

**Great Lakes Binational Toxics Strategy (GLBTS)
(Step 4)**

**Management Assessment for Octachlorostyrene (OCS),
perchlorinated hydrocarbon trace byproduct**

**U.S. Environmental Protection Agency
Great Lakes National Program Office
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This Assessment relies on primary studies that collectively represent a great deal of work by many scientists, from many nations, across three decades. Many are cited among Footnotes. In the Great Lakes region, contributors have included EPA's D. W. Kuehl, Environment Canada's B. G. Oliver, from the State University of New York at Buffalo, E. M. Schulman and H. Klingele, and Susan Heustis of Canada's Department of Fisheries and Oceans.

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The Council of Great Lakes Industries prepared a 40-page report on OCS, steered by Dale Phenicie, Werner Braun, and George Kuper. Contributors included Robert E. Bailey (Bailey Associates) and Dr. Daniel W. Smith (Conestoga Rovers).

Executive Summary

Background [Framework Crosswalk Section 1]: The Great Lakes Binational Toxics Strategy (GLBTS, 1996) aims to promote reduced releases of 13 selected substances, via information and public participation. These substances were nominated by the International Joint Commission. One substance is octachlorostyrene (OCS). OCS is a trace-yield byproduct of processes that bring together carbon, chlorine, and energy. Circumstances of temperature, concentrations, and perhaps catalysis need to align to produce OCS. OCS is a perchlorinated aromatic hydrocarbon, closely akin to hexachlorobenzene (HCB) in its molecular structure. OCS may be co-created whenever HCB is also formed as a byproduct. PCDDs (polychlorinated dibenzo-p-dioxins) and PCDFs (polychlorinated dibenzo-p-furans) are also sometimes indicative of OCS formation.

GLBTS Goals for OCS [Framework Crosswalk Section 2]: The United States goal was to “confirm by 1998 that there is no longer use or release from sources that enter the Great Lakes Basin of five bioaccumulative pesticides and of the industrial byproduct/contaminant octachlorostyrene. If on-going, long-range sources of these substances from outside of the U.S. are confirmed, work within international frameworks to reduce or phase-out releases of these substances.” Canada’s similar goal was to “report by 1997 that there is no longer use, generation, or release from Ontario sources that enter the Great Lakes of five bioaccumulative pesticides and of the industrial byproduct/contaminant octachlorostyrene. If on-going, long-range sources of these substances from outside of Canada are confirmed, work within international frameworks to reduce or phase-out releases of these substances.”

To restate these more succinctly, each nation aimed to:

- evaluate whether there is ongoing use of OCS;
- evaluate whether there is ongoing release of OCS from sources of OCS in the U.S. or Canada that reach the Great Lakes

Assessing progress toward goals [Framework Crosswalk Section 2]:

Under the GLBTS process, the U.S. and Canada have pooled available information regarding potential sources of OCS. If we regard each nation as having pledged to study whether there are active sources of OCS in each nation, then it may now be concluded that each nation has indeed undertaken such a study.

Furthermore, each nation has determined by its review that OCS is currently generated as an unintended byproduct of a potentially diverse variety of industrial processes (though, be it noted, generation does not necessarily imply release to the environment). Pursuant to a recent regulation, five U.S. firms have reported generation and management of OCS wastes. (It is plausible that additional processes may generate OCS, but are either not obliged to report this or may well be unaware of trace generation of OCS, since OCS is neither an input material nor a commercial product.)

If we regard an implicit goal of each nation to be that they encourage minimal release of OCS, then diverse evidence indicates that OCS levels in Lake Ontario have fallen from their peak forty plus years ago by about two orders of magnitude (i.e., 95+ percent). Though there is a shorter chronological perspective for other lakes, in recent years OCS has generally continued to ebb across the Great Lakes system. By these metrics, the implicit goal has been handsomely met.

In summation:

1. Is there ongoing use of OCS? This goal is met. There has been and is no known intended use of OCS.

2. Are there ongoing releases of OCS? It is known that some production processes produce OCS. It is possible that there may be others that are not known. Yet, do releases of OCS reach the Great Lakes from sources in Canada or in the U.S.? This cannot be definitively answered, because molecules of OCS present in the Great Lakes or its air-shed cannot be definitively backtracked to their place or date of origin. However, temporal perspectives on OCS abundance in the Great Lakes indicate a massive and continuing decline. This implies that sources of OCS to the Great Lakes have massively declined.

Geographic Distribution and Temporal Trends [Framework Crosswalk Section 3.1, 3.3., and 3.5]: OCS levels have long been highest in Lakes Ontario and Erie. For the water-body with the longest chronological perspective, Lake Ontario, diverse evidence indicates that there has been a massive (i.e., circa two-orders of magnitude) decline in OCS since the 1960s. Considering the preponderance of evidence, there also continues to be ebbing of residual OCS levels across the Great Lakes.

ES-1: Geographic comparison, OCS in herring gulls and sport fish¹

	L. Ontario	Erie	Huron	Michigan (Upper)	Superior
Gulls (1987)	17 ppb	17 ppb	5 ppb	5 ppb	5 ppb
Gulls (2001)	6 ppb	6 ppb	2 ppb	1 ppb	3 ppb
Trout (1999)	19.5 ppb		4 ppb	1.6 ppb	Non-detect
Walleye (1999)		2.5 ppb			

OCS levels are higher on the lower lakes. From gull monitoring, it is evident that OCS levels fell on all lakes between 1987-2001.

ES-2: Temporal focus on Lake Ontario

	1970s	1977-1993	1987 and 2001	2002
Sediment cores	65+% ²			
Lake trout		10% per year ³		
Herring Gulls			67% ⁴	
Tributary sediments				No detection at 112 tributaries ⁵

¹ Weseloh, D.V., Havelka, T., and Pekarik, C. "Trends in Great Lakes Herring Gull Eggs." In: *Great Lakes Binational Toxics Strategy Annual Progress Report, 2002*. USEPA and Environment Canada. Lake trout/walleye data from Elizabeth Murphy, USEPA, unpublished and preliminary. (OCS is measured on a whole fish basis.)

² Durham, R. W. and B. G. Oliver. 1983. "History of Lake Ontario contamination from the Niagara River by sediment radiodating and chlorinated hydrocarbon analysis." *J. Great Lakes Res.* 9(2): 160-168. Also, Kaminsky, R and Hites, R. 1984. "Octachlorstyrene in Lake Ontario." *Environ. Sci. Technol.*, 18, 275-279.

³ Huestis, S. Y., Servos, M.R., Whittle, D.M., and Dixon, D.G. 1996. "Temporal and age-related trends in levels of polychlorinated biphenyl congeners and organochlorine contaminants in Lake Ontario lake trout." *J. Great Lakes Res.* 22(2): 310-330

⁴ Weseloh, D.V., Havelka, T., and Pekarik, C. "Trends in Great Lakes Herring Gull Eggs." In: *Great Lakes Binational Toxics Strategy Annual Progress Report, 2002*. USEPA and Environment Canada.

⁵ Environment Canada, unpublished, provided by A. Waffle.

A massive decline in OCS is evident in the lake with the longest chronological record, provided through several indicators viewed together

ES-3: Temporal focus, lake trout, Lake Ontario

Year	OCS mean	Std dev.	Reference
1977	263 ppb	156	Heustis <i>et al</i> , 1996. Trout (4 yrs old) caught at Main Duck Island; whole fish; wet weight
1977	281		Kuehl <i>et al</i> , 1981. Whole fish, wet weight. Sampled Cape Vincent, NY
1978	98.6	39.8	Heustis <i>et al</i> , 1996.
1979	86		Kuehl <i>et al</i> , 1981. Sampled at Stony Island, NY.
1980	96.7	68.3	Heustis <i>et al</i> , 1996.
1981	54	17.6	Heustis <i>et al</i> , 1996.
1982	79.4	23.4	Heustis <i>et al</i> , 1996.
1983	54.4	18.1	Heustis <i>et al</i> , 1996.
1984	106	106	Heustis <i>et al</i> , 1996.
1986	43.7	12.1	Heustis <i>et al</i> , 1996.
1987	30.5	7.73	Heustis <i>et al</i> , 1996.
1988	43	16.3	Heustis <i>et al</i> , 1996.
1989	36.7	14.3	Heustis <i>et al</i> , 1996.
1990	31.6	7.73	Heustis <i>et al</i> , 1996.
1991	33.5	9.38	Heustis <i>et al</i> , 1996.
1992	29.4	12.3	Heustis <i>et al</i> , 1996.
1993	31.3	8.3	Heustis <i>et al</i> , 1996.
1999	19.5		Murphy, 2004, preliminary, unpublished. Whole fish, wet weight. Caught at North Hamlin.
2000	9.6		Murphy, 2004, preliminary, unpublished. Caught at Oswego, NY

OCS levels in lake trout sampled from Lake Ontario have declined. Initial sampling began in 1977

ES-4: Examples of temporal indicators, by lake

Medium	Lake	Time Frame	OCS % Decrease
Sediment core	Ontario	1900-80	90+% (Durham and Oliver, 1983)
Sediment cores (11)	Ontario	1960-1980	65% to 1980 (Kaminsky and Hites, 1984)
Lake trout	Ontario	1977 – 1993	10 % per year (Heustis <i>et al</i> , 1996)
Water	Ontario	1984 – 1996	20 % per year (Env. Canada, unpublished)
Surface sediments	Ontario	2001-03	No detection at 112 tributaries (EC, unpublished)
Herring gull egg	Ontario	1987 and 2001	67% (Weseloh <i>et al</i> , 2003).
Herring gull egg	Ontario	1987 through 1998	17% per year. Council of Great Lakes Industries, 1999, report on

			Octachlorostyrene at: http://www.cgli.org/BiToxOxy.pdf .
Spot-tail shiner	L. Niagara River	1985 - 1995	8 % per year (100% recent non-detects) (EC, unpublished, CGLI, 1999)
Water	Niagara River	1989 – 1995	16 – 21 % per year (EC, unpublished, CGLI, 1999)
Herring gull egg	Erie	1987 and 2001	68 % (Weseloh <i>et al</i> , 2003)
Atmospheric deposition	Erie	1999 - 2002	67 % (Hulting, unpublished, preliminary)
Herring gull egg	Detroit River	1987 - 2003	86 % decrease (Weseloh, personal conversation, 2004).
Herring gull egg	Huron	1987 and 2001	61 % (Weseloh <i>et al</i> , 2003)
Herring gull egg	Superior	1987 and 2001	52 % (Weseloh <i>et al</i> , 2003)
Atmospheric deposition	Superior	1999-2002	40 % (Hulting, unpublished, preliminary)
Herring gull egg	Upper Michigan	1987 and 2001	79 % (Weseloh <i>et al</i> , 2003)

OCS has declined in Lake Ontario by two orders of magnitude. Continuing declines are also seen across the Great Lakes system as a whole.

Criteria/Risk [Framework Crosswalk 3.2]: There are generally no regulatory criteria for OCS, save a water criterion in the State of New York. Nevertheless, there are regulations pertaining to HCB and especially dioxin. During the past several decades, steps to manage these substances will have had the collateral effect of reducing OCS releases. This provides one reasonable explanation for the general decline in OCS levels seen across the 800-mile wide Great Lakes system. [Another possible contributing explanation is structural economic change within the chemical industry (i.e., reduced output of certain products in the vicinity of the Great Lakes).]

Health Canada has assessed estimated exposures of the general population of the Great Lakes basin in relation to a calculated Maximum Risk Intake (MRI) for OCS. These ranged from under one percent of the MRI to, at the high end of the range estimate, four percent of the MRI.⁶ Thus the human population generally has 25-fold to 100-fold safety margins, under conservative risk assumptions and estimates.

Sources (past potential) [Framework Crosswalk 4.1.1]: It has been reported that OCS was present in wastes generated during electrolytic manufacture of chlorine (before circa 1975).⁷ Chlorine factories have since improved their production process, no longer employing graphite anodes. The erosion of graphite anodes once provided carbon that served to form chlorinated hydrocarbon wastes.

Sources (potential current) [Framework Crosswalk 4.1.2]: There is likely continued generation of OCS, in keeping with potential current sources of HCB and PCDD. Recently, OCS was explicitly added as a reporting parameter to the U.S. Toxics Release Inventory (TRI). During 2002, five facilities reported generation of 808 pounds of OCS, including three inorganic pigment producers, one chemical and

⁶ Laube, V., Arvanitakis, A., Jordan, S., Haines, D., and Gupta, S. 1998. "Octachlorostyrene." In: *Persistent Environmental Contaminants and the Great Lakes Basin Population: an exposure assessment*. Health Canada.

⁷ Kaminsky, R and Hites, R. 1984. "Octachlorostyrene in Lake Ontario." *Environ. Sci. Technol.*, 18, 275-279.

vinyl producer, and one magnesium metal producer.⁸ These are located in Mississippi, Tennessee, Delaware, Louisiana, and Utah, respectively.

- **Magnesium (via electrolysis):** Electrolytic magnesium factories are known to have generated OCS, also its close relation hexachlorobenzene (HCB), and PCDDs. The U.S. has one electrolytic magnesium factory (in Utah). [One Canadian factory likely generates lower quantities of chlorinated hydrocarbon wastes, owing to a different source of raw magnesium.]
- **Titanium and titanium compounds:** Two factories may produce titanium via a production stage that involves electrolytic manufacture of magnesium. These are located in Oregon and Nevada. The U.S. also produces titanium dioxide.
- **Chemicals:** In 1998, chemical firms reported, to EPA's TRI, 1.5 million pounds of waste containing HCB (principally in Texas and Louisiana).⁹ It is likely OCS is present in HCB-containing wastes.
- **Other potential candidates:** Aluminum foundries and secondary smelters; incineration; niobium and tantalum; vanadium; semi-conductors; nickel; sodium; secondary copper smelting; graphite.

Government activities concerning OCS [Framework Crosswalk 4.4]: USEPA and Environment Canada co-hosted a forum with North American electrolytic magnesium firms in December 2000. This shared perspectives regarding management of chlorinated hydrocarbon wastes generated during production of magnesium.

EPA has issued a MACT rule governing air emissions from the U.S. electrolytic magnesium factory. In addition, it has been reported that this factory has invested in new production technologies¹⁰ that may reduce formation of chlorinated hydrocarbon wastes.

Also, EPA added the magnesium and titanium sectors to its dioxin inventory. In addition, EPA has established regulations for classes of incinerators, which offer promise of reduced emissions of chlorinated hydrocarbons. Also, EPA added OCS as a reporting parameter to the TRI.

Opportunities to Achieve Further Reductions [Framework Crosswalk 4.4]:

Owing to little risk-based grounds for concern about OCS, coupled with its evident general, sustained, and massive decline in the Great Lakes, the case for seeking further reductions based solely on trace generation of OCS or potential trace generation seems modest.

During the GLBTS review of OCS sources, it became apparent from scientific literature that OCS is co-formed with HCB (among other chlorinated hydrocarbons, including dioxin.) Potential opportunities to reduce OCS are generally the same as opportunities to reduce other trace chlorinated hydrocarbon byproducts.

PCDD has many toxicological and risk studies, regulations and criteria, whereas HCB has more toxicological studies and regulations than OCS. Given more awareness of dioxin and HCB, opportunities to encourage reduced releases of chlorinated hydrocarbon byproducts will, practically speaking, be driven by dioxin and secondarily by HCB. There are no known reduction opportunities that rely on OCS as their justification.

Management Outcome [Framework Crosswalk 4.5]: Continue suspension of GLBTS activities for OCS, begun during 2000.

⁸ USEPA, *Toxics Release Inventory, 2002*, provided by A. Thomas, Battelle Memorial Institute

⁹ USEPA, *Toxics Release Inventory, 1998*, provided by A. Thomas, Battelle Memorial Institute

¹⁰ *Platt's Metals Week*, 19 April 1999, p. 5

Referral to Another Forum [Framework Crosswalk 4.5.1]: This assessment will be provided to the dioxin and HCB workgroups, for their information. However, these groups will not be asked to add OCS to their scope.

Number of Lakes Impacted [Framework Crosswalk 4.5.2]: OCS has traditionally been highest on Lakes Ontario and Erie, though seems declining everywhere.

New Goals [Framework Crosswalk 4.5.3.]: There are no known risk-based grounds for new activities or new challenge goals regarding OCS, under the GLBTS process.

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Management Assessment for Octachlorostyrene (OCS)

1. Introduction [Framework Crosswalk 1]

The purpose of the Great Lakes Binational Toxics Strategy (1996) is to promote reduced releases of certain targeted substances, via information and public participation. One substance is octachlorostyrene (OCS).

The Strategy envisioned a 4 step analytic process: gather information; analyze current regulations and programs which manage or control target substances; identify cost-effective options to achieve further progress; and implement actions to work toward the goal of virtual elimination.

During 1998, the U.S. Environmental Protection Agency (USEPA) drafted a report on potential sources of OCS.¹¹ (This in turn drew partly on two earlier reports regarding chlorinated styrenes.¹²) A public comment period for EPA's draft paper on potential sources was announced in the Federal Register and comments were received during the first half of 1999.

Continuing the Strategy analytic process, in September 2000, the USEPA drafted a Step 3 report for OCS. This report reviewed information regarding OCS levels in the environment, potential sources, and ideas to further reduce OCS exposures within the Great Lakes watershed. It was provided to all who had expressed interest regarding OCS in the GLBTS process.

Now, this document assesses progress in relation to the U.S. challenge for OCS. As such, it documents completion of the 4-step analytic process as regards OCS.

This document follows a "General Framework for Preparing Assessments to Manage GLBTS Level 1 Substances." (Numeric headings are provided to cross-walk to this Framework.)

Perchlorinated aromatic hydrocarbons, including OCS and HCB

Styrene [100-42-5], also known as vinyl benzene, occurs naturally in some plants (e.g., cinnamon, coffee beans, and peanuts). Since the 1930s, styrene has been synthesized as an important industrial chemical, used in production of rubber and plastic. The feedstock for styrene manufacture is ethylbenzene. Structurally, styrene consists of six carbon atoms arranged in an aromatic, six-sided benzene ring to which are attached five hydrogen atoms and a two carbon side-chain (vinyl) bearing three hydrogen atoms.

Polychlorinated styrenes are a class of compounds in which chlorine atoms displace hydrogen ones in the styrene (vinyl benzene) structure. Monochlorinated styrenes, for instance, have one chlorine atom. With octachlorostyrene, all eight hydrogen atoms have been replaced by chlorine ones.

OCS and HCB are structurally close. Both are "perchlorinated" in that each molecule holds as many chlorine atoms as it can structurally accept. HCB is a fully chlorinated benzene structure, whereas OCS is a fully-chlorinated vinyl benzene.

¹¹ USEPA-Great Lakes National Program Office. "OCS: A review of potential sources." Draft for public comment, 11/5/98.

¹² Schulman, E. M. and Klingele, H. "Sources of Polychlorinated Styrenes in the Great Lakes and their tributaries." USEPA-Great Lakes National Program Office, Grant R00-5764-01, SUNY-Buffalo, draft final report, 1984. Also, Daugherty, M. L. "Chlorinated Styrenes: Chemical Hazard Information Profile." Draft report, June 13, 1986, EPA Office of Pesticides and Toxic Substances.

The Chemical Abstract Service number for OCS is 29082-74-4.

2. Challenge Goals Status [Framework Crosswalk 2]

Under the Great Lakes Binational Toxics Strategy, the United States enunciated the following goals:

- “Confirm by 1998 that there is no longer use or release from sources that enter the Great Lakes Basin of five bioaccumulative pesticides and of the industrial byproduct/contaminant octachlorostyrene.
- If on-going, long-range sources of these substances from outside of the U.S. are confirmed, work within international frameworks to reduce or phase-out releases of these substances.”

This challenge does not set a numeric goal. Rather it implicitly encourages zero release of OCS, on various geographic scales: local, regional, national, and international.

Similarly, Canada’s goal was to “Report by 1997 that there is no longer use, generation, or release from Ontario sources that enter the Great Lakes of five bioaccumulative pesticides and of the industrial byproduct/contaminant octachlorostyrene. If on-going, long-range sources of these substances from outside of Canada are confirmed, work within international frameworks to reduce or phase-out releases of these substances.”

Have the goals of verifying no releases of OCS been achieved? Yes, the issue has been reviewed. Under the GLBTS process, the U.S. and Canada have pooled available information regarding potential sources of OCS. If we regard each nation as having pledged to study whether there are active sources of OCS in the U.S. and Canada, then it may now be concluded that each nation has indeed undertaken such a study.

Furthermore, these studies indicate that there is ongoing generation of OCS by industrial processes. Each nation has determined by this review that OCS is currently generated as an unintended byproduct of a potentially diverse variety of industrial processes (though generation does not necessarily imply current release). Five U.S. firms have recently reported generation and management of OCS wastes.

As will be discussed in Section 4 below, it is plausible that there may be additional industrial processes that generate OCS. Some potential sources may either not be required to report or may be unaware of trace generation of OCS, since OCS is neither an input material nor commercial product.

If we regard the implicit goal of each nation to be that they encourage minimal release of OCS, on various geographic scales (local, regional, national, and global), then during the past 45 years there is diverse evidence (to be presented in Section 3) that robustly indicates that OCS levels in Lake Ontario have massively fallen and that OCS levels elsewhere across the Great Lakes generally continue to ebb. By this yardstick, the implicit goal has been handsomely met.

Discussion of barriers [Framework Crosswalk 2]

The general guidance regarding GLBTS reports, such as this one, asks that there be a discussion of barriers to achieving a goal. Barriers to achieving zero release of OCS to the Great Lakes include:

- Few regulations pertain specifically to OCS, thus potential sources of OCS have been modestly assessed;
- Toxicological information, albeit limited, suggests that OCS is not highly hazardous. [Note: the USEPA and Environment Canada did not

include OCS in the GLBTS program based on a risk assessment, but at the request of the International Joint Commission.]

- The preponderance of environmental data suggests that OCS levels in the Great Lakes have substantially declined since 1970, with continued ebbing today. There seems no compelling case for commissioning OCS-specific regulations, toxicological studies, or seeking reductions from potential distant atmospheric sources.

Canadian perspective¹

There is no reported generation or release of OCS within the Province of Ontario. There were industrial processes in Ontario which likely generated OCS in the past (e.g., chlor-alkali with graphite anodes; chlorinated solvent production). There are or may be soils and bottom sediment sites within Ontario that once received OCS wastes.

Efforts to fill OCS source "data gaps" should continue, outside of an OCS BTS workgroup. Processes that form hexachlorobenzene and dioxins/furans are likely to be potential OCS sources. Filling OCS "data gaps" should be referred to the hexachlorobenzene and/or dioxin/furan workgroups. When possible, OCS emissions should be included with their ongoing efforts to generate more accurate inventories. Source sectors which are common to OCS, HCB and D/F are many: including, base metal smelting (copper, nickel, and magnesium), aluminum foundry and secondary smelting, waste incineration, semiconductor mfg., chlorinated pesticide mfg., and high temperature metal production processes using chlorine/carbon.

Also, an assessment should be carried out to confirm that the GLBTS sediment challenge is dealing adequately with the remediation of priority sites having OCS contaminated bottom sediments. Also, landfills likely to have accepted wastes from the chlorinated solvent and chlor-alkali (using graphite anodes) production sectors need to be identified, and an assessment carried out to confirm that appropriate long-term monitoring and reporting measures are in place to control OCS releases.

This report will indicate that OCS can be transported via the atmosphere and is probably ubiquitous at very low levels across the basin. The door needs to be closed on the issue of atmospheric deposition from these known sources located outside of the basin (i.e., the Quebec plant, the plants in Mississippi, Tennessee, Delaware, Louisiana and Utah). Are they significant from the Basin perspective, should the GLBTS be working with others to reduce releases as mandated by challenge goals? The issue of long-range transport from known out-of-basin OCS air sources should be referred to the Long-Range Transport Workgroup for assessment to establish if GLBTS activities are warranted.

Discussion from a U.S. perspective

Air releases of OCS from reporting U.S. sources are less than one pound per year. Also, there are not grounds for the U.S. to view air emissions of OCS, even if they are in actuality much larger, with risk-based concern. As will be discussed, there is robust evidence that OCS has massively decreased in the Great Lakes since the 1960s. There seem sufficient grounds to conclude that distant OCS air emissions are unimportant today to the Great Lakes.

In addition, as will be discussed, Health Canada has assessed estimated OCS exposures of the general population in the Great Lakes basin in relation to a calculated Maximum Risk Intake (MRI). These ranged from under one percent of the MRI to, at the high end of the range estimate, four percent of the MRI. Thus the human population generally has 25-fold to 100-fold safety margins, under

conservative risk assumptions and estimates. Also, there are no known existing, site-specific exceedances of health criteria.

For such reasons, the United States does not plan to seek more information regarding OCS releases.

3. Environmental Analysis: Geographic Distribution, Temporal Perspectives, Criteria/Risk [Framework Crosswalk 3]

Geographic distribution within the Great Lakes [Framework Crosswalk 3.1]

An unknown compound with 8 chlorine atoms was first noted in the tissue of eider ducks sampled in 1966 from the Rhine River in the Netherlands.¹³

This mystery compound was subsequently identified as octachlorostyrene.¹⁴

OCS was thereafter noted around the Great Lakes, in blue herons from Lake St. Clair¹⁵ and in fish.¹⁶ The latter study reported OCS levels were highest in fish from Lake Ontario; Lake St. Clair; Ashtabula, Ohio; and Saginaw Bay.

In the Great Lakes region, the highest OCS levels have been found downstream of factories near Midland, MI; Sarnia, Ontario¹⁷; Ashtabula, Ohio¹⁸; Niagara Falls, NY; and Massena, New York.¹⁹

The uneven geographic distribution of OCS across the Great Lakes is nicely indicated by monitoring of herring gull eggs at colonies across the Great Lakes watershed.²⁰ OCS levels in gull eggs from Lakes Ontario and Erie are higher than in Lakes Superior, Huron, and Michigan.

During 2001 to 2003, Environment Canada conducted surveys of surface sediments at Canadian tributaries to Lake Erie and Lake Ontario. OCS was detected in just 5 of 101 tributaries to Lake Erie, whereas among 112 tributaries to Lake Ontario OCS was found at none!²¹

A Health Canada study found detectable OCS residues only in human breast milk samples from the Province of Ontario. OCS was not detected in breast milk samples from nine other Canadian Provinces.²²

Table-1: Geographic comparison, OCS in herring gulls and sport fish²³

¹³ Koeman, J. H., ten Noever de Brauw, M. C., and de Vos, R. H. 1969. *Nature*, 221, 1126

¹⁴ ten Noever De Brauw, M. C. and Koeman, J. H. 1973. "Identification of chlorinated styrenes in cormorant tissues by a computerized gas chromatography-mass spectrometry system." *Science of the Total Environment*, 1, 427-432

¹⁵ Reichel, W. L., Prouty, R. M., and Gay, M.L. 1977. "Identification of polychlorinated styrene compounds in Heron tissues by gas-liquid chromatography-mass spectrometry." *J. Assoc. Off. Anal. Chem.* 60: 60-62.

¹⁶ Kuehl, D. W., Johnson, K.L., Butterworth, B.C., Leonard, E.N., and Veith, G.D. 1981. "Quantification of octachlorostyrene and related compounds in Great Lakes fish by gas chromatography-mass spectrometry." *J. Great Lakes Res.* 7(3): 330-335

¹⁷ Oliver, B. G. and K. Kaiser. 1986. *Water Poll. Re. J. Canada*, 21, 3, 344-350

¹⁸ Kuehl, D. W., Johnson, K.L., Butterworth, B.C., Leonard, E.N., and Veith, G.D. 1981. "Quantification of octachlorostyrene and related compounds in Great Lakes fish by gas chromatography-mass spectrometry." *J. Great Lakes Res.* 7(3): 330-335

¹⁹ 6th highest OCS value in USEPA's national survey of chemical residues in fish, 1992.

²⁰ Bishop, C. *et al.* 1992. *An atlas of contaminants in eggs of fish eating colonial birds of the Great Lakes*. Technical Report Series No. 152, Canadian Wildlife Service, Ontario Region.

²¹ "Sediment quality in tributaries to the Great Lakes", Env. Canada, unpublished, 2004

²² Mes, J., Davies, D. J., Doucet, J., Weber, D., and McMullen, E. 1993. "Levels of chlorinated hydrocarbon residues in Canadian human breast milk and their relationship to some characteristics of the donors." *Food Additives and Contaminants*, 10, 4, 429-441

²³ Weseloh, D.V., Havelka, T., and Pekarik, C. "Trends in Great Lakes Herring Gull Eggs." In: *Great Lakes Binational Toxics Strategy Annual Progress Report, 2002*. USEPA and Environment Canada. Lake trout/walleye data from Elizabeth Murphy, USEPA, unpublished and preliminary. (OCS is measured on a whole fish basis.)

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Gulls (1987)	17 ppb	17 ppb	5 ppb	5 ppb	5 ppb
Gulls (2001)	6 ppb	6 ppb	2 ppb	1 ppb	3 ppb
Trout (1999)	19.5 ppb		4 ppb	1.6 ppb	Non-detect
Walleye (1999)		2.5 ppb			

OCS levels are higher on the lower lakes. From gull monitoring, it is evident that OCS levels fell on all lakes between 1987-2001.

Geographic distribution on a wider basis [Framework Crosswalk 3.1]

Other studies also support a general picture of uneven distribution of OCS in the environment:

- In a nationwide U.S. survey of chemical residues in fish sampled during the late 1980s, OCS was detected in only 9% of fish sampled, presumably in locations relatively near sources.²⁴ [Similar results have been obtained for fish surveyed during 1999-2000.]²⁵
- OCS could not be detected in mosses sampled near the Austrian city of Linz.²⁶
- OCS levels in Atlantic cod decrease from the southern to the northern North Sea.²⁷
- OCS was detected in fish from the North Sea, but not detected in fish species sampled from the Mediterranean, North Atlantic, and the Red Sea.²⁸
- In milk samples from cows in Switzerland, OCS levels varied by a factor of 20.²⁹
- OCS was only detected in eggs from one of seven colonies of herring gulls across Norway, in the colony closest to an electrolytic magnesium factory.³⁰ Another study found the indication of pollution from this factory as recorded in crabs to extend up to 31 miles downstream.³¹

Relatively high environmental OCS levels indicate proximity to sources. The highest OCS level noted in a national survey of chemical residues in fish sampled during the late 1980s was 0.14 part per million (ppm) in a catfish from Bayou D'Inde (near Lake Charles, Louisiana).³² The second highest level (0.07 ppm) was in a catfish from the Brazos River near Freeport, Texas. Both rivers are proximate to clusters of chemical factories. A magnesium factory employing electrolysis operated in Freeport from 1940 to 1998. Another study during the mid-1980s found OCS and

²⁴ USEPA-Office of Water. 1992. *National Study of Chemical Residues in Fish*.

²⁵ <http://epa.gov/waterscience/fishstudy/>

²⁶ Chovanec, A., Vogel, W.R., Lorbeer, G. Hanus-Ilmar, A. and Seif, P. 1994. "Chlorinated organic compounds, PAHs, and heavy metals in sediments and aquatic mosses of two upper Austrian rivers." *Chemosphere*, 29, 9-11, 2117-2133

²⁷ de Boer, J. 1989. "Organochlorine compounds and bromodiphenylethers in livers of Atlantic cod (*Gadus Morhua*) from the North Sea, 1977-1987. *Chemosphere*, 18, 11/12, 2131-2140

²⁸ Ernst, W., Weigelt, V. and Weber, K. 1984. "Octachlorostyrene—a permanent micropollutant in the North Sea." *Chemosphere*, 13, 1, 161-168

²⁹ Rappe, C., Nygren, M., Lindstrom, G., Buser, H.R., Blaser, O., and Wuthrich, C. 1987. "Polychlorinated dibenzofurans and dibenzo-p-dioxins and other chlorinated contaminants in cow milk from various locations in Switzerland." *Environ. Sci. Technol.*, 21, 964-970

³⁰ Moksnes, M. T. *et al.* 1986. *Environ. Pollut. Ser. B*, 11, 109-116

³¹ Oehme, M. *et al.* 1990. "Estimation of PCDF and PCDD Contamination of a Coastal Region Using Isomer Profiles in Crabs." *Environ. Sci. Technol.*, 24, 1836-1841

³² 5th highest level was recorded in catfish from nearby Calcasieu River

greater quantities of penta- and hexa-chlorobenzene in bottom sediments of the Bayou D'Inde.³³

Relatively high levels of OCS in Europe have been reported in fish³⁴ and in human blood samples³⁵ along the River Elbe, near Hamburg, Germany.

The Council of Great Lakes Industries advises that the distribution of OCS through Europe has recently been reported and shows a localized distribution (Chu, S., Covaci, A., Voorspoels, S., Schepens, P. 2004. "The Distribution of Octachlorostyrene in environmental samples from Europe. *J. Environ. Monit.*, 5, 619-625).

Atmospheric deposition [Framework Crosswalk 3.1]

OCS can be transported via the atmosphere, as indicated by its presence in Siskiwit Lake on Isle Royale within Lake Superior, suggestive of atmospheric dispersion or transport.³⁶

OCS was intermittently detected in only 34% of air samples collected at Egbert, Ontario during 1988-89.³⁷ (The annual mean was reported to be 0.71 pg/m³, with a high value of 31 pg/m³.) Intermittence suggests that OCS is found at higher levels when air is received from the direction of a source. It may further suggest that air emissions have local dispersion, in keeping with the spotty geographic distribution of OCS indicated by analysis of OCS levels in fish and birds.

EPA added OCS to five monitoring stations in 1999. There are now four years of data, through 2002. OCS has been found in nearly all samples, suggesting a ubiquitous atmospheric presence detectable with sufficiently sensitive and selective analytic method.

Geographically, OCS deposition is higher at two sites (Chicago and near Lake Erie) than three sites near Lake Superior and Michigan. This suggests higher levels are found in urban air-sheds.

In terms of temporal change, all the sites indicated a decline between 1999 and 2002.

Table 2: Geographic comparison, atmospheric deposition³⁸

	Superior	L. Michigan (Upper)	Chicago, IL	L. Erie
OCS (1999)	0.789 pg/m ³	1.758	1.511	2.677
OCS (2002)	0.526	0.551	0.855	0.856

Urban air-sheds have higher OCS deposition, while all monitoring sites have seen recent declines

³³ Pereira, W. E. *et al.* 1988. *Environ. Sci. Technol.*, 22, 772-778

³⁴ Luckas, B. and Oehme, M. 1990. "Characteristic contamination levels for polychlorinated hydrocarbons, dibenzofurans, and dibenzo-p-dioxins in bream (*Abramis Brama*) from the River Elbe." *Chemosphere*, 21, 1-2, 79-89.

³⁵ Lommel, A., Kruse, H., Muller, E., Wasserman, O. 1992. "Organochlorine pesticides, octachlorostyrene, and mercury in the blood of Elb River residents, Germany." *Arch. Environ. Contam. Toxicol.*, 22, 14-20

³⁶ Swackhamer, D. A. and Hites, R. A. 1988. "Occurrence and bioaccumulation of organochlorine compounds in fishes from Siskiwit Lake, Isle Royale, Lake Superior." *Environ. Sci. Technol.*, 22, 5, 543-548.

³⁷ Hoff, R. H., Muir, D.C., and Grift, N. P. 1992. "Annual cycle of polychlorinated biphenyls and organohalogen pesticides in air in southern Ontario." *Environ. Sci. Technol.*, 26: 266-275

³⁸ M. Hulting, USEPA, preliminary, unpublished data.

Discussion of the sufficiency of geographic data [Framework Crosswalk 3.4]

The herring gull monitoring covers all lakes across the Great Lakes system. This program provides sufficient geographic scope. It is high quality data, at a biological endpoint.

Lake Ontario has historically been most studied for OCS, because its OCS levels were highest. Lake Ontario received OCS from Lake Erie and from sources along the Niagara River. There are three studies of OCS in Lake Ontario bottom sediment cores.

Areas (Midland, Sarnia, Ashtabula, Niagara Falls, and Massena) that once probably contained sources of OCS have been identified.

OCS was added to the gull monitoring in 1987. From available Lake Ontario sediment cores, OCS levels peaked during the 1960s and likely declined by 90 percent before 1987. While the herring gull program can show geographic variability, by itself it cannot show the full magnitude of OCS reduction across all water-bodies during the past 40 years.

Should sediment cores be obtained from the upper four lakes to show the longer-term temporal picture on the four upper lakes? Given the lack of risk-based cause for concern regarding OCS, there does not seem a compelling case for investing dollars in sediment cores from other lakes.

Temporal trends [Framework Crosswalk 3.3]

There are indicators of temporal trends in the abundance of OCS in the Great Lakes:

- One study dated and analyzed a Lake Ontario bottom sediment core obtained in 1981.³⁹ OCS first appeared at a depth corresponding to the 1920s. OCS concentrations increased, with one peak of 65 parts per billion (ppb) corresponding to the late 1940s, and a marked peak of 166 ppb corresponding to the short timeframe of 1959-1962. Subsequently, OCS levels declined, reaching 13 ppb during the mid-1970s, **a decline of 90+%**. (This history was similar to that for total chlorinated benzenes; the concentration of combined di- through hexa- chloro-benzenes peaked in 1959-62 and by the late 1970s had fallen about 85%, from 4,200 to 500 ppb.)
- Another core, taken in 1995 from the Niagara Bar of Lake Ontario, provided good agreement with the earlier study, noting an OCS peak in 1960 and a subsequent 13.5% per year decline until the detection limit was reached in 1981.⁴⁰
- Another study analyzed OCS in 11 sediment cores from all across Lake Ontario.⁴¹ OCS was found in 8 of the cores, with some variance in results, as would be expected. Two indicated a peak near 1960, but five others indicated a peak near 1970. Since 11 cores were obtained, this study may present a fuller picture of OCS trends than the studies with just one sample. **By 1980, the average OCS decline shown by the 8 cores was about 65%.**
- **From 1977 through 1993, OCS levels fell in lake trout from Lake Ontario by 10% per year, from 0.1 ppm to 0.03 ppm.**⁴²

³⁹ Durham, R. W. and B. G. Oliver. 1983. "History of Lake Ontario contamination from the Niagara River by sediment radiocarbon and chlorinated hydrocarbon analysis." *J. Great Lakes Res.* 9(2): 160-168

⁴⁰ Council of Great Lakes Industries, March 1, 1999, report on Octachlorostyrene available at: <http://www.cgli.org/BiToxOxy.pdf>.

⁴¹ Kaminsky, R and Hites, R. 1984. "Octachlorostyrene in Lake Ontario." *Environ. Sci. Technol.*, 18, 275-279

⁴² Huestis, S. Y., Servos, M.R., Whittle, D.M., and Dixon, D.G. 1996. "Temporal and age-related trends in levels of polychlorinated biphenyl congeners and organochlorine contaminants in Lake Ontario lake trout." *J. Great Lakes Res.* 22(2): 310-330

- A wide picture of OCS temporal trends across the Great Lakes is provided by herring gull egg sampling by the Canadian Wildlife Service.⁴³ OCS was added as a parameter in 1987. Between 1987 and 1998, among all 15 colonies across the five Great Lakes, OCS levels declined by an average of 18% per year.⁴⁴
- For the GLBNS Progress Report (2002), scientists at the Canadian Wildlife Service reported OCS burdens in gull colonies from 1987 through 2001, a fuller period.⁴⁵ OCS burdens in gulls declined at all colonies, from 22 percent to 86 percent.⁴⁶ In relation to a chosen goal for statistical confidence, the declines in OCS at 6 gull colonies were statistically significant, whereas OCS declines at 9 additional colonies did not achieve the same degree of statistical significance. On balance, the gull monitoring program appears to indicate continuing, gradual OCS declines.

Discussion of sufficiency of temporal data [Framework Crosswalk 3.4]

The strongest declining trend in any substance should occur immediately after a large reduction in loadings. From the sediment cores in Lake Ontario, it appears likely that the steepest declines in OCS levels in the Great Lakes took place during the 1970s. OCS was added to some monitoring programs, after this period of steepest decline.

Herring gull and lake trout are relatively high in the aquatic food web and acquire relatively high levels of OCS. They are valuable integrators of OCS within the food web, since OCS levels are often too low to be detected in other media.

Another valuable source of temporal data are dated bottom-sediment cores, sampled from deep water. There are three studies and multiple (13) cores pertaining to Lake Ontario. These provide especially useful perspectives, since large declines took place before lake trout and herring gull monitoring programs began to measure OCS.

The fullest long-term picture of OCS pertains to Lake Ontario. Sediment cores indicate a decline of 60-90%, by the late 1970s. Recent data from herring gulls and trout show subsequent decline, adding to the total decline since levels during the 1960s.

Viewed together, these indicators point to a massive decline in OCS levels in Lake Ontario biota since the 1960s. This one-lake picture is also consistent with the general decline in OCS levels in herring gulls noted across the 800 mile-wide Great Lakes watershed between 1987 - 2001.

Table 3: OCS from a temporal perspective, chronologically by lake

Waterbody	Medium	Time Frame	OCS% Decrease	Discussion
St. Lawrence River	Water	1989-96	N/A 90% recent non-detects	Intermittent detection w/river flow, low OCS concentration. (EC, unpublished)
L. Ontario	Sediment core	1900-80	90%+ (cumulative to 1980)	Strong confidence, endpoint indicator. Published (Durham and Oliver, 1983)
L. Ontario	OCS found in 8 of 11 sediment	1960-80	65 % (cumulative to 1980)	Strong confidence, endpoint indicator, multiple cores. Published (Kaminsky and

⁴³ Petit, K. E. *et al.* 1994. *Atlas of contaminants in eggs of fish-eating colonial birds of the Great Lakes (1989-1992)*. Technical Report No. 193, Canadian Wildlife Service

⁴⁴ Council of Great Lakes Industries, March 1, 1999, report on Octachlorostyrene available at: <http://www.cgli.org/BiToxOxy.pdf>.

⁴⁵ Weseloh, D.V., Havelka, T., and Pekarik, C. 2002. "Trends in Great Lakes Herring Gull Eggs." In: *Great Lakes Binational Toxics Strategy Annual Progress Report*. USEPA and Environment Canada.

⁴⁶ C. Weseloh, Canadian Wildlife Service, personal conversation, 2004

	cores			Hites, 1984)
L. Ontario (Niagara Bar)	Sediment core	1960–81	12 % per year OCS beneath detection after 1981	NYDEC, 1995, unpublished, reported by Smith, 1999, available at: http://www.cgli.org/BiToxOxy.pdf .
L. Ontario	Lake trout	1977–93	10 % per year 100% detection	Strong confidence, endpoint indicator. Published (Heustis, <i>et al</i> , 1996).
L. Ontario	Water	1984–96	20% per year 100% recent non-detects	EC, unpublished? Smith, 1999 at: http://www.cgli.org/BiToxOxy.pdf .
L. Ontario	Herring gull egg	1987-98	17% per year	Strong confidence, endpoint indicator. Smith, 1999: http://www.cgli.org/BiToxOxy.pdf .
L. Ontario	Herring gull egg	1987 and 2001	67% cumulative	Decline not statistically significant (Weseloh, Havelka, Pekarik, 2002).
L. Ontario	Lake trout (U.S.)	1999-2000	No trend, since OCS just added.	Lake Ontario fish had 10-fold higher levels (0.01 to 0.02 ug/g) relative to other lakes (0.001 to 0.006). (Murphy, EPA, 2004, unpublished, preliminary data)
L. Ontario	Water, dissolved phase	1998, 99, 01	Non-detect	Unpublished? EC (EHD, ECB, Ontario Region), 2004
L. Ontario	Tributary surface sediment	2001-2003	No detection at 112 Canadian tributaries sampled	Unpublished? EC, 2004
Lower Niagara River	Spot-tail shiner	1985-95	8 % per year (Smith, unpublished, 1999) (100% recent non-detects)	Program described by Suns <i>et al</i> (1982, 1992, 1993).
Niagara River	Herring gull egg	1987-98	17% per year	Strong confidence, endpoint indicator. Smith, 1999: http://www.cgli.org/BiToxOxy.pdf .
Niagara River	Herring gull egg	1987 and 2001	22.33% cumulative	Decline not statistically significant (Weseloh, Havelka, Pekarik, 2002).
Lower Niagara River	Water	1987–95	16 – 21 % per year (50% recent non-detects)	Fast flowing connecting channel, no equilibrium; local versus whole-lake measure. EC, unpublished, reported by Smith, 1999: http://www.cgli.org/BiToxOxy.pdf .
Lower Niagara River	Whole water and suspended sediment	1989-2000	Suspended sediment decline from 7.8 ng/g to 0.9 ng/g. (88 percent, cumulative). Water decline from 0.065 to 0.003 (95 percent decline)	Env. Canada, USEPA, MOE, NYSDEC. Upstream/Downstream Niagara River Monitoring Reports (1989-2000)
Lake Erie	Herring gull egg	1987-98	16 % per year	Strong confidence, endpoint indicator. Smith, 1999: http://www.cgli.org/BiToxOxy.pdf .
Lake Erie	Herring gull egg	1987 and 2001	68.08% cumulative	One Erie colony has statistically significant decline; one decline not so statistically robust. (Weseloh <i>et al</i> , 2002)
Lake Erie	Water, dissolved phase	1998, 2000	Non-detect	Unpublished? EC, 2004
Lake Erie	Tributary surface sediments	2001-03	Non-detect at 96 of 97 Canadian tributaries	Unpublished? EC, 2004
Lake Erie	Atmospheric deposition	1999-2002	Two-thirds decline (cumulative) from 2.7 pg/m ³ to 0.86.	Hulting, unpublished, preliminary, 2004
Detroit River	Herring gull egg	1987 - 1998	20% per year	Strong confidence, endpoint indicator. Smith, 1999:

				http://www.cgli.org/BiToxOxy.pdf .
Detroit River	Herring gull egg	1987 - 2003	86% decline (cumulative)	Weseloh, CWS, 2004, unpublished
Lake St. Clair	Sediment core	Unreported	74 % decline (cumulative)	St. Clair is shallow, increasing chance of a disturbed core. Reported by Painter, EC, 2002. Moderate confidence, yet credible, in light of declines observed elsewhere.
St. Clair R. Mouth (Port Lambton)	Suspended sediment	1989-96	15% per year (95% recent non-detects)	"Results are scattered, typical of sediment data. Levels are generally lower in the late 1990s." EC, unpublished, 2004
St. Clair River	Tributary surface sediments	2001-03	Detected at 4 Canadian tributaries	Unpublished? EC, 2004
St. Clair River	Whole-water	2002-03	New program, no trend yet	0.011 ng/L OCS at mouth, Canadian side. Non-detect U.S. side and headwater. EC, unpublished, 2004
Lake Huron	Herring gull egg	1987-98	16 % per year	Strong confidence, endpoint indicator. Smith, 1999: http://www.cgli.org/BiToxOxy.pdf .
Lake Huron	Herring gull egg	1987 and 2001	61 % decline (cumulative)	Decline not statistically significant (Weseloh, Havelka, Pekarik, 2002).
Lake Huron	Water, dissolved phase	1999, 2000	Non-detect	Unpublished? EC, 2004
Lake Superior	Herring gull egg	1987-98	17 % per year	Strong confidence, endpoint indicator. Smith, 1999: http://www.cgli.org/BiToxOxy.pdf .
Lake Superior	Herring gull egg	1987 and 2001	51.46% decline cumulative	Decline not statistically significant (Weseloh <i>et al</i> , 2002).
Lake Superior	Water, dissolved phase	1996, 97, 01	Non-detect	Unpublished? EC, 2004
Lake Superior	Atmospheric deposition	1999-2002	40 percent decline cumulative (0.8 to 0.5 pg/m3)	Hulting, unpublished, preliminary, 2004
Upper Lake Michigan	Herring gull egg	1987-98	20% per year	Strong confidence, endpoint indicator. Smith, 1999: http://www.cgli.org/BiToxOxy.pdf .
Upper L. Michigan	Herring gull egg	1987 and 2001	78.84% (cumulative)	Decline statistically significant for one colony, not significant at the other (Weseloh <i>et al</i> , 2002).
Lake Michigan	Atmospheric deposition	1999-2002	Two-thirds decline (cumulative) from 1.8 to 0.55 pg/m3	Hulting, unpublished, preliminary, 2004
L. Michigan (Chicago)	Atmospheric deposition	1999-2002	40 percent decline (cumulative) (1.5 to 0.85 pg/m3)	Hulting, unpublished, preliminary, 2004

Table 4: Temporal focus on Lake Ontario

	1970s	1977-1993	1987 and 2001	2002
Sediment cores	65+% ⁴⁷			
Lake trout		10% per year ⁴⁸		

⁴⁷ Durham, R. W. and B. G. Oliver. 1983. "History of Lake Ontario contamination from the Niagara River by sediment radiodating and chlorinated hydrocarbon analysis." *J. Great Lakes Res.* 9(2): 160-168. Also, Kaminsky, R and Hites, R. 1984. "Octachlorstyrene in Lake Ontario." *Environ. Sci. Technol.*, 18, 275-279.

Herring Gulls			67% ⁴⁹	
Tributary sediments				No detection at 112 tributaries ⁵⁰

A massive decline in OCS is evident in the lake with the longest chronological record, provided through several indicators

Table 5: Temporal focus, lake trout, Lake Ontario

Year	OCS mean	Std dev.	Reference
1977	263 ppb	156	Heustis <i>et al</i> , 1996. Trout (4 yrs old) caught at Main Duck Island; whole fish; wet weight
1977	281		Kuehl <i>et al</i> , 1981. Whole fish, wet weight. Sampled Cape Vincent, NY
1978	98.6	39.8	Heustis <i>et al</i> , 1996.
1979	86		Kuehl <i>et al</i> , 1981. Sampled at Stony Island, NY.
1980	96.7	68.3	Heustis <i>et al</i> , 1996.
1981	54	17.6	Heustis <i>et al</i> , 1996.
1982	79.4	23.4	Heustis <i>et al</i> , 1996.
1983	54.4	18.1	Heustis <i>et al</i> , 1996.
1984	106	106	Heustis <i>et al</i> , 1996.
1986	43.7	12.1	Heustis <i>et al</i> , 1996.
1987	30.5	7.73	Heustis <i>et al</i> , 1996.
1988	43	16.3	Heustis <i>et al</i> , 1996.
1989	36.7	14.3	Heustis <i>et al</i> , 1996.
1990	31.6	7.73	Heustis <i>et al</i> , 1996.
1991	33.5	9.38	Heustis <i>et al</i> , 1996.
1992	29.4	12.3	Heustis <i>et al</i> , 1996.
1993	31.3	8.3	Heustis <i>et al</i> , 1996.
1999	19.5		Murphy, 2004, preliminary, unpublished. Whole fish, wet weight. Caught at North Hamlin.
2000	9.6		Murphy, 2004, preliminary, unpublished. Caught at Oswego, NY

OCS levels in lake trout sampled from Lake Ontario have declined. Initial sampling began in 1977

Criteria and risk [Framework Crosswalk 3.2]

Likely owing to the higher levels of OCS in Lake Ontario, the State of New York has set a water quality criterion for OCS of 6×10^{-6} ug/L. (This is supported by an acceptable daily intake of 0.03 ug OCS/kg/day for non-oncogenic effects.⁵¹)

There were exceedances of this criterion on a "whole-water" basis at the mouth of the Niagara River during 1989-91 and during 1998. On a positive note,

⁴⁸ Huestis, S. Y., Servos, M.R., Whittle, D.M., and Dixon, D.G. 1996. "Temporal and age-related trends in levels of polychlorinated biphenyl congeners and organochlorine contaminants in Lake Ontario lake trout." *J. Great Lakes Res.* 22(2): 310-330

⁴⁹ Weseloh, D.V., Havelka, T., and Pekarik, C. "Trends in Great Lakes Herring Gull Eggs." In: *Great Lakes Binational Toxics Strategy Annual Progress Report, 2002*. USEPA and Environment Canada.

⁵⁰ Environment Canada, unpublished, provided by A. Waffle.

⁵¹ New York Dept. of Env. Conservation. 1997. OCS, ambient water quality value, fact sheet.

during the 1990s, there was a decreasing trend in OCS in the Niagara River. Recent data indicate that the criterion is being marginally met.

There are no sediment quality criteria.

Should OCS-specific criteria be developed for sediments or other media? As mentioned previously, toxicological information, albeit limited, suggests that OCS is not highly hazardous. [Note: the USEPA and Environment Canada did not include OCS in the GLBTS program based on a comparative risk assessment among the full breadth of trace chemical exposures.] In addition, the preponderance of environmental data suggests that OCS levels in Lake Ontario have massively declined, with recent ebbing generally seen across all lakes. There is no evident risk-based rationale for now commissioning OCS-specific regulations or toxicological studies. Though one substance, OCS, can often be detected by analytic chemists at very low levels, this alone does not constitute strong grounds for considering that a trace exposure to OCS constitutes a priority risk to living things, especially in relation to many other, unmonitored trace chemical exposures.

There are few studies on the potential health effects of OCS, probably in part because OCS has never been a commercial product that warranted testing. One study investigated acute effects of OCS on nitocra spines (an aquatic organism).⁵² There are also studies with OCS dosing of rats.⁵³

It is sometimes assumed that substances under the Great Lakes Binational Toxics Strategy are “bad actors.” The limited toxicological information does not suggest that OCS is more toxic than a great number of other substances.

Nonetheless, Health Canada has established a Minimum Risk Intake for OCS of 0.31 ug/kg body weight/day (= to 310 ng/kg bw/day). According to Health Canada: “The estimated exposures for the general population of the Great Lakes basin from this assessment, ranging from 0.02 ng/kg bw/day in adults to 12.86 ng/kg bw/day in exclusively breast-fed infants, constitute from <1% to 4% of the MRI, respectively.”⁵⁴ Therefore, there seems no concern regarding human health exposures in the Province of Ontario.

Data sufficiency? (Framework Crosswalk 3.4)

This section is said to be a “safety check for cases where sufficient monitoring data is (sic) not available; or where environmental trends are decreasing and criteria have either not been established or are not being exceeded.”

There are sufficient monitoring data on OCS for the purposes of management decisions under the GLBTS process.

The second condition mentioned above generally holds. OCS levels seem to be declining in the Great Lakes; generally there are not criteria in existence; and for the few that do exist, there are generally not exceedances of those criteria. (That there are no exceedances of a New York water quality criterion or a Health Canada MRI seem welcome.)

This section seems to ask if the absence of criteria might hide recognition of an underlying problem? Since current OCS levels are likely under 5% of their levels in the 1960s, it may be inferred that a problem, if there was one, is now 20-fold smaller.

⁵² Tarkpea, M. et al. 1985. “Mutagenicity, acute toxicity, and bioaccumulation potential of six chlorinated styrenes.” *Bull. Environ. Contamin. Toxicol.*, 35, 525-530.

⁵³ Chu, I., Secours, V. E., Villeneuve, D.C. and Valli, V. E. 1982. “Acute and subacute toxicity of octachlorostyrene in the rat.” *J. Toxicol. Env. Health*, 10, 285-296. Also, Chu, I., et al. 1984. “Octachlorostyrene: a 90 day toxicity study in the rat.” *Fundamental and Applied Toxicology*, 4, 547-557. Also, Chu, I. 1986. “Long-term toxicity of octachlorostyrene in the rat.” *Fundamental and Applied Toxicology*, 6, 69-77

⁵⁴ Laube, V., Arvanitakis, A., Jordan, S., Haines, D., and Gupta, S. 1998. “Octachlorostyrene.” In: *Persistent Environmental Contaminants and the Great Lakes Basin Population: an exposure assessment* by Health Canada.

There are continuing sources of OCS, though many are likely distant from the Great Lakes and generation of OCS does not necessarily signify its release to the environment. Section 4 will discuss some potential current sources of OCS formation.

Environmental assessment conclusions (Framework Crosswalk 3.5)

OCS levels have been relatively high in Lakes Erie and Ontario, because of sources along the Niagara River and further upstream. Sediment cores indicate that OCS levels in Lake Ontario peaked during the 1960s. Sediment, gull and trout data collectively indicate that the decline in Lake Ontario, where levels were once highest, has exceeded 90 percent.

There has also been a widespread decline in OCS across all lakes since 1987, principally indicated by herring gull data. The herring gull monitoring program is uncommonly valuable, in duration, broad geographic coverage, and for measuring a trace chemical burden at a biological receptor.

A sediment core from Lake St. Clair also indicates a 75 percent reduction,⁵⁵ though a core from shallow water is an indicator with more attendant uncertainty.

4. Potential Sources, Past or Current [Framework Crosswalk 4.0]

This section will review environmental and industrial literature to consider potential generators of OCS, in the past and currently. Considering how human activities may have released OCS during the past helps to explain why levels have declined in the Great Lakes.

Formation

Octachlorostyrene is unknown to have been synthesized, on an industrial scale. Rather OCS is thought a byproduct of circumstances that bring together chlorine, carbon, and sufficient energy. This suggests that a variety of reaction conditions and mechanisms yield OCS.

Table 6: Some conditions associated with OCS formation⁵⁶

Process	Temp	Energy Source	Carbon Source	Chlorine Source
Chlor-alkali, w/graphite anodes (obsolescent)	220F	Electricity	Carbon anodes with tar binder; Rubber cell liners	NaCl input & Cl ₂ produced
Magnesium: (1) purification stage; (2) electrolysis of molten MgCl stage	800C	Electricity	(1) Added (2) Electrodes	1. Cl ₂ atmosphere 2. MgCl; Cl ₂ produced
Aluminum Foundries	600C		Hexachloroethane	HCE & Cl ₂
Secondary copper smelting	700C		Coal	8% NaCl under reducing conditions
Carbon tetrachloride	550-600C		Propylene	Cl ₂

Some laboratory-scale syntheses of OCS have been published:

- Chlorination of benzo[b]thiophene, followed by oxidation of a product, followed by pyrolysis at 300C.⁵⁷

⁵⁵ Painter, S. 2002. "Trends in Great Lakes Sediment." In: *Great Lakes Binational Toxics Strategy Annual Progress Report*. USEPA and Environment Canada.

⁵⁶ For references, see footnotes corresponding to later discussion

- This reaction was mechanistically similar to pyrolysis of octachlorobenzocyclobutene to OCS.⁵⁸
- Another study reported 20% formation of OCS (and 40% formation of hexachlorobenzene) via high temperature (600C) chlorination, in carbon tetrachloride diluent, of n-propylbenzene.⁵⁹
- Chlorination of perchlorophenylacetylene.⁶⁰
- Reaction of perchlorotoluene with cuprous chloride, diethylphosphite, and carbon tetrachloride, yielding 55% OCS.⁶¹
- Vaporization of 2-vinyl-pyridine in carbon tetrachloride, then mixed with chlorine gas at 595C.⁶²
- Mixing dichlorostyrene in carbon tetrachloride for 20 hours at room temperature, distillation, SbCl₅ added, and heated for four hours at 190C.⁶³

Shulman and Klingele (1984) considered possible chemical reaction mechanisms for forming polychlorinated styrenes, including OCS, based on interpretations of published literature. They hypothesized:

"It is highly probable that the mechanism of polychlorinated styrene formation involves stepwise condensation or addition reactions leading to increasingly conjugated, increasingly chlorinated species. Each reaction in the stepwise formation of polychlorinated styrenes could fall into two broad categories: 1) ultra-trace concentrations of reactants combine in high yields; or 2) high concentrations of reactants combine in ultra-trace yields.

In the former case, the free energy of formation of the product at each step is lower than the free energies of reactants and other competing products. Reaction conditions favoring the former would probably involve high-energy environments where polychlorinated aromatics like polychlorinated styrenes would be stable relative to other molecular configurations. Such conditions would be likely to prevail in high-energy electro-, pyro-, photo-, and thermo-chemical reaction environments.

In the latter case, the free energies of formation of reactants and other products are lower than the polychlorinated styrene precursor products, but the statistics of the reaction chemistry assure that some of each of the successive precursor products will be generated in some amounts. Reaction conditions favoring the latter case would involve lower energy reactions in which polychlorinated organic substances are reactants or intended products. Further, if polychlorinated styrenes were removed from the reaction environment faster than other, more stable products, say via physical processes such as sorption to the walls or bottom of a reactor vessel or to particulate matter in the reaction matrix, significant quantities of polychlorinated styrenes could still be generated, even though not thermo-chemically favored....

Whatever the details of the mechanism, it seems likely that a carbon-chlorine reaction can and will build up per-chloro-aromatics under the right conditions, including hexachloro-benzene, octa-chloro-styrene, octa-chloro-naphthalene, octa-chloro-dibenzo-furan, and octa-chloro-dibenzo-p-dioxin, due to the increasing stability and decreasing reactivity toward oxygen of increasingly conjugated, increasingly chlorinated free radicals... Whenever a carbon source is exposed to chlorine and large energy flux, as either electricity or heat, and indicator compounds such as carbon tetrachloride, per-chloro-ethylene [highly chlorinated ethylene compounds], and per-chloro-benzene [highly chlorinated benzene compounds] are produced, polychlorinated styrenes are a suspected byproduct. [Or] Whenever aromatic compounds, particularly chlorinated ones, are

⁵⁷ Raasch, M. S. 1980. *J. Org. Chem.*, 45, 856

⁵⁸ Roedig, A., et al. 1972. *Tetrahedron Lett.*, 2613-5

⁵⁹ Ruetman, S. H. 1975. "Synthesis of perchlorinated indene and 5H-1-Pyridine." *Synthesis*, 382-384

⁶⁰ Ballester, M. et al. 1977. *Tetrahedron Letters*, 2353

⁶¹ Ballester, M. et al. 1980, reported in *Chem Abstr* 95: 4206W

⁶² Sieber, J. N. 1971. *J. Org. Chem.*, 36, 2000

⁶³ Bieneik and Korte 1978, reported in CAS Online: CA90: 54582t

exposed to conditions where chloroalkyl radicals may be present, polychlorinated styrenes are a suspected byproduct.”⁶⁴

Other chlorinated hydrocarbons as indicators of OCS

In an earlier review of OCS sources, EPA proposed that HCB and PCDD could each serve as indicators of potential OCS formation.⁶⁵ In this earlier document, EPA estimated OCS air emissions by extrapolating from national air emissions inventories for PCDD and HCB by OCS multipliers (653 and 0.15, respectively), derived from the ratio of PCDD to OCS in a sample of fish tissue and the ratio of HCB to OCS in a sediment sample.

There are reasonable grounds for considering that processes known to yield chlorinated hydrocarbons may, among these, produce OCS. HCB and OCS have close structural similarity. **All studies known to have analyzed for both compounds have found both.** (Table 5 provides a cross-reference to literature on OCS, HCB, and PCDD from various sources.)

EPA has long regarded PCDD as indicative of a wide range of chlorinated compounds. Many more studies have evaluated potential sources for PCDD/F than for the unregulated OCS, hence the usefulness of viewing PCDD a possible indicator of OCS generation. Yet, the OCS relationship with dioxin is likely to be less consistent as the relationship with HCB.

Unlike EPA's earlier review of potential OCS sources, this Assessment does **not** offer a numeric estimate of OCS air emissions. To include such might suggest unwarranted exactitude.

Table 7: Literature cross-reference regarding potential sources

Sector	OCS	HCB	PCDD/F
Chlor-alkali (discontinued anodes)	Footnotes 41	64	63
Chemicals	65, 66, 67, 69, 70, 71	65, 66, 67, 68, 69, 70, 71, 72	
Magnesium (via electrolysis)	74, 75, 76, 78, 79	74, 75, 76, 78, 79	75, 76, 79
Titanium, titanium tetrachloride	Magnesium applies	Magnesium applies	EPA dioxin inventory
Niobium, Tantalum	84	84	
Sodium	85		
Nickel			74
Aluminum foundries and secondary smelters	88, 89, 90	88, 89, 90	88, 89, 90
Secondary copper smelting	95	95	95, 96
Graphite	100		
Incineration	101, 102, 103, 104	101, 102, 103, 104	
Semi-conductors	105	105	

OCS, HCB, and PCDD/DF are often found near the same potential sources

Past potential source: chlor-alkali

A reported past source of OCS was the chlor-alkali industry, which produces chlorine and sodium or potassium hydroxide from brine. From the 1890s into the

⁶⁴ Schulman, E. M. and Klingele, H. “Sources of Polychlorinated Styrenes in the Great Lakes and their tributaries.” USEPA Great Lakes National Program Office, Grant R00-5764-01, SUNY-Buffalo, draft final report, 1984.

⁶⁵ USEPA-Great Lakes National Program Office. “OCS: A review of potential sources.” Draft for public comment, 11/5/98.

1970s, this industrial technology employed graphite anodes, which eroded, forming “taffy tar” wastes. OCS was reported in a sample of spent chlor-alkali taffy tar.⁶⁶

Another study reports chlor-alkali taffy tar included PCDFs.⁶⁷ PCDFs have been reported from magnesium production via electrolysis, a known OCS source.

Two studies at a former chlor-alkali site report PCBs, HCB, and polychlorinated naphthalenes, attributed to taffy tar wastes.⁶⁸ (It is likely OCS would have been detected had it too been analyzed.)

Potential current OCS sources (Framework Crosswalk 4.1 and 4.2)

Chemical Production: Some chemical factories have in the past seemed plausible sources of water and/or air releases of OCS. Subsequent process improvements may have prevented or reduced potential past releases.

A number of studies illustrate the potential for OCS formation by chemical factories:

- OCS and HCB were reported in the groundwater beneath a chemical complex in Sarnia, Ontario.⁶⁹
- The highest levels of OCS in Great Lakes biota have been downstream of clusters of chemical factories near Sarnia, Ontario; Ashtabula, Ohio; and Niagara Falls, NY.
- HCB and (much lower levels of) OCS were detected in sediments from the Bayou D’Inde near to a factory producing trichloroethylene and perchloroethylene.⁷⁰
- HCB and OCS were principal components found in wastes from production of carbon tetrachloride and perchloroethylene, two solvents and intermediates.⁷¹ (Lesser constituents included hexachlorobutadiene, octochloronaphthalene, decachlorobiphenyl, and octachlorodibenzofuran.)
- Manufacture of chlorinated solvents and pesticides have been reported to generate HCB.⁷²
- Studies in Spain reported OCS and HCB, plus trichloroethylene and carbon tetrachloride, in river water downstream of a solvent factory.⁷³ HCB was also detected in the nearby atmosphere and, with OCS and PCBs, in food produce grown within the area influenced by atmospheric emissions.⁷⁴

OCS used to be found near Ashtabula, Ohio. Schulman and Klingele (1984) reviewed chemical production plants in this area for processes that they thought could have emitted OCS as a component within waste streams. They hypothesized that 2,4-toluenedisocyanate production may have been a source, because of the presence of chlorobenzenes and styrene in a settling basin.⁷⁵ They suggested phenolic resin production via the Raschig-Hooker process might generate HCB and

⁶⁶ Kaminsky, R and Hites, R. 1984. “Octachlorostyrene in Lake Ontario.” *Environ. Sci. Technol.*, 18, 275-279

⁶⁷ Svensson, B-G, *et al.* 1993. “Exposure of PCDD and PCDF from Graphite Electrodes in a Chlor-alkali Plant.” *Chemosphere*, 27, 1-3, 259-262

⁶⁸ Kannan, K., *et al.* 1998. *Environ. Sci. Technol.*, 1214-1221 and 2507-2514

⁶⁹ Oliver, B. G., *et al.* 1986. “Chlorinated contaminants in St. Clair River sediments.” *Water Poll. Res. J. Canada*, 21, 3, 344-350. Also, Canadian Chlorine Coordinating Committee, <http://www.cfour.org/case/dow.html> (4/3/98)

⁷⁰ Pereira, W. E. *et al.* 1988. *Environ. Sci. Technol.*, 22, 772-778

⁷¹ Markovec, L. *et al.* 1984. *Analyst*, 109, 497-501

⁷² Quinlivan, S. C. *et al.* 1977. *J. Hazardous Materials* 1, 343-359. Also, Jacoff, F.S. *et al.* 1986. Proceedings HCB Conference. Oxford Univ. Press.

⁷³ Amaral, O. *et al.* 1996. *Wat. Res.*, 30, 8, 1876-84

⁷⁴ Otero, R. *et al.* 1994. *Toxicological and Environmental Chemistry*, 46, 61-72

⁷⁵ Schulman, E. M. and Klingele, H. “Sources of Polychlorinated Styrenes in the Great Lakes and their tributaries.” USEPA Great Lakes National Program Office, Grant R00-5764-01, SUNY-Buffalo, draft final report, 1984.

OCS. Other processes that they identified as potential OCS emitters near Ashtabula were production of titanium tetrachloride, phosgene, polyvinyl chloride, and chlor-alkali products.

Nowadays, there is no known evidence of ongoing releases of OCS in the vicinity of Ashtabula.

The U.S. Halogenated Solvents Alliance advises that chlorinated solvents production appears to have been a source of OCS in the past, but there have been changes in the manufacturing process during the past 10 to 15 years. Also, waste products from solvent manufacture are reused or incinerated.

The Alliance does not necessarily disagree with using HCB as an indicator for OCS, but advises that the ratio of HCB to OCS should be based on measurements within waste streams rather than environmental levels, and on actual measures of HCB, which in 1996 were estimated by its members to be 250 pounds to water and 201 pounds to air.⁷⁶

During 1998, 1.5 million pounds of wastes that contained HCB were reported by chemical manufacturers in Texas and Louisiana to EPA's Toxic Release Inventory.

During 2002, five facilities reported generation of 808 pounds of OCS, including three inorganic pigment producers, one chemical and vinyl producer, and one magnesium metal producer.⁷⁷ These are located in Mississippi, Tennessee, Delaware, Louisiana, and Utah, respectively. These reporting facilities estimated that only 0.2 pounds of OCS were released to the atmosphere, whereas the predominant remainder was transferred to landfills or surface impoundments.

Magnesium: Electrolytic production of magnesium was among the first recognized sources of OCS and a factory in Norway was highly studied during the 1970s and 1980s:⁷⁸

- Fish in a nearby fjord were found to contain octachlorostyrene, HCB, PCBs, and other chlorinated benzenes and styrenes.⁷⁹
- Air pollution control scrubber water was calculated to contain, on an annual basis, 500 grams of 2,3,7,8-TCDD TEQ, 65% contributed by PCDFs, which were ten times greater in quantity than PCDDs.⁸⁰
- This effluent also contained 7 kg/week of HCB and OCS, 75% of which was HCB. "Hexachlorobenzene, octachlorostyrene, and other highly chlorinated compounds are formed under similar conditions as PCDD/DF, and their presence in the emissions of a technical process should therefore be a good indicator for reaction mechanisms which may also create PCDD/DF...Collected water samples contained about 200-500 mg (dry) of black fine particles per liter...Diffuse losses of process gases to the atmosphere also occurs."⁸¹
- Between 1951-75, the Norwegian factory used coke, probably generating 10 times more HCB/OCS. The authors estimate up to 50-100 kg of 2,3,7,8-TCDD may have been discharged between 1951-88 year period.⁸²
- HCB and OCS were reported in blood samples of magnesium workers.⁸³

⁷⁶ Comments on OCS report, Halogenated Solvents Industry Alliance, March 1, 1999

⁷⁷ USEPA, *Toxics Release Inventory, 2002*, provided by A. Thomas, Battelle Memorial Institute

⁷⁸ Lunde, G *et al.* 1976. *Fresenius Z. Anal. Chem.*, 282, 395-399

⁷⁹ Ofstad, E. B., Lunde, G., and Martinsen, K. 1978. "Chlorinated aromatic hydrocarbons in fish from an area polluted by industrial effluents." *Sci. of the Total Environment*, 10, 219-230.

⁸⁰ Knutzen, J. and Oehme, M. 1989. "Polychlorinated dibenzofuran and dibenzo-p-dioxin levels in organisms and sediments from the Frierfjord, southern Norway." *Chemosphere*, 19, 12, 1897-1909

⁸¹ Oehme, M., Mano, S. and Bjerke, B. 1989. "Formation of polychlorinated dibenzofurans and dibenzo-p-dioxins by production processes for magnesium and refined nickel." *Chemosphere*, 18, 7-8, 1379-1389

⁸² Knutzen, J. and Oehme, M. 1989. "Polychlorinated dibenzofuran and dibenzo-p-dioxin levels in organisms and sediments from the Frierfjord, southern Norway." *Chemosphere*, 19, 12, 1897-1909

Production of magnesium ingots is a multi-stage process. Two stages favor production of chlorinated hydrocarbons: purification in the melter; and the electrolytic stage, both discussed as follows in an industrial encyclopedia:

- Purification stage: Magnesium powder is “melted in an electrically heated, brick-lined melt cell and treated with carbon and chlorine gas to lower the content of magnesium oxide, water, bromine, sulfate, aluminum, and heavy metals. In a second reactor vessel, impurities are further reduced with chlorine gas in the presence of carbon at 830C...Off-gases containing chlorine, hydrogen chloride, sulfur dioxide, magnesium chloride dust, and chlorinated hydrocarbons are scrubbed with milk of lime.”⁸⁴
- Electrolysis stage: “Magnesium chloride is electrolyzed in a molten mixture with alkali chlorides at 700-800C...The brick-lined cell is divided into four to six compartments by semi-submerged refractory partition walls termed semi walls...The semi walls separate the magnesium metal and the chlorine gas...Cells operated at 750-780C have a life of about one year... Anode consumption is 15-20 kg per ton of magnesium.”
- “In electrolytic processes, carbon is used as a reductant in preparation of anhydrous magnesium chloride and as an anode material in electrolysis. The presence of carbon, water, chloride or hydrogen chloride, even in low concentrations, at elevated temperature leads to formation of chlorinated hydrocarbons and other organic compounds. Chloromethanes, chlorobenzenes, polychlorinated biphenyls (PCBs), chlorodibenzofurans, and chlorodibenzo-p-dioxins are highly toxic and are only slowly degraded in nature. Although such compounds only occur in liquid effluents from scrubber systems at low concentrations (a few micrograms per liter), collection and destruction are mandatory.”

An EPA national survey of chemical residues in fish⁸⁵ during the late 1980s reported the second highest recorded OCS levels in a fish near Freeport, Texas, in the vicinity of a then operational magnesium factory. The highest HCB level, by an order of magnitude, was the same sample, also one of the highest for various PCDF isomers and hexachlorobutadiene.

The only electrolytic magnesium factory in the United States, located in Utah, often places among the highest in quantities of substances released, as reported to EPA's Toxics Release Inventory. In 1998, the facility reported 55 million pounds in stack air emissions of chlorine gas.

More recently, in the 2002 TRI, this plant specifically estimated 173 pounds of OCS were placed in surface impoundments. No OCS was reported as volatilizing to air or as emitted to water.

There is one electrolytic magnesium factory operating in the Province of Quebec.

There has also been a recent article regarding formation of OCS during electrolysis of magnesium chloride, not factored above, only because unknown during preparation of this report.⁸⁶

Titanium metal and tetra-chloride: Titanium ore is refined by reaction with chlorine gas and carbon at 925-1,010C to yield titanium tetrachloride.⁸⁷ Conducted in a fluidized-bed reactor, this process emits volatile byproducts. The

⁸³ Lunde, F. and Bjorseth, A. 1977. “Human blood samples as indicators of occupational exposure to persistent chlorinated hydrocarbons.” *Science of the Total Environment*, 8, 241-246

⁸⁴ Hoy-Petersen, N., Aune, T., Vralstad, T., Andreassen, K., Oymo, D., Haugerod, T., Skane, O. “Magnesium.” *Ullmann's Encyclopedia of Industrial Chemistry*, c. 1989.

⁸⁵ USEPA 1992, EPA 823-R-92-008a

⁸⁶ Deutscher, R. L., Cathro, K.J. 2001. “Organochlorine formation in magnesium electrowinning cells.” *Chemosphere*, 43, 147-155.

reaction of abundant chlorine and available carbon in this temperature range is likely to form OCS.

One step in the production of metallic titanium is electrolytic separation of molten MgCl₂, using graphite anodes, akin to a step in magnesium production. This step is likely to generate OCS.

Two U.S. facilities produce titanium by electrolysis. Under EPA's Toxics Release Inventory, each of these facilities have in recent years reported combined air emissions of chlorine and HCl in the vicinity of 50,000 pounds.

In the 2002 TRI, three titanium tetrachloride producers in the United States reported 0.2 pounds of OCS released to surface water and 634 pounds to land disposal.

In addition, the Council of Great Lakes Industries advises that these three facilities have committed to a significant reduction in generation of wastes characterized by the USEPA as "Persistent, Bioaccumulative Toxicants", including OCS.

Niobium and tantalum: These metals are used as alloys in steel. One method of refining ore containing niobium reacts chlorine gas with ore and carbon at 500-1,000C.⁸⁸ One study seems to report that water showered on exhaust fumes from this process contained HCB, OCS, and decachlorobiphenyl.⁸⁹ As of 1993, there were five U.S. producers of niobium and tantalum, two of these extracting from ore.

Sodium: One process for production of sodium is electrolysis of fused sodium chloride in a Downs cell. One such factory is indeed located in Niagara Falls, NY, an area with a number of candidate processes that may have contributed to past environmental releases of OCS. This cell uses a graphite anode and operates at 580C. Carbon tetrachloride boils off the cells and may be a marker for formation of OCS.⁹⁰

Vanadium and compounds: Vanadium metal production entails roasting ore at 850C with sodium chloride or carbonate, followed by water/acid leaching and solvent extraction.⁹¹ OCS emissions, if any, would depend on a carbon source and on management of off-gases.

Vanadium oxytrichloride is produced from vanadium pentoxide by chlorination with charcoal at high temperature. Vanadium tetrachloride is produced by chlorination of vanadium compounds in the presence of carbon at 800C. Both processes would have potential to form OCS.

Nickel: One process for producing nickel reportedly entails chlorine leaching of Ni-Cu; followed by precipitation processes employing chlorine gas and alkylbenzene; followed by electrolysis of NiCl and CoCl. The temperatures employed do not normally exceed 150-200C. However, "Formation of PCDD/F due to catalytic effects of heavy metals such as Ni, Co, and Cu cannot be excluded."⁹² (It is unknown if this process is used in the United States.)

Aluminum foundries and secondary smelters: Several studies have documented that chlorinated hydrocarbons (including OCS, HCB, and less chlorinated benzenes) formed when hexachloroethane (HCE) was used, in Germany, to remove

⁸⁷ "Titanium." *Kirk-Othmer Encyclopedia of Chemical Technology*, 1996

⁸⁸ *Kirk-Othmer Encyclopedia of Chemical Technology*, 1996

⁸⁹ Vogelgesang, Jurgen. 1986. "HCB, OCS, and other organochlorine compounds in waste water from industrial high temperature processes involving chlorine." *Z. Wasser- Abwasser-Forsch.*, 19, 140-144.

⁹⁰ Schulman, E. M. and Klingele, H. "Sources of Polychlorinated Styrenes in the Great Lakes and their tributaries." USEPA Great Lakes National Program Office, Grant R00-5764-01, SUNY-Buffalo, draft final report, 1984.

⁹¹ *Kirk-Othmer Encyclopedia of Chemical Technology*, 1996

⁹² Oehme, M., Mano, S. and Bjerke, B. 1989. "Formation of polychlorinated dibenzofurans and dibenzo-p-dioxins by production processes for magnesium and refined nickel." *Chemosphere*, 18, 7-8, p. 1379-1389

hydrogen gas during the melting of aluminum for casting into final forms.^{93 & 94} This process dates to the 1930s. In one facility to produce aluminum pistons, aluminum logs were melted and cast in moulds made of clay and graphite, which eroded and required biweekly replacement. The process operated at 500-600C. When the source of aluminum includes post-consumer scrap, such as beverage cans, this input may contain chemical coatings that contain chlorine.

Another study attempted to quantify air emissions of organochlorine compounds from a small foundry.⁹⁵ Major organochlorine emissions were HCB (4,300 ug/g HCE), OCS (780 ug/g HCE), and unreacted HCE (550 ug/g HCE). Other chlorobenzenes, chlorophenols, PCDDs (0.034 ug/g) and PCDFs (0.036 ug/g) were also measured. The largest emission was hydrogen chloride (330,000 ug/g). Based on this test and HCE use in the United Kingdom, the study estimated annual OCS emissions from the United Kingdom to be 1,200 pounds per year at that time, and HCB air emissions to be 6,000 pounds per year at that time, from this sector.

An occupational health study reported nine foundry workers from six different foundries in Sweden had significantly higher OCS burdens (54.6 ng/g) than control subjects (0.7 ng/g).⁹⁶

In 1992, the Oslo-Paris Commission recommended phase out of HCE in the secondary aluminum industry and in the primary industry with integrated foundries. In some instances, inert gases like argon can be used by foundries.⁹⁷

In 1999, the Aluminum Association reported that use of HCE was rare in the United States. In 1992, only 13 small secondary furnaces among 686 furnaces in the U.S. reported HCE use.⁹⁸

Currently, the Council of Great Lakes Industries advises that the Aluminum Association reports that now none of its members employ HCE for degassing. The Association also notes that the use of chlorine flux has been reduced in recent years, but is still vital for the recycling and processing of some aluminum products, especially to remove certain impurities, such as magnesium. No substitute is available to serve such purposes. The Association further reports that OCS has not been reported in emissions associated with use of fluxing agents other than HCE, including chlorine. This is thought to be because the HCE contains highly chlorinated alkanes or alkenes necessary to facilitate formation of OCS. Organic materials present on the charged materials are removed before introduction of chlorine, salts, and other fluxing agents.

Primary aluminum: The Council of Great Lakes Industries advises that chlorine is used in primary aluminum degassing operations and a developing MACT rule will reduce the quantity of chlorine used. This process change would result in lower releases of all volatile compounds, including OCS if present.⁹⁹

Secondary copper smelting: A German study has reported copper gravel, extracted from old mine tailings via a roasting process in which 8% sodium chloride and coal were reacted with tailings, contained PCDFs and PCDDs, and larger

⁹³ Vogelgesang, J. *et al.* 1986. "The origin of a contamination of fish from the river Neckar with hexachlorobenzene, octachlorostyrene, and pentachlorobenzene: formation in an industrial process." *Z. Lebensm Unters Forsch*, 182, 471-474.

⁹⁴ Vogelgesang, J. 1986. "Formation of contaminants in the degassing of an aluminum foundry with chlorine." *Z. Wasser- Abwasser-Forsch.*, 19, 140-144.

⁹⁵ Westberg, H.B., Selden, A.I., and Bellander, T. 1997. "Emissions of some organochlorine compounds in experimental aluminum degassing with hexachloroethane." *Appl. Occup. Environ. Hyg.*, 12, 3, 178-183.

⁹⁶ Selden, A. I., Floderus, Y., Bodin, L.S., Westberg, H.B., and Thunell, S. 1999. "Porphyrin status in aluminum foundry workers exposed to hexachlorobenzene and octachlorostyrene." *Archives of Environmental Health*, 54, 4, 248-253

⁹⁷ Kanicki, D. P. *et al.* 1990. "Processing Molten Aluminum: cleaning up your metal." *Modern Casting* 80, 55-58

⁹⁸ Comments on Draft OCS report, Aluminum Association, Feb 25, 1999.

⁹⁹ Council of Great Lakes Industries, March 1, 1999

quantities of HCB, OCS, and decachlorobiphenyl.¹⁰⁰ The production process took place at 700C. Another study reported PCDD/Fs in grass, cows milk, and human blood near a copper reclamation plant.¹⁰¹

Incineration has in the past been used to recover metals out of wire scrap coated with plastics, according to a U.S. study that found PCDD/Fs and HCB near a wire reclamation incinerator.¹⁰²

The Council of Great Lakes Industries advises that "open burning of wire for copper recovery is no longer an industry practice. Insulation is removed from scrap wire before recycling."¹⁰³

In the U.S., primary copper smelting does not entail extraction with chlorine.¹⁰⁴

Graphite: A process for producing high purity graphite entails baking carbon in an Acheson-type furnace at 2,200 to 3,000C. The furnace is flushed with chlorine gas during this baking in order to convert metals, mostly iron, to volatile chlorides and thus remove them from the graphite. Exhaust gas at one factory was vented to a caustic scrubber and chlorinated hydrocarbons would likely have been captured in scrubber liquid. This process having once been employed in Niagara Falls, NY, was hypothesized as a source of OCS to Lake Ontario.¹⁰⁵

Incineration: Under certain incineration conditions, OCS and other chlorinated hydrocarbon byproducts are created.¹⁰⁶

In one study, combustion of plastics at various temperatures (400, 600, 800C) yielded HCB and OCS, the authors concluding that "in all combustion processes involving chlorinated substances, the formation of OCS should be expected."¹⁰⁷

An experiment burning polyvinylchloride at various temperatures, found the OCS and HCB yield relatively low between 880-1,090C.¹⁰⁸

Elevated levels of OCS and HCB were found in bottom sediments from an area of the North Sea in which ocean-based combustion took place, prior to the adoption of improved combustion methods.¹⁰⁹

There are many types of incineration processes. The environmental performance of many of these has been improved during the past two decades, in part pursuant to development and promulgation of various regulations. These regulations are usually based on minimization of PCDD/F emissions and by their implementation, past and pending, have had or will have the collateral effect of lowering OCS emissions. This review is focusing on consideration of processes that have been less rigorously evaluated and regulated in terms of trace chlorinated hydrocarbon releases. Reductions in historic emissions from incineration sources

¹⁰⁰ Doring, J., Damberg, M., Gamradt, A., and Oehme, M. 1992. "Screening method based on the determination of perchlorinated aromatics for surface soil contaminated by copper slag containing high levels of polychlorinated dibenzofurans and dibenzo-p-dioxins." *Chemosphere*, 25, 6, 755-762.

¹⁰¹ Riss, A. *et al.* 1990. "Comparison of PCDD/PCDF levels in soil, grass, cows milk, human blood, and spruce needles in an area of PCDD/PCDF contamination through emissions from a metal reclamation plant." *Chemosphere*, 21, 1451

¹⁰² Hryhorczuk, D. O., Withrow, W. A., Hesse, C.S., and Beasley, V.R. 1981. "A wire reclamation incinerator as a source of environmental contamination with tetrachlorodibenzo-p-dioxins and tetrachlorodibenzofurans." *Archives of Environmental Health*, pp. 228-234

¹⁰³ Council of Great Lakes Industries, OCS report, March 9, 1999

¹⁰⁴ Buonicore, A. J. and Davis, W. T. 1992. *Air Pollution Engineering Manual*.

¹⁰⁵ Schulman, E. M. and Klingele, H. "Sources of Polychlorinated Styrenes in the Great Lakes and their tributaries." USEPA Great Lakes National Program Office, Grant R00-5764-01, SUNY-Buffalo, draft final report, 1984.

¹⁰⁶ Ballschmiter, K. *et al.* 1983. *Chemosphere*, 12, 585-594

¹⁰⁷ Lahaniatis, E.S. *et al.* 1989. "Hazardous halogenated substances formed during combustion process." *Toxicological and Environmental Chemistry*, 20-21, 501-506

¹⁰⁸ Ahling, B. *et al.* 1978. *Chemosphere*, 10, 799-806

¹⁰⁹ Lohse, J. 1988. "Ocean incineration of toxic wastes: a footprint in North Sea sediments." *Marine Pollution Bulletin*, 19, 8, 366-371

may be an important factor in the reduction of OCS and other chlorinated hydrocarbons in the Great Lakes region.

Semi-conductors: In some plasma etching processes, layers of material are removed from the surface of a silicon wafer, using gases containing chlorine, under irradiation with radio frequency energy. Byproducts condense and are removed as waste oils.

Constituents have been determined to include HCB and much lower quantities of OCS.¹¹⁰ These waste oils are recognized as a workplace hazard, yet this assessment is not aware of evidence that they are released to the environment.

Less likely potential sources

This Assessment has drawn on available published articles concerning OCS to consider productive processes that may yield OCS as an unwanted byproduct. There are many more societal circumstances that bring together carbon, chlorine, and energy, in various amounts. However, specific circumstances of temperature, concentrations, and perhaps catalysis need to be aligned so as to form OCS.

OCS is not found uniformly in the environment. A national survey of OCS found the substance in only 9% of fish sampled. This uneven geographic distribution suggests that little OCS, if any, would be released by widespread products (e.g., pesticides) or processes (e.g., fuel combustion, paper-making and other broadly distributed varieties of industrial production).

In EPA's November, 1998 draft, some additional potential sources of OCS emissions were hypothesized.¹¹¹ Following review, these are now seen as unlikely.

Coke: *The American Coke and Coal Chemicals Institute advises "coke formation is not like the other processes identified as emitting OCS. The coking process is not incinerative and does not involve the addition of chlorine. Coke is formed by thermally treating coal in the absence of excess oxygen (pyrolysis)...Formation of OCS in coal pyrolysis systems is not favored because 1) chlorine free radicals cleaved from the coal surface during thermal cracking will combine with the nascent hydrogen to form hydrochloric acid, 2) nascent hydrogen abstracts chlorine from the hot coal surface (dehydrochlorination) forming HCl, and 3) alkylchloride free radicals will combine with nascent hydrogen or other alkyl free radicals to produce low molecular weight organochloride compounds such as chloromethane, chloroethane, etc. The immediate consumption of chlorine and alkyl chloride free radicals by nascent hydrogen eliminates a multi-step chlorination reaction involving styrene to produce the fully chlorinated compound OCS."*

[Clarify with CGLI whether to retain.] Also, studies have shown the absence of PCDDs and HCB as byproducts.¹¹²

Metal degreasing with chlorinated solvents: The Halogenated Solvents Industry Alliance advises that temperatures routinely encountered in vapor degreasing are 121C or less; this does not provide sufficient energy to facilitate reactions necessary to produce OCS; and waste generated is subject to strict storage, handling, and disposal requirements under U.S. hazardous waste regulations.¹¹³

Pentachlorophenol: The Pentachlorophenol Task Force has advised that one of its members has analyzed this product for OCS and has not detected any OCS with a limit of quantification of 10 parts per billion.¹¹⁴

¹¹⁰ Schmidt, R. *et al.* 1995. *Toxicology and Industrial Health*, 11, 1, 49-61. Also, Bauer, S., *et al.*, p. 523-541

¹¹¹ USEPA-Great Lakes National Program Office. "OCS: A review of potential sources." Draft for public comment, 11/5/98.

¹¹² Comments, American Coke and Coal Chemicals Institute, March 22, 1999

¹¹³ Comments on OCS report, Halogenated Solvents Industry Alliance, March 1, 1999

¹¹⁴ Comments on OCS report, Pentachlorophenol Task Force, Feb. 26, 1999

In addition, the Council of Great Lakes Industries advises that the temperatures involved in chlorination of phenol to pentachlorophenol, less than 200 degrees Centigrade, are insufficient to rearrange carbon-carbon bonds to form OCS.

In addition, the Council of Great Lakes Industries advises:

“Generally, the incidental formation of PCDDs during pentachlorophenol (PCP) manufacturing is thought to be due to the strong basic conditions and condensation of the chlorophenolate salts with each other. The initial condensation forms polychlorodiphenyl ether, which then undergoes an inter-molecular reaction to form polychloro-p-dibenzo-dioxin. Since technical PCP has significant levels of tetrachlorophenols, the PCDD distribution is predominated by OCDD, followed by varying amounts of HpCDD and HxCDD. Generally, PCDFs are at much lower levels... This fingerprint or product distribution does not resemble any product distribution associated with known sources of OCS. There is no similarity in the reactions responsible for PCDD formation in PCP manufacturing... There is no indication that any of the other OCS precursors are present.” [Clarify retention with CGLI.]

Other pesticide products: HCB has been a micro-contaminant in some chlorinated pesticides.¹¹⁵ Dr. Bailey further advises that the formation of HCB has resulted from specific chemical reactions, so there is no reason to expect that OCS would also be produced. He reports that manufacturers have made process changes to dramatically reduce or eliminate HCB concentrations; and EPA regulates the maximum concentration of HCB allowed in various pesticide products and current manufacturing methods produce materials with HCB well under these concentrations.

Plastics: The Vinyl industry has advised that its production is primarily located outside the Great Lakes watershed; that existing control technologies would minimize any OCS emissions that might be formed during ethylene dichloride or vinyl chloride monomer manufacture; and that, recognizing that OCS emissions are unmeasured, under a worst case estimate, they might be 20.4 kg/yr, or 0.01 percent of national OCS emissions as estimated in EPA’s 1998 report. The Vinyl industry also advises that it has undertaken an extensive evaluation of its various manufacturing and process control technologies, which show that the vinyl industry is a minor source of PCDDs/PCDFs.

Pulp and paper: The Council of Great Lakes Industries advises that OCS and HCB have not been detected in mill waste-streams and that pulp and paper processes have never “favored” formation of such highly chlorinated compounds. In addition, the use of high or complete substitution of elemental chlorine with chlorine dioxide virtually eliminates the tendency. All U.S. bleached-kraft pulp mills have been converted to complete chlorine dioxide bleaching.

Rubber: The Rubber Manufacturing Association has advised that the great preponderance of data indicates that HCB is not emitted during the tire manufacturing process; thus, a derivative assumption of OCS formation is unjustified.¹¹⁶

(Canada) Past, Current, and Potential OCS Sources in Ontarioⁱⁱ

Table 8

Ontario Past, and Potential OCS Sources	Basis for Concern About Possible Releases	Number of Facilities
Likely, Past Sources of OCS in Basin		
Chlor-alkali Production using Graphite Anodes	None. Chlor-alkali production using graphite anodes discontinued in basin ^{a,b}	0
Chlorinated Solvent Production	None. Chlorinated solvents no longer	0

¹¹⁵ Bailey, R. E. 2001. “Global hexachlorobenzene emissions.” *Chemosphere*, 43, 167-182.

¹¹⁶ Comments on OCS report, Rubber Manufacturers Association, February 1999

Ontario Past, and Potential OCS Sources	Basis for Concern About Possible Releases	Number of Facilities
	produced in basin ^{a,c}	
Current Sources Reporting OCS Releases in Basin		
None confirmed	OCS releases not generally monitored; magnitude of point and non-point releases unknown.	No sources confirmed
Potential OCS Sources in Basin		
Primary Aluminum Production	None. No primary aluminum production in Ontario ^a	0
Aluminum Foundries, Secondary Smelting (Al degassing with hexachloroethane)	In general, secondary Al smelting sector no longer using hexachloroethane for aluminum degassing ^a Extent of hexachloroethane use in basin still questionable; audit needed to verify current use and potential magnitude of OCS releases.	7 aluminum smelters, approx. 45 aluminum foundries ^k
Primary Copper Production	Limited OCS release data for primary copper smelting and refining sector ^l	3 ^d
Secondary Copper Smelting	None. No secondary copper smelting facilities in basin.	0
Niobium, Tantalum, Titanium or Vanadium Production	None. No Niobium, Tantalum, Titanium or Vanadium Production in Ontario ^a	0
Magnesium Production (using electrolysis)	None	0 ^e
Primary Nickel Production	No OCS or chlorinated compounds release information for primary nickel smelting and refining operations.	2 ^l
Incineration	Limited OCS release data from incineration sector: (i) Municipal solid waste and biomedical waste incinerators operating with state-of-the-art air pollution control, NPRI 2002 reported dioxin & furan, and HCB releases suggest facilities may be minor OCS sources; (ii) Hospital incinerators approved prior to December 6, 2002 required by Ontario regulation to cease operation by December 6, 2003. ^j (iii) Human crematoria and animal cremators not considered significant OCS sources ⁱ . (iv) One primary hazardous waste incinerator operating with state-of-the-art control; 1997 stack test detected no OCS released.	1 Municipal solid waste incinerator ^g 1 Biomedical incinerator ^h 2 Hazardous waste incinerators ⁱ Number of hospital incinerators operating unavailable Number of crematoria and cremators in sector unavailable
Semiconductor/Microelectronics (Aluminum plasma etching with chlorinated solvents)	No Ontario information regarding sector operations or releases.	Number of facilities unavailable
Reservoir Sources	Landfill sites that in the past accepted OCS	Number of facilities

Ontario Past, and Potential OCS Sources	Basis for Concern About Possible Releases	Number of Facilities
	wastes, and contaminated lake/river sediments adjacent to past sources of OCS.	unavailable
Other Potential Source Sectors	Sectors reporting HCB releases also considered as potential OCS sources include: (i) Pesticide & herbicide application (ii) Open burning household waste (iii) Use of ferric/ferrous chloride byproducts (iv) Iron & steel production (v) Cement production (vi) Municipal STP wastewater discharges and sludge disposal (vii) Wood combustion (viii) Thermal power generation (ix) Use preserved wood products (x) Pulp & paper and forest products (xi) Chemical production	-

(a) Octachlorostyrene Sources, Regulations and Programs for the Province of Ontario, 1988, 1998, and 2000 Draft Report (No.1), June 30, 2000, prepared by Benazon Environmental Inc. for Toxics Prevention Division, Environmental Protection Branch, Environment Canada.

(b) Former chlor-alkali plants: American Can of Canada Ltd. (Marathon); Canadian Industries Ltd./ICI Forest Industries Ltd. (Cornwall); (Hamilton); Dow Chemical of Canada Ltd. (Thunder Bay); Dow Chemical of Canada Ltd. (Sarnia); and Dryden Chemical Company (Dryden).

(c) Former chlorinated solvent production facility: Dow Chemical (Sarnia)

(d) Primary copper smelters: Falconbridge Limited, Kidd Metallurgical Division (Timmins); Falconbridge Limited, Sudbury Division (Sudbury); Inco Limited, Sudbury/Copper Cliff Operations (Copper Cliff).

(e) One Ontario primary magnesium facility using a thermal reduction process, located outside of the basin, Timminco Limited (Haley).

(f) Primary nickel production: Falconbridge Limited, Sudbury Division (Sudbury)

(g) KMS Peel Inc. Peel Energy from Waste Facility, Brampton

(h) Metal Waste Management Inc., Brampton

(i) Clean Harbors Canada Inc., Lambton Facility; Ontario Power Generation, Western Waste Management Facility, Kincardine

j) Environment Canada's voluntary BTS stack testing initiative from 2000 to 2003 detected no OCS releases from a number of facilities including a crematorium, two animal cremators, a kraft pulp & paper recovery boiler, an iron induction furnace, a steel electric arc furnace, and a copper smelter; method detection limit <0.001ug/m³. A test at a hospital incinerator in 2000 detected no OCS release, however, tests at another biomedical waste incinerator facility, now since closed, found traces of OCS.

(k) Environment Canada report, "Inventory Update for Release of Selected Toxic Substances from Secondary Metal Production in Ontario, May 26, 2003," by Environmental Health Strategies.

5. Management Assessment (Framework Crosswalk 4.0)

(Binational) Recent activities to reduce chlorinated hydrocarbons, including OCS

Under the GLBNS, USEPA and Environment Canada co-hosted an information-sharing forum with North American electrolytic magnesium firms in December 2000.

This shared perspectives regarding management of chlorinated hydrocarbon wastes generated during production of magnesium.

EPA issued a MACT rule governing air emissions from this factory. In addition, this factory has invested in new production technologies that may reduce formation of chlorinated hydrocarbon wastes, including PCDD, HCB, and OCS. In addition, EPA added magnesium and titanium production to its dioxin inventory. In addition, EPA added OCS to as a reporting parameter of the Toxics Release Inventory.

In addition, during recent years, EPA has established regulations for various classes of incinerators with 99 percent plus reduction in PCDD/F emissions. This suggests a similar dramatic reduction in any OCS emissions from incineration.

(Binational) Opportunities to achieve further reductions (Framework Crosswalk 4.2)

Potential opportunities to reduce OCS are similar to opportunities to reduce other trace chlorinated hydrocarbon byproducts, PCDD and HCB.

TCDD has many toxicological and risk studies, regulations and criteria, whereas HCB also has more toxicological studies and regulations than OCS. Given higher awareness of dioxin and HCB, opportunities to encourage reduced releases of chlorinated hydrocarbon byproducts will, practically speaking, be driven by dioxin and secondarily by HCB. There are no known reduction opportunities that rely on OCS as their sole justification.

Owing to little risk-based grounds for concern about OCS and its evident massive and prolonged decline in the Great Lakes, the case for making reductions based solely on OCS would seem modest.

Sectors that undertake actions to reduce releases of dioxin and of HCB will necessarily thereby reduce OCS releases as well. Just as one likely cannot generate the former two substances without OCS (discussed in Section 4), by the same logic, one cannot prevent releases of dioxin and HCB without preventing releases of OCS as a collateral consequence.

There are no known opportunities for the GLBTS program to reduce OCS, per se, beyond the electrolytic magnesium sector forum that took place during 2000.

The GLBTS analytic process valuably helped identify sectors that had previously not been recognized for release of dioxin and HCB. Any future opportunities with these sectors can be pursued on grounds of dioxin and HCB.

Table 9: Province of Ontario Opportunities to Characterize Potential Sourcesⁱⁱⁱ

Potential Sources	Opportunities to Better Characterize Potential Sources
Aluminum Foundries and Secondary Smelters (Al degassing with hexachloroethane)	Audit aluminum foundry and secondary smelting sector to verify that further actions to reduce hexachloroethane usage in basin are unwarranted.
Primary Copper Production	Further characterization of facility releases of chlorinated compounds, including OCS. To date, limited stack testing at one of three primary copper smelters found undetectable OCS levels.
Primary Nickel Production	Characterization of facility releases of chlorinated compounds, including OCS.
Incineration	(1) Audit Ontario's hospital waste incineration sector to verify that obsolete incineration facilities are no longer operating, and to determine current number and control status of those remaining in operation. (2) Update characterization of releases of chlorinated

	compounds, including OCS, from Ontario's hazardous waste incineration facilities.
Semiconductor/Microelectronics (Aluminum plasma etching with chlorinated solvents)	(1) Audit Ontario's semiconductor/microelectronics sector to identify facilities using plasma etching of aluminum with chlorinated solvents. (2) If warranted, characterization of facility releases of chlorinated compounds, including OCS.

(Canada) Additional Province of Ontario Opportunities regarding OCS^{iv}

Contaminated Sediment: continue support for sediment clean-up in known Ontario OCS "hot spots"; i.e., in waters adjacent to former chlorinated solvent and chlor-alkali production facilities.

Landfill Sites: identify landfill sites likely to have accepted wastes from Ontario's former chlorinated solvent and chlor-alkali (using graphite anodes) production sectors; and assess adequacy of site environmental controls. Former chlor-alkali plants: American Can of Canada Ltd. (Marathon); Canadian Industries Ltd./ICI Forest Industries Ltd. (Cornwall); (Hamilton); Dow Chemical of Canada Ltd. (Thunder Bay); Dow Chemical of Canada Ltd. (Sarnia); and Dryden Chemical Company (Dryden). Former chlorinated solvent manufacturing: Dow Chemical (Sarnia).

Long Range Air Transport: assess potential for long range air transport of OCS from Canadian magnesium production (electrolytic process) plants located outside of the GLs basin.

(Canada) Opportunity Assessment Conclusions

- Opportunities exist within a number of Ontario sectors to characterize releases; i.e., base metal smelting (copper, nickel, and magnesium), aluminum foundry and secondary smelting, waste incineration, and semi-conductor manufacturing sectors. These opportunities deal with filling OCS data gaps rather than improving the accuracy of current release estimates.
- Opportunities exist within the magnesium production sector to assess the impact of long range air transport from known Canadian OCS sources located outside of the Great Lakes basin; i.e., sources producing magnesium using an electrolytic process.
- Opportunities exist to impact on known exposure pathways associated with OCS reservoir sources: landfill sites which in the past accepted wastes from facilities involved in the production of chlor-alkali (using graphite anodes) and chlorinated solvents; and contaminated bottom sediments adjacent to such facilities.

Management Outcomes (Framework Crosswalk 4.5)

Binational Outcome: Continue suspension of GLBTS activities for OCS, begun during 2000.

(Canada) Management Outcomes:

- There are no current OCS releases reported in Ontario. OCS levels in the Great Lakes environment have shown a major decline over the last several decades and the decline continues; Most Great Lakes media are now at or below detection limits.
- Opportunities exist to characterize potential OCS releases from a number of sectors that have also been found to release other chlorinated hydrocarbons; notably, dioxins/furans and hexachlorobenzene. This effort to fill OCS "data gaps" should continue.

- The GLBTS sediments challenge is dealing with the remediation of priority sites with contaminated bottom sediments in the Basin, and the adequacy of the challenge commitment in addressing OCS contaminated sediments should be verified.
- Landfill sites containing OCS wastes from past disposal practices are a major potential OCS source in the Basin. As such, an assessment is needed to identify landfill sites most likely containing OCS wastes, and to verify that appropriate leachate control and monitoring measures are in place.
- To date, little evidence to suggest that Long Range Air Transport of OCS is an issue in the Great Lakes Basin.
- Based on current release information, the Canadian Challenge “that there is no longer use, generation or release from Ontario sources that enter the Great Lakes of the industrial byproduct/contaminant octachlorostyrene” has been achieved. It is recommended that the GLBTS OCS workgroup be suspended.

(Binational) Referral to another forum (Framework Crosswalk 4.5.1.)

This assessment will be provided to the dioxin and HCB workgroups, for their consideration of candidate sources of dioxin and HCB. (These workgroups will not be asked to add OCS to their portfolios.)

(Canada) Referral to another forum (Framework Crosswalk 4.5.1.)

OCS “data gaps” and reservoir sources should be referred to other GLBTS workgroups or commitments, or to other environmental programs, as follows:

- (i) Filling data gaps: Processes that form hexachlorobenzene and dioxin/furan are also those most likely to be potential OCS sources, as such, filling “OCS “data gaps” should be referred to the hexachlorobenzene and/or dioxin/furan workgroups to be done in conjunction with their efforts to close similar data gaps associated with the same sectors.
- (ii) Sediments: GLBTS sediments challenge workgroup should verify that OCS sediment “hot spots” in the basin are identified and being appropriately addressed.
- (iii) Landfill sites likely containing OCS wastes: Those sites within Areas of Concern should be dealt with through the RAP program; Those sites outside Areas of Concern, through the Lake Management Program.

(Binational) Number of lakes impacted (Framework Crosswalk 4.5.2.)

OCS has traditionally been highest on Lakes Ontario and Erie.
Environmental management activities along the Niagara and St. Clair Rivers are not impacted by this GLBTS review of OCS.

(Binational) New OCS Challenge Goals (Framework Crosswalk 4.5.3)

There are no known risk-backed grounds for new activities or new challenge goals regarding OCS, under the GLBTS.

ⁱ Darryl Hogg, Ontario Ministry of the Environment

ⁱⁱ Darryl Hogg, Ontario MoE

ⁱⁱⁱ Darryl Hogg, Ontario MoE

^{iv} D. Hogg, Ontario MoE