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INCIDENCE OF CHLORINATED STYRENES IN GREAT LAKES HERRING GULLS (PRE-PUBLICATION DRAFT) AND SOURCES OF POLYCHLORINATEDSTYRENES IN THE GREAT LAKES AND THEIR TRIBUTARIES W/LETTERS

Chemical Category

CHLORINATED STYRENES

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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
REGION V

DATE: AUG 20 1985

SUBJECT: Polychlorinated Styrenes Review

FROM: Larry E. Fink, Chemist
Remedial Programs Staff, 5GL

RECEIVED 8/22/85 TOB/CSB

TO: Al Wiedow
Existing Chemicals Assessment Division (TS-778)
Office of Toxic Substances (OTS)

This memo conveys the attached draft final report "Sources of Polychlorinated Styrenes in the Great Lakes and their Tributaries" by Schulman and Klingele.

I would appreciate it if you and the process chemists in OTS's Industrial Chemistry Branch could read and evaluate the report, as it has been substantially rewritten from the earlier draft forwarded to OTS by Mitch Wrich, Chief, Toxic Materials Branch, Region V. Any comments or recommendations you or they may have as to content, format, etc. would be of assistance.

The authors concur with the conclusion of the ICB process chemists that octachlorostyrene (OCS) and hexachlorobenzene are likely to be generated by the same chemistries and thus be associated in the environment, as well. Environmental monitoring data cited by the authors seem to support this conclusion.

Information which has come to my attention since the report was circulated for peer review indicates that one significant source of OCS in the Great Lakes environment is the discharge of wastewater associated with the manufacture of chlorinated solvents such as chlorinated ethenes. Representatives of Dow Chemical Ltd. in Sarnia, Ontario, Canada have indicated to Ontario Ministry of the Environment staff that waste "hex tars" from Dow-Sarnia chlorinated solvent manufacturing processes are contaminated with significant levels of OCS. They discounted the significance of chlor-alkali process sources, based on analyses of Dow-Sarnia process waste streams. They claim that changes in hex tar disposal practices have now significantly reduced the discharge of OCS from the Dow-Sarnia Complex.

The above is consistent with the conclusions drawn by Schulman and Klingele in their process characterization analysis of likely polychlorinated styrene sources.

OCS has been detected in fish and birds in Lake St. Clair and the Detroit River down stream of the Dow Sarnia Complex.

I have also attached a pre-publication draft report by Brecher and Hallett titled "Incidence of Chlorinated Styrenes in Great Lakes Herring Gulls" for your consideration. While publication appears imminent, I would ask that you contact Dr. Doug Hallett prior to citing or quoting from the report. His telephone number is 416-973-5840.

Should you have any questions, call me at FTS: 353-0117.

Attachments

cc: V. Saulys, 5GL (w/o Attachments)
M. Wrich, 5SP[illegible]

PRE-PUBLICATION

DRAFT

DO NOT CITE OR QUOTE

INCIDENCE OF CHLORINATED STYRENES IN GREAT LAKES HERRING GULLS

R.W. BRECHER[1]

AND

D.J. HALLETT[2]

1. Chemist
Canadian Wildlife Service
Ontario Region
100 Gamelin Boulevard
HULL, Quebec K1A 0E7
Canada

2. Scientific Advisor
Department of Environment
Ontario Region
7th Floor
55 St. Clair Avenue East
TORONTO, Ontario M4T 1M2
Canada

INTRODUCTION

The chlorinated styrenes are a group of 110 congeners having the general formula $C_8H_{8-x}Cl_x$ where x is the number of chlorine atoms. Isomers of heptachlorostyrene (HCS) and octachlorostyrene (OCS) have been identified in a number of environmental and biological samples in various locations throughout the Northern Hemisphere. In Europe, residues have been detected in the blood of workers from a Norwegian magnesium reduction plant (Lunde and Bjørseth, 1977), in cormorants from the Netherlands (ten Noever de Brauw and Koeman, 1972-1973) and in sprat collected in Eastern Norway (Lunde and Ofstad, 1976).

In North America, chlorinated styrenes have been found in Lake Ontario alewife and Herring Gull tissues (Kuehl et al, 1976; IJC Water Quality Board Report, 1978). Heron eggs and carcasses collected from Lake St. Clair in 1973 and 1976 showed three isomers of HCS (Reichel et al, 1977).

Octachlorostyrene has generally been confirmed by co-chromatography with authentic standard and by mass spectrometry. The mass spectrum of OCS is characterized by an 8-chlorine cluster at m/e 376 (molecular ion) and fragments indicative of sequential loss of chlorine. The $[M-2Cl]^+$ ion cluster is the most intense in the spectrum.

No analytical standards are available for HCS isomers, making positive structural assignments impossible. The mass spectra of compounds tentatively identified as HCS show a 7-chlorine molecular ion cluster at m/e 342, and other fragments characteristic of the successive loss of chlorine atoms. As for OCS, the $[M-2Cl]^+$ ion cluster is the most abundant (ten Noever de Brauw and Koeman, 1972-1973; Lunde and Ofstad, 1976; Kuehl et al, 1976; Reichel et al, 1977; Lunde and Bjørseth, 1977).

The chlorinated styrenes are not produced commercially. They have been found associated with the electrolytic reduction of magnesium oxide in Norway (Lunde and Bjørseth, 1977) and OCS has been confirmed as a combustion product of polyvinyl chloride (PVC) (Ahling et al, 1978). Although magnesium reduction is a relatively localized industrial process, the combustion of PVC is a widespread phenomenon associated with the incineration of both industrial and municipal waste (Ahling et al, 1978). Photochemical degradation of PVC has also been shown to produce chlorinated styrenes (Weir and Milkie, 1979). Chlorine-carbon electrode processes including electrolytic reduction of metals have recently been implicated as potential sources of chlorinated styrenes to the environment (Veith et al, 1979; Kuehl et al, 1981; Kuehl et al, 1981).

The Canadian Wildlife Service routinely monitors contaminants in the Great Lakes by gas chromatography - mass spectrometry (GC/MS) using Herring Gull eggs (Larus argentatus) and tissues as indicators. In eggs collected from 1978 to 1980, several early-eluting compounds having mass spectra consistent with chlorostyrenes were detected in samples from Lake Ontario and the Detroit River. In 1981, a more systematic GC/MS survey was made for the widespread incidence of these compounds. While no quantitative data were obtained, this paper reports the presence of HCS and OCS in the Great Lakes Herring Gulls.

Ten eggs were randomly selected from each of five colonies at key locations within the Great Lakes Basin. Samples from Channel Shelter Island, Saginaw Bay, Fighting Island in the Detroit River and Hamilton Harbour were chosen due to their proximity to heavy industrialization and high population density. By contrast, Agawa Rock, Lake Superior and Chantry Island, Lake Huron, were chosen for their proximity to low industrialization and urbanization. As a control colony, Kent Island in the Bay of Fundy on the Atlantic coast was used.

MATERIALS AND METHODS

Homogenization and Extraction

Five gram aliquots from each of 10 egg homogenates from individual colonies were pooled and homogenized in a Sorval omnimixer for 1.5 minutes. Then 25.0 $\pm$ 2.5 g of the homogenate was accurately weighed into each of two glass mortars containing 150 g anhydrous Na_2SO_4 (Fisher Scientific, U.S.A., heated at 400°C for 4 hours). Each subsample was ground until the mixture was a free-flowing powder. The two subsamples were combined in a large glass column (75 cm X 3 cm I.D.) and extracted with 300 ml hexane (Caledon Labs, Canada, Distilled in Glass). The extract was reduced in volume on a rotary evaporator and adjusted to a final volume of 40.0 ml with hexane.

Column Chromatography

Four glass columns (35 cm X 2.1 cm I.D.) were plugged with glass wool (pre-washed 3 times with methanol, 3 times with CH_2Cl_2) filled with 27.0 g Florosil (PR grade, Floridin Company, U.S.A., heated at 550°C for 6 hours and deactivated with 1.2% (v/w) hexane extracted distilled water) and then 2-3 cm Na_2SO_4 was layered on top. Each column was pre-eluted with hexane. 10.0 ml of the egg extract was loaded onto each column. The four columns were then each eluted as follows: 150 ml hexane, 75 ml 15% (v/v) CH_2Cl_2/hexane, 75 ml 15% (v/v) CH_2Cl_2/hexane, 150 ml 30% (v/v) CH_2Cl_2/hexane. Similar fractions from each column were combined in large flasks, and each combined fraction was reduced in volume to about 5 ml with a rotary evaporator. Each fraction was then transferred to a 15 ml graduated centrifuge tube and reduced to 0.2 $\pm$ 0.1 ml under a gentle stream of ultra-pure nitrogen (Central Oxygen Limited, Ottawa, Canada). Concentrates were transferred to 0.3 ml Reacti Vials (Pierce, U.S.A.), blown just to dryness, and redissolved in 100 $\pm$ 1µl hexane. The vials were capped with Mininert valves (Pierce, U.S.A) and stored at -20°C until analysis.

Analysis

Analysis was performed on a Hewlett-Packard 5985B GC/MS system using a flexible fused silica capillary column (J & W Scientific, California, U.S.A., SE-54, 0.2 mm I.D. X 30 m) and electron impact ionization (electron energy 70 eV). GC temperature program was as follows: 80°C hold for 2 minutes, 20°C/min for 2 minutes, 5°C/min for 30 minutes, hold at 270°C for 10 minutes. Ions were scanned over the range 50 to 450 amu with a scan time of 1.1. sec.

RESULTS AND DISCUSSION

Figure 1 shows the total ion chromatogram of the hexane fraction from the Hamilton Harbour egg sample. Peak 1 was identified as

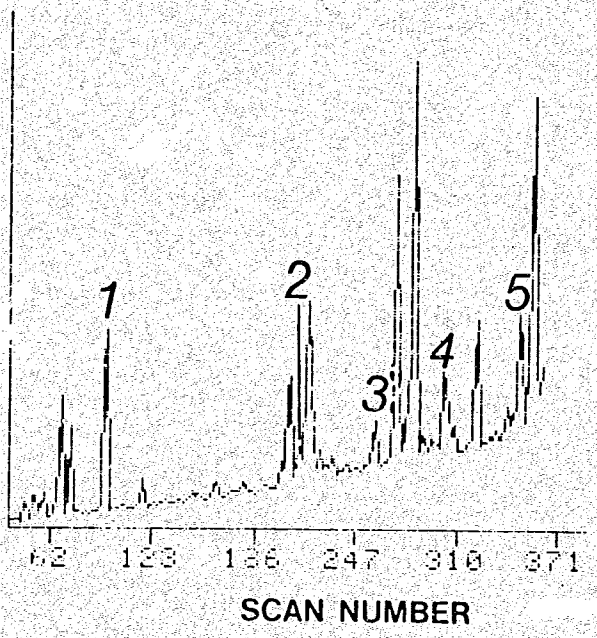

Figure 1 - Hamilton Harbour egg extract, hexane fraction. Peak 1 - HCB, Peaks 2,3,4, - HCS, Peak 5 - OCS. See text.

hexachlorobenzene (HCB) by co-chromatography with authentic standard and by mass spectrometry (6-chlorine molecular ion cluster at m/e 282 and successive loss of chlorine). Peaks numbered 2, 3, and 4 represented compounds with molecular ions at m/e 342, bearing 7 chlorine atoms. A typical EI-mass spectrum is shown in Figure 2. Fragmentation was characterized by successive loss of chlorine with the $[M-2Cl]^+$ ion cluster being the most intense, therefore these compounds were tentatively identified as isomers of HCS. Peak 5 was identified as OCS by mass spectrum and GC retention time relative to an authentic standard. OCS had a molecular ion cluster at m/e 376 with 8 chlorine atoms and showed successive loss of chlorine atoms.

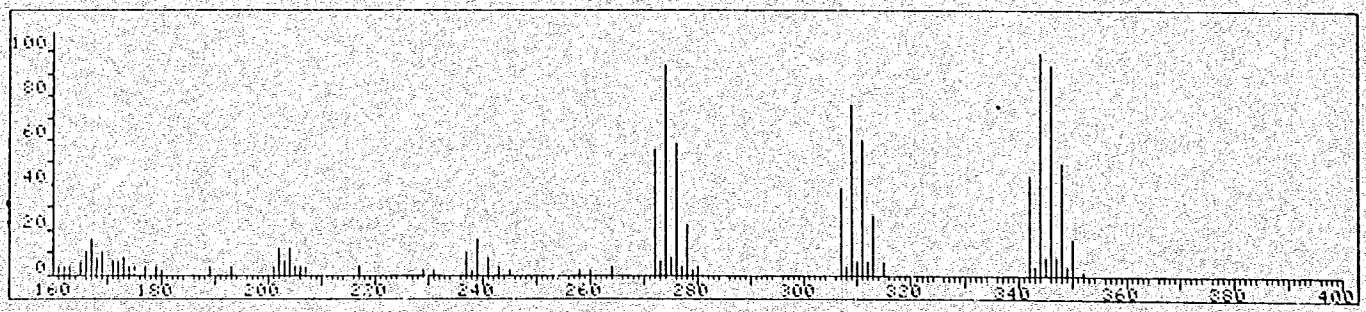

Figure 2 - EI-mass spectrum of a tentatively identified HCS isomer.

On the basis of the mass spectra obtained, it was not possible to distinguish the particular structure of any of the HCS peaks, or to determine whether the single hydrogen atom was on the ring or the sidechain.

Egg samples from colonies on four Great Lakes contained at least one HCS peak (Figure 1,. Chantry Island, Lake Huron, was the only colony which did not contain any HCS isomers. OCS was detected in all the Great Lakes samples except that from Lake Superior. No chlorostyrenes were detected in the extracts from eggs collected at the Bay of Fundy. These data are summarized in Table 1. Relative retention times (to OCS) of each of the HCS peaks identified are also given. They were consistent in each colony.

Table 1 - Presence of HCS and OCS in Great Lakes Herring Gull Colonies

COLONY, AND LOCATION	HCS #1 RRT = .832	HCS #2 RRT = .892	HCS #3 RRT = .946	OCS RRT = 1.000
Hamilton Harbour (Lake Ontario)	✓	✓	✓	✓
Agawa Rock (Lake Superior)	✓	-	-	-
Fighting Island (Detroit River)	✓	-	✓	✓
Chantry Island (Lake Huron)	-	-	-	✓
Saginaw Bay (Lake Michigan)	✓	-	-	✓
Bay of Fundy (Control)	-	-	-	-

Table 1 - checkmark indicates that the isomer was identified by GC/MS. '-' indicates not detected. RRT = Relative Retention Times (relative to OCS).

Point sources of chlorostyrene entry into the Great Lakes have not been identified. The fact that these compounds have been found in each of the Great Lakes suggests that there may be many sources and routes through which the chlorinated styrenes may gain access to the Great Lakes, and that chlorinated styrenes are persistent contaminants.

Given the relatively urbanized geography of the land surrounding the lower Great Lakes, many sources of chlorostyrenes probably exist. As already discussed, an important widespread airborne source could be the incineration of wastes containing PVC.

The impact of the chlorinated styrenes on the Great Lakes ecosystem is not known. Since its relatively recent identification as an environmental contaminant, OCS has been the subject of several toxicological investigations. Strik and Koeman found that OCS induces a variety of hepatic enzymes and causes liver histological changes in male Wistar rats (Strik and Koeman, 1976). Chu and co-workers found OCS to be resistant to metabolic degradation in rats (Chu et al, 1982). In another study, diet levels of 5 ppm OCS/day for 28 days caused liver hypertrophy and liver microsomal changes, while 50 ppm OCS/day diet levels caused mixed function oxidase induction and histological changes in the thyroids and livers of rats (Villeneuve et al, 1982). OCS has been estimated to have a bioconcentration factor of 33,000 in fish (Veith et al, 1979). Although the toxicological information on OCS is still incomplete, it appears that OCS is similar to the chlorobenzenes in several respects, as might be expected from the similarity of chemical structures of these compounds. Due to the lack of HCS standards, no toxicological data are available for these compounds.

We estimated the concentration of HCS (sum of all isomers) to be in the order of 0.2 to 0.5 ppm in the samples studied, assuming a total ion GC/MS response similar to HCB. The OCS concentration was estimated to be in the order of 1 ppm in the Herring Gull eggs analyzed.

The high bioaccumulation potential of OCS (and probably HCS) may present a potential hazard to higher trophic levels in the ecosystem, extending even to the human population which consumes fish from the Great Lakes. The HCS isomers found should be synthesized to provide standards for quantitative studies and for investigating the toxicology of HCS so that a scientifically defensible environmental impact assessment can be made.

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SOURCES OF POLYCHLORINATED STYRENES IN THE GREAT LAKES AND THEIR TRIBUTARIES

U.S. Environmental Protection Agency

Grant No. R00-5764-01

FINAL REPORT

Submitted to:

Remedial Programs Staff
Great Lakes National Program
536 South Clark Street
Chicago, Illinois 60604

by

Dr. Edward M. Schulman

and

Dr. Harold Klingele

Great Lakes Laboratory

State University of New York College at Buffalo
1300 Elmwood Avenue
Buffalo, New York 14222

July 1985

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SOURCES OF POLYCHLORINATED STYRENES IN THE GREAT LAKES

AND THEIR TRIBUTARIES

ABSTRACT

The polychlorinated styrenes (PCS), 147 chlorinated derivatives of styrene, have never been intentionally produced by any industrial process. However, they are found in sediment, water, aquatic organisms, and man both in North America and Europe. By analogy to other chlorinated aromatics, they are a potential health hazard. Since these compounds are not produced intentionally, and are not naturally occurring, they must be the by-product of industrial processes.

By evaluating the chemical literature, known sources of PCS, known occurrences of PCS in the environment, and current industrial processes, we are able to suggest the most likely sources of introduction of PCS to the environment and thereby guide future monitoring and regulation.

While some literature suggests that the PCS problem may be of more historic than current importance, we disagree. We believe that current ongoing processes are adding to the PCS burden of the environment, and that regulation should follow.

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SECTION I

INTRODUCTION

Of the more than 550 anthropogenic chemicals verifiably detected in water, sediment or fish from one or more Great Lakes locations, polychlorinated styrenes (PCSs) are perhaps the most enigmatic. The sources of the vast majority of the Great Lakes contaminants can be traced to the manufacture, use or disposal of pesticides and industrial chemicals. However, PCSs have never been intentionally manufactured by anyone in the world for commercial market. Apparently, they are unintended byproducts of chemical manufacture, use, or disposal.

Available data on the toxicities and environmental fate of octachlorostyrene are sparse and non-existent for the other PCS congeners. Nevertheless, by analogy to PCBs, the higher chlorinated PCSs can be inferred to be extremely persistent, highly bioaccumulative and potentially genotoxic. Thus, the systematic identification of potential sources of PCSs in the Great Lakes ecosystem warrants priority attention. If the introduction of PCSs into the Great Lakes environment is to be controlled, it is important that possible sources of these chemicals be characterized.

The objective of this report is to identify the potential generators of chlorostyrenes in the Niagara River-Lake Ontario and the Ashtabula, Ohio regions of the U.S. By reviewing the literature, we intend to find the processes which are known to form chlorostyrenes or which, on the basis of what is known about carbon-chlorine chemistries, are likely to introduce chlorostyrenes into the environment.

In Section II, background information is presented which defines the class of chlorinated aromatic compounds known as polychlorinated styrenes, summarizes their widespread distribution in the environment and describes their measured and inferred physical, physicochemical, chemical, biological and toxicological properties. Carbon-chlorine chemistries affecting the routes and rates of chlorinated organic chemical formation and destruction are discussed in Section III. Section IV inventories and describes known intended and unintended routes and conditions of PCS formation. In Section V the mechanisms and controlling factors of the chemistries of PCS formation are inferred from the principles of carbon-chlorine chemistry discussed in Section III and observed reactions set forth in Section IV. Section VI identifies candidate PCS source manufacturing and waste disposal processes. Sections VII and VIII focus on locations of PCS contamination along the Niagara Frontier and in the Fields Brook-Ashtabula River system, respectively, and present an inventory of likely industrial sources of the historical and on-going PCS load. Conclusions based on this analysis and recommendations for directions in future research are set forth in Section IX. Section X references literature citations.

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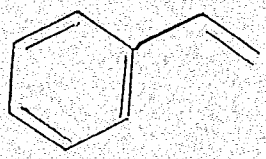
SECTION II

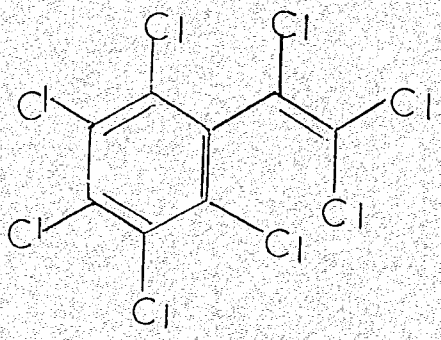
BACKGROUND

The polychlorostyrenes (PCSs) are a class of organic compounds containing carbon, hydrogen, and chlorine. There are 147 such compounds all based on the styrene (vinyl benzene) skeleton illustrated below.

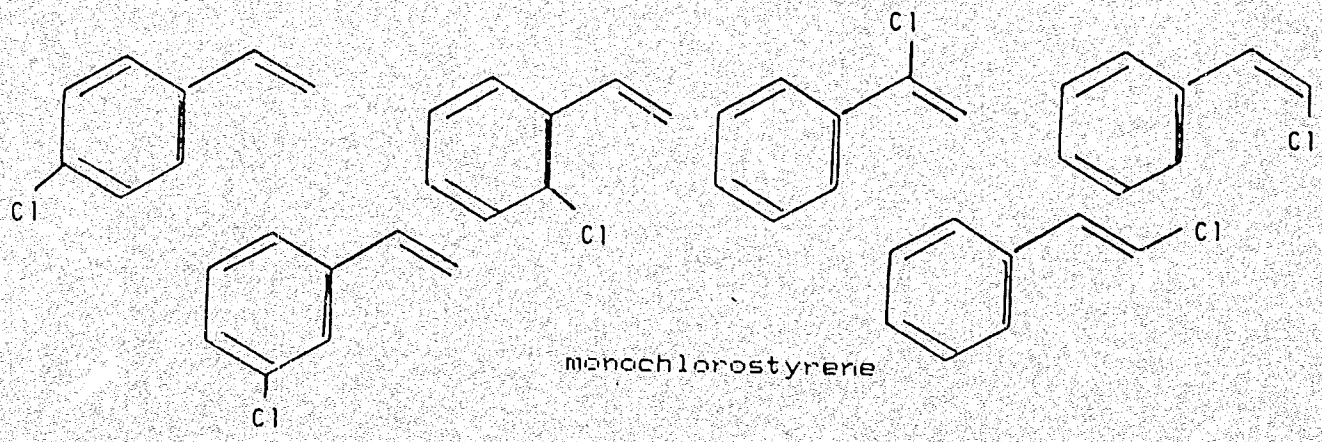


STYRENE

The parent compound, styrene (C_8H_8), consists of a six-membered benzene ring bearing five hydrogen atoms, denoted as aromatic hydrogens, and a two-carbon side chain bearing three hydrogen atoms, denoted as vinylic hydrogens. Each of the hydrogens on the styrene molecule can be replaced by a chlorine to produce the family of 147 PCS molecules. There is thus only one compound possible with all eight hydrogens replaced by chlorine, octachlorostyrene (OCS).



However, if only one hydrogen is replaced by a chlorine to produce monochlorostyrene, then the replacement can take place at any of three aromatic positions or any of three vinylic positions to produce six different isomers.



monochlorostyrene

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Similarly, if seven hydrogens are replaced by chlorine, the remaining hydrogen could be at any of three aromatic or three vinylic sites to again produce six isomers of heptachlorostyrene. The same logic can be used to produce the summary table below.

Name	Empirical Formula	No. of Compounds
Octachlorostyrene	C_8Cl_8	1
Heptachlorostyrene	C_8HCl_7	6 isomers
Hexachlorostyrene	$C_8H_2Cl_6$	18 isomers
Pentachlorostyrene	$C_8H_3Cl_5$	34 isomers
Tetrachlorostyrene	$C_8H_4Cl_4$	30 isomers
Trichlorostyrene	$C_8H_5Cl_3$	34 isomers
Dichlorostyrene	$C_8H_6Cl_2$	19 isomers
Chlorostyrene	C_8H_7Cl	6 isomers

Few studies have been published on any of these 147 different compounds, so our background summary of relevant properties will focus mainly on one example taken from the list: OCS.

No measured melting point for OCS has been reported in the available literature and no accepted methods for estimating melting point presently exist. Vapor pressure data are also unavailable. De Foe reported a water saturation solubility for OCS of 7 parts per billion at 20°C (1). Veith and co-workers (2) measured an n-octanol/water partition coefficient of 1.9×10^6, from which a sediment/water partition coefficient can be estimated according to the method of Karickhoff et al. (3) to be 25,000-49,000 for sediment material containing 2-4 percent organic carbon by weight. Both Durham and Oliver (4) and Kaminsky and Hites (5) have measured octachlorostyrene in Lake Ontario sediments. Corresponding water concentrations have not been measured. Thus, it is not possible to confirm this estimate for Great Lakes sediments. However, Ofstad et al. (6) have measured OCS water and sediment concentrations in a Norwegian fjord on the North Sea and Ofstad (7) reports a sediment/water partition coefficient value of 7×10^5, within an order of magnitude of the estimated value.

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In a 28-day flow-through laboratory biouptake study Veith et al. (2) measured an OCS bioconcentration factor (partition coefficient between fathead minnow, Pimephales promelas, and water) to be 33,000 (approximately 65,000 on a fat weight basis). This value was similar to those observed for PCBs, HCB and DDT - all of which are well established as highly bioaccumulative contaminants in fresh water and marine ecosystems. However, Ofstad et al. (6) measured the concentrations of OCS in sediment, water and biota in two Norwegian fjords, one of which was impacted by a magnesium manufacturing facility, from which Ofstad (7) calculated biota bioconcentration factors ranging from 1.3×10^7 in crab to 7×10^7 in cod on a fat weight basis. The discrepancy between the laboratory and field fish bioconcentration factors can probably be explained by the short duration of the laboratory test and the lack of a food chain contribution to the steady state body burdens.

By analogy to PCBs and HCB, OCS is expected to be highly persistent in fresh and marine waters and underlying sediments, being particularly resistant to hydrolysis and biological degradation.

Several polychlorinated styrene (PCS) species, particularly the higher chlorinated congeners, have been detected in water, sediment and biota in a wide variety of environments in the Great Lakes Basin.

Specifically, fish from the Saginaw River and Bay in Michigan, the Detroit River, Fields Brook, and the Ashtabula River in Ohio and Lake Erie, the Niagara River and Lake Ontario (8) have been shown to contain residues of octachlorostyrene (OCS), heptachlorostyrenes (H_1CS), hexachlorostyrenes (H_2CS) or pentachlorostyrene (H_3CS). Octa- and heptachlorostyrene have also been detected in herring gull eggs from Fighting Island (Detroit River) colonies (9). Table I summarizes the extent of the PCS contamination problem in Great Lakes.

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NOTE—OCTACHLOROSTYRENE IN GREAT LAKES FISH

TABLE 1 *Results of quantification of octachlorostyrene and related chemicals in Great Lakes fish. All values are in parts-per-billion whole fish wet weight and are mean values of duplicate analyses using two ions for each chemical*

			1,3,5-Trichlorobenzene[1]	1,2,4-Trichlorobenzene[1]	1,2,3-Trichlorobenzene[1]	1,2,4,5-Tetrachlorobenzene[2]	1,2,3,4-Tetrachlorobenzene[2]	Pentachlorobenzene[2]	Hexachlorobenzene[2]	Hexachlorobutadiene[2]	Heptachlorostyrene[1]	Heptachlorostyrene[1]	Heptachlorostyrene[1]	Octachlorostyrene[1]	
Relative Retention Time*			0.196	0.296	0.379	0.737	0.869	1.329	1.687	0.429	1.860	1.927	1.975	2.033	
Waterbed	Date (year)	Fish Species													
Lake Superior Apostle Islands, WI	1974	Lake trout	ND**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	12.2
Lake Superior Copper Harbor, MI	1980	Lake trout	ND	1.2	ND	ND	ND	ND	6.5	ND	ND	ND	ND	ND	23.8
Lake Michigan Grand Traverse Bay, MI	1980	Lake trout	ND	2.0	ND	ND	ND	ND	6.3	ND	ND	ND	ND	ND	26.4
Lake Huron Mackinac, MI	1974	Chub	ND	1.4	ND	ND	ND	ND	11.5	ND	ND	ND	ND	ND	20.2
Lake Huron Saginaw Bay, MI	1977	Lake trout	ND	NQ***	ND	ND	ND	ND	NQ	ND	ND	ND	ND	2.0	16.9
		Composite													
Lake Huron Saginaw Bay, MI	1980	Catfish Carp	ND	NQ	ND	ND	ND	ND	5.0	ND	ND	ND	ND	110.7	11.3
Lake Erie Woodtic, MI	1980	Carp	ND	ND	ND	ND	ND	ND	20.9	ND	ND	ND	ND	33.8	9.6
Lake Ontario Cape Vincent, NY	1977	Lake trout	NQ	36.0	9.5	12.0	17.0	17.0	230	2.5	46.0	30.0	27.0	281	17.1
Lake Ontario Oswego, NY	1978	Brown trout	NQ	2.8	1.1	2.5	5.0	11.0	115	1.7	4.5	NQ	NQ	35	10.1
Lake Ontario Stony Island, NY	1979	Lake trout	NQ	2.4	NQ	2.9	4.5	9.1	117	NQ	28	NQ	NQ	86	20.0
Lake St. Clair Anchor Bay, MI	1980	Carp	ND	NQ	ND	ND	ND	ND	48.8	ND	NQ	NQ	ND	227	11.0
		Composite													
Ashtabula River Ashtabula, OH	1976	Alewife Shad Bass Perch Bullhead	16	4.7	NQ	81	17	221	1,600	323	124	62	NQ	144	x
		Composite													
Ashtabula River Ashtabula, OH	1978	Sucker Roller Carp	2.1	NQ	3.9	7.0	1.3	33	466	61	105	NQ	NQ	152	x
Ashtabula River Ashtabula, OH	1979	Smelt	2.1	2.1	NQ	15	3.7	19	48	NQ	NQ	NQ	NQ	NQ	5.0
Ashtabula River Ashtabula, OH	1979	Northern pike	11.0	7.5	NQ	96.0	20.0	157	1,140	445	335	171	4.9	405	5.4
Fields Brook Ashtabula, OH	1979	Sucker	75	124	20	1,150	205	789	1,530	3,250	12	6.9	NQ	256	x
		Composite													
Fields Brook Ashtabula, OH	1980	Carp Bass	31	14	1.9	193	43	352	2,210	811	117	104	NQ	184	x

* Relative to *p,p'*-diiodobenzene; **ND = not detected, ***NQ = detected but not quantifiable, x = not determined. 1. Detection limit 1 ppb wet weight whole fish. 2. Detection limit 5 ppb wet weight whole fish. All values are in ppb wet weight whole fish

00018

Using radiodating techniques, Durham and Oliver (4) determined that the maximum concentration of OCS occurred in Lake Ontario sediments in about 1960.

Outside the Great Lakes Basin, PCSs have been detected in fish from several sites, including the Muskingum River, Ohio (10) and the Delaware River, Pennsylvania (11). OCS was also reported detected in a sample of oil applied to Iowa roads for dust suppression in 1977 (12). In Europe, OCS has been detected in duck, stern, fish, and seals in the Netherlands (13, 14), and in Norwegian fish, sediments, and water (15, 6, 7, 16).

The widespread occurrence of PCS contaminants in aquatic and marine biota and sediments is disconcerting, given the fact that PCSs are nowhere reported to have been commercially manufactured.

At present the U.S. Food and Drug Administration has issued no formal residue action levels or informal guidelines for any of the PCSs accumulating in fish; nor has the U.S. Environmental Protection Agency developed a PCS Water Quality Criteria document as guidance to the states in promulgating toxic substances Water Quality Standards. Nevertheless, the structural similarities between PCS and polychlorinated benzenes and polychlorinated biphenyls (PCBs) are cause for concern.

Despite the observation of environmental accumulation in biota, very few reports are available on the toxic effects of these chemicals. In the currently published literature, Strik and Koeman (17) observed porphyria in rats and Japanese quail fed at 500 mg/kg/day. In addition to increased levels of porphyrin in livers, observations included megalocytosis, basophilic spots, whorls and hypertrophy of hepatocytes as well as increased in cytochrome P-450 and δ-aminolevulinic acid synthetase.

Recently Chu et al. (18) have examined acute and subacute effects and Villeneuve et al. (19, 20) the subchronic effects of OCS in rats. While OCS accumulated in fat and liver and caused biochemical and histopathological changes, no deaths were observed within 14 days at dose levels as high as 3710 mg/kg. Doses of 1690 mg/kg or higher caused increased liver weight, increased activity of hepatic microsomal aniline hydroxylase and aminopyrine demethylase and elevated serum cholesterol and uric acid levels. When fed at dietary levels of 50 ug/g for 28 days, liver hypertrophy and hepatic microsomal changes were observed and even at 5 ug/g, liver and thyroid histological changes were found as well as induction of mixed function oxidases.

Styrene is known to be metabolically converted to styrene oxide (21) which is considered to be responsible for the mutagenic activity of the parent compound (22-26). As in the case of styrene, it is expected that PCSs will be converted to reactive chloro-epoxides. Since chemicals which are subject to metabolic conversion to epoxides are suspected to possess mutagenic/carcinogenic activity, polychlorinated styrenes may present a potential hazard not only to fish and other aquatic organisms but also to humans if the fish contaminated with PCSs were consumed by man.

00019

A brief notation in Chu et al. (27) states that "...OCS is resistant to metabolic degradation..." in the rat. No further details were provided. A study of OCS and HCSs in workers in a probable occupation exposure situation (78) indicates that these substances can accumulate to at least 5 ug/L in the blood (means 1.5) of humans. Exposure levels were not reported. It is disturbing, however, that these chemicals were also found in the blood of groups with less probability of exposure (a polyvinyl chloride plant: mean 0.7 ug/L). PCSs may therefore be more widespread than might otherwise be expected.

Measured or estimated physical, chemical, biological and toxicological properties of OCS relevant to the characterization of its intrinsic environmental and public health hazards are summarized in Table II from Dr. Gilman Veith's Quantitative Structure Activity Relationship System (QSARS), a computerized data base accessible via Montana State University.

The IJC's Aquatic Ecosystem Objectives Committee (29) has indicated that the presence of PCSs in the Great Lakes ecosystem is problematic and recommended further studies of the extent of their distribution and their mechanism(s) of entry into the waters of the Great Lakes.

Based on quantitative structure activity relationships (QSAR), it can be inferred that the persistence, bioaccumulation factor, and toxicological activity increase with increasing degree of chlorination on the aromatic ring and the vinyl substituent, reaching a maximum at octachlorostyrene.

Kuehl et al. (30) speculated that PCSs were unintended byproducts of chlorine manufacture. More recent work by Kaminsky and Hites (5)indicates that this is potentially one historically significant route of entry of PCSs into the Great Lakes ecosystem.

Due to their inferred persistence and high bioaccumulation potential, the assimilative capacities of the Great Lakes for the higher chlorinated PCS congeners may be quite small. Thus, seemingly insignificant sources may have an accumulatively significant effect.

In spite of the wide distribution of PCSs, very little is known regarding the source(s) of these chemicals in the Great Lakes. PCSs are not produced commercially, nor are they known to be byproducts from any particular industrial process. However, it is believed that polychlorostyrenes are formed as byproducts in industrial processes involving high-energy carbon-chlorine reaction.

In the next section, we review those aspects of carbon-chlorine chemistry which have a direct bearing on the routes and rates of formation of polychlorinated alkenes and arenes under various high energy reaction conditions.

00020

TABLE II

QSARS

CAS #: 29082-74-4

NAME: Octachlorostyrene

#	Data	Value	Units	Source	Error
1	MW	379.0	GM/MOL	Calc.	
2	Pr	572.00			
3	Mol. Refr.	68,80		Calc.	
4	Mol. Vol.	252.00		Calc.	
5	Log P	7.94		Clog D (Calc.)	
6	M.P.	- -		- -	
7	B.P. (^{o}C)	342.00	760	Calc.	2%
8	Vap. Press	- -		- -	47%
9	Ht. Vap.	7485.00		Calc.	1.85
10	pKa	- -		- -	
11	Log(s)	.41 ug/L		Calc.	
12	Surf. Area	- -		- -	

00021

TABLE II (Cont'd)

ECOTOX

NAME: Octachlorostyrene

QSAR Estimation of Values for Exposure Assessment

Water solubility	=	0.40 ug/L
Log RCF	=	5.0
BCF	=	100,000.00
Adsorption Coef. (Log Ku)	=	5.65
Hydrolysis Half Life	=	1000 days

Hydrolysis is not likely to be an important mechanism for this chemical.

Biodeg $t_{1/2}$ 100 days

Water solubility too low to reliably estimate partitioning

QSAR Estimation of Aquatic Toxicity

Daphnia	Fathead Minn.	Rainbow Trout
	2.58	

Catfish	Goldfish	Bluegill	Mosquito Fish
		1.87	2.58

No effect level 0.129 mg/1

Not phytotoxic

Possible carcinogenicity

00022