

# **Proposed Chlorine Sunsetting in the Great Lakes Basin:**

## **Policy Implications for New York State**

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## Introduction

The International Joint Commission (IJC) first made a recommendation to “develop timetables to sunset the use of chlorine and chlorine-containing compounds” in the Great Lakes Basin in its Sixth Biennial Report on Great Lakes Water Quality (1992). In its Seventh Biennial Report (IJC, 1994), the IJC accepted the findings of the Virtual Elimination Task Force (IJC, 1993) and confirmed the recommendation of the Sixth Biennial Report when it recommended that the governments of Canada and the United States “...consult with industry and other interests to develop timetables to sunset the use of chlorine and chlorine containing compounds as industrial feedstocks and examine the means of reducing and eliminating other uses, recognizing that socio-economic considerations must be taken into account in developing the strategies and timetables” (IJC 1992). Other International Organizations took similar steps. The Paris Commission, composed of 15 nations, and the 21-nation Barcelona Convention have taken the stance that toxic, persistent and bioaccumulative substances, particularly organohalogens, which class includes chlorinated organic substances, should be eliminated or substituted where possible. On the other hand, the American College of Occupational and Environmental Medicine, the American Chemical Society, the American Medical Society, and the Society of Toxicology while recognizing that several organohalogens are on most lists of priority pollutants, have none the less opposed treating chlorine and chlorinated chemicals as a class noting concern over the potential economic repercussions of a ban on chlorine. Their position is that not all chlorinated have been shown to be dangerous, and many yield proven health benefits. Debate over the eventual elimination of chlorinated organic compounds and chlorine used in industrial feedstocks, pesticides and many other applications (sometimes referred to as a Chlorine “sunsetting”) is a complicated one; various positions have been staked on either side of the issue.

The International Joint Commission is a binational treaty organization with the responsibility to report on progress in achieving the goals and objectives of the Canada-US Great Lakes Water Quality Agreement. The IJC's biennial reports on Great Lakes Water Quality are issued in response to this obligation. One of the goals of the Agreement, established in Article II of the 1978 revisions, is to virtually eliminate persistent toxic chemicals from the Great Lakes. Half of the 362 synthetically-produced chemical compounds that were found in the Great Lakes basin were chlorinated organics (MESB 1994). Due to the persistent, toxic nature of many of these compounds, the uncontrollable mixing that has occurred in the environment, and limited scientific understanding about the effects of mixtures in the environment, the Commissioners of the IJC believed that rather than treat these chemicals individually, they should be treated as a class for the sake of government action. Adopting this recommendation would mean a dramatic change in the way environmental contaminants are regulated. In standard practice, chemicals must be evaluated individually for toxicity, carcinogenicity, persistence and bioaccumulation potential before regulatory action is taken. This tends to be costly and time consuming and therefore only a small percentage of chemicals released to the environment are tested. In 1997, the US and Canada took steps toward the elimination of toxics in the Great Lakes; the stated goal is the elimination of 5 chlorine-based pesticides, a 90% reduction in PCB, and a 75% reduction in dioxin by the year 2006. Part of the current debate is the question of whether or not it is sufficient or safe to consider each compound separately - a process that, it has been suggested, would take 1 billion laboratories over 130 billion years to complete - or whether it would be prudent to combine all chlorinated chemicals in the same class, with the recommendation for an immediate though gradual phase out of the class. The onus of proof would thus be on the potential user or manufacturer of a certain compound to prove it safe for human health and the environment; without this proof each chlorinated compound would be assumed too risky for release into the environment and therefore too risky for use. There are convincing arguments for both sides, as well as conflicting findings. Several issues surfaced as a result of the IJC's recommendation including: human health and environmental risks, costs and benefits, terminology (i.e. ban vs. phase out, individual vs. class),

scope, state of knowledge, and plan of action for chlorinated chemicals. Considering the fact that US production of chlorine had reached **an** all time high of more than **12** million tons per year (Hilleman, et al. 1994) the recommendation had far-reaching implications and became highly controversial immediately after **the** IJC made it.

This report is the product of an effort by the Great Lakes Program at the University of Buffalo along with the cooperating institutions of the New York Great **Lakes** Research Consortium to consider the implications of the IJC recommendations **as** they might affect the environment and economy of the Great Lakes region of New York State. Our goal in this study is to synthesize available scientific, economic and policy information about the impact of a chlorine ban specifically on New York. Section One provides the context within which to consider the IJC recommendation. **Are** the human health and environmental consequences of **certain** chlorinated organic compounds, particularly persistent and bioaccumulative toxic substances, of such a degree that a radical departure from conventional pollution control strategies is desirable? If so, does it make sense to treat chlorinated organic compounds **as** a class for regulatory and policy purposes? What impact might a Chlorine ban have on the inadvertent production and release of Dioxins and Furans? Section Two looks at the economics of Chlorine and potential economic impact of substitutes for chlorinated substances in commerce. It focuses particularly on the New York **State** economy and includes **an** appraisal of the contributions of Chlorine related industries. Section **Three** reviews the available data on the release of chlorinated compounds to New York's environment. A numerical model is used to demonstrate the behavior of a number of chlorinated compounds in Lake Ontario under various loading scenarios. The report concludes with recommendations for **NY** DEC in pursuing the issues associated with reducing and eventually eliminating the release of toxic chlorinated compounds into New York's Great Lakes region.

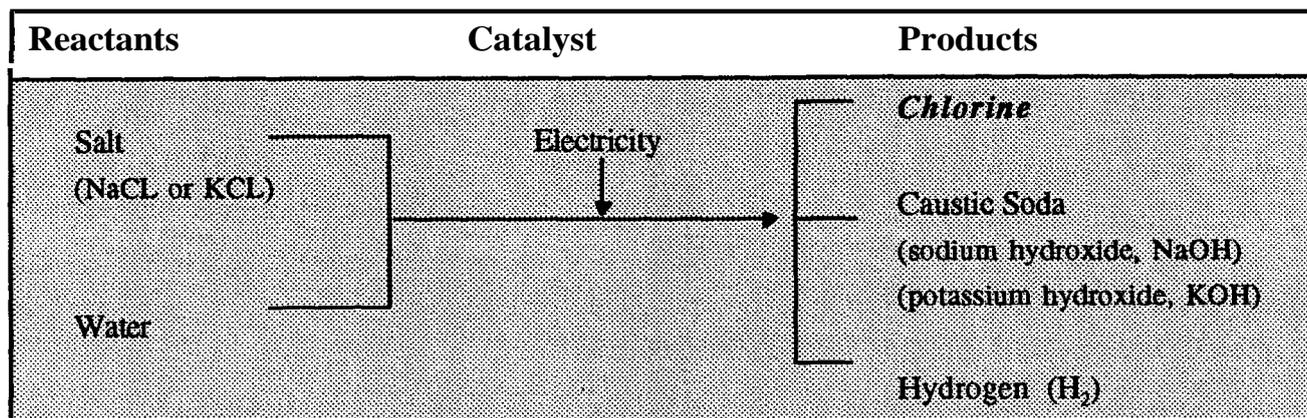
## Section One: About Chlorine and Chlorinated Compounds

Chlorine is widely used in the US in water disinfection systems (98% of all water disinfection and 1% of **all**  $\text{Cl}^-$  use), pharmaceuticals (**85%** of **all** pharmaceuticals), and crop protection pesticides (96% of **all** pesticides) (Holland 1995). Chlorine is inexpensive and simple to manufacture. Chlorinated plastics became important originally during World War II because of a need to replace natural rubber. During the gasoline crisis, lighter weight plastic substitutes were found to reduce fuel consumption in automobiles. Water treatment experts quickly discovered that chlorine was easy to use, killed deadly disease-causing bacteria and provided a residual that helped to disinfect throughout the water network. Chlorinated pesticides ensured "High quality" produce at low cost. The major use of chlorine, PVC, provided lighter products for construction.

### *How is chlorine produced?*

The manufacture of chlorine is one of the more basic chemical processes. The electrolysis of salt water, or brine, (74% in diaphragm cells, 13% in mercury cells, 11% in membrane cells) made up 97% of 1995 chlorine manufacturing. While the byproduct of sodium and magnesium (by decomposition of HCL) manufacturing comprised the **remaining** 3% of chlorine manufacturing (Mannsville 1995). Electrolysis involves using electricity to break down salt water into chlorine ( $\text{Cl}_2$ ), caustic soda (sodium hydroxide-NaOH) or caustic potash (potassium hydroxide-KOH), and other by-products (i.e. hydrogen) (see Figure 1). A more detailed description of chlorine production can be found in other reports (Charles River Associates, 1993; Holland 1995).

Figure 1. The Production of Chlorine\*

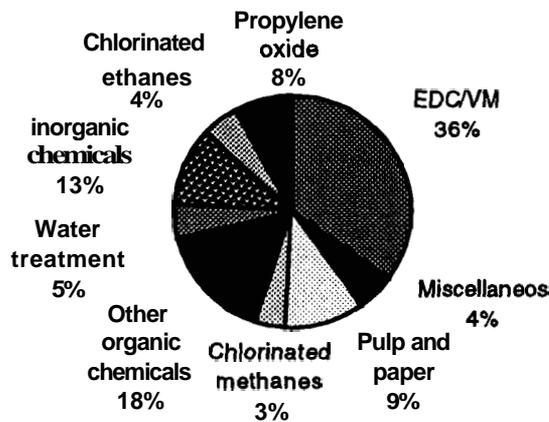


\* Source: Charles Rivers Associates 1993.

### *How is Chlorine Used?*

Chlorine has been used in three ways: 1) direct use (i.e., waste water treatment), 2) as a catalyst, but not in final product (i.e., many pharmaceuticals and pesticides), and 3) manufacture of chlorine containing products (i.e., PVC). "Over **50** percent of **all** commercial chemicals either contain chlorine or chlorine chemistry was used in their manufacture, and consequently chlorine has come to be known as the single most important chemical" (Holland 1995).

Figure 2 End-use Estimates for Chlorine in 1995\*



\*Source: US EPA 1994.

An estimated 15,000 synthetically-produced chlorinated compounds are currently in commerce (Ehrenfeld et al. 1993). Chlorine results in thousands of applications or end-uses. The major applications of chlorine are ethylene dichloride/vinyl chloride or EDC/VCM (35%) and the pulp and paper (9%) (see Figure 2). The US pulp and paper industry, the second largest application of elemental chlorine, is experiencing a massive switch from elemental chlorine use to elemental chlorine free or chloride dioxide (Mannsville 1995). This trend in the pulp and paper industry will lower future estimates of chlorine use, as the amount of chlorine required in the chloride dioxide process is much less. The largest chlorine use, EDC/VCM, is actually an intermediate for polyvinyl chloride or PVC. Figure 3 shows one of the thousands of applications that result from chlorine chemistry. The Charles River Associates (1993) provide a more detailed look at flow from chlorine to end products.

Figure 3. Chlorine to PVC\*

Base Commodity	Intermediate Product	End Product
Chlorine (reacted with ethylene)	Ethylene Dichloride (cracked) ↳ Vinyl Chloride (polymerized) ↳ Polyvinyl Chloride (or PVC) (compounded with plasticizers, fillers, and others)	Luggage, Shoes, Raincoats, belts, strollers, chairs, containers, Pipes, Flooring

\* Source: Charles River Associates 1993; Holland 1995.

Chlorine's extreme reactivity is the same quality which yields both its value to public health, the economy and industry and its dangers in the environment. In its elemental form, pure chlorine is highly reactive and therefore extremely rare in nature. In order to produce elemental chlorine, an electric current is passed through a salt solution, or brine which separates the chlorine from the sodium yielding elemental chlorine, caustic soda and hydrochloric acid for market. When Chlorine and other halogens form chemical bonds with Carbon (forming organochlorines) these bonds are among the strongest, most stable and long-lasting in Nature. Most chlorinated organics are also highly soluble in other organic molecules and lead to complex strings of chlorine-carbon

bonds. Since Carbon chemistry dominates all life activities, organochlorines find themselves easily caught up in living tissues which is how they bioaccumulate and biomagnify. Since many of the resulting compounds are new to the planet and life has not evolved in their presence, present-day organisms may not have the necessary enzymes to catalyze their breakdown or use. Often partial metabolism occurs which can lead to new, highly reactive metabolites in the body. The toxicity associated with certain chlorinated organic compounds is ultimately related to these fundamentals of chlorine chemistry. Because of this, the proponents of a chlorine ban have argued for a regulatory approach that addresses organochlorines as a class.

The chlorine debate encompasses **both** deliberately manufactured chemicals such as pesticides and polyvinyl chloride **as well as** a wide range of organochlorines inadvertently produced as unintended by-products (i.e. dioxin). Pressure to prevent dioxin formation is being addressed, more recently, on **an** industry-by-industry basis. The pulp bleaching industry and the PVC industry, for example, are both under heavy scrutiny. Many environmental groups which initially responded favorably to a complete chlorine phase-out are moderating their stance to focus on specific industries and are proposing exceptions for specific applications, especially in water disinfection and the production of pharmaceuticals.

Chlorine **was** first produced for industrial **use** in 1893 in a process by which electric current is passed through water. The resulting elemental Cl<sup>2</sup> readily reacts with carbon (usually obtained from petroleum), yielding numerous chlorinated organic compounds (around 11,000 have been manufactured or inadvertently created). These range from simple molecules like chloroform (a single carbon atom with one hydrogen and **three** chlorine atoms attached) to the chlorinated phenols (consisting of a six-pack of carbons in a ring with various chlorinated arrangements attached), to the polychlorinated biphenyls (two attached hexagonal **rings** of carbon atoms with chlorines at the corners).

Because Cl<sup>2</sup> is so highly reactive, the bonds it forges tend to be extremely stable and hence persistent in the environment. The combination of biological activity and persistence creates the potential for problems. ~~Sixty-seven~~ percent (**22** of 33) of the persistent toxic substances targeted for virtual elimination by the Great Lakes Binational Toxics Strategy **are** organochlorines. Most of these substances are or were deliberately manufactured. For several (DDT, PCBs **and** Mirex most prominently) the manufacture for domestic use **has** been banned for many years but they persist in the environment. Some like Dioxin, a substance that is toxic at extremely low quantities and measurable in the body tissues of virtually every human in the United **States**, have never been deliberately produced but **arise** from chemical reactions in certain conditions where elemental chlorine is available. **This** makes dioxin extremely difficult to **eliminate** from **the** environment through conventional regulatory efforts.

The IJC's recommendation that governments and industry begin a process toward the eventual sunsetting of Chlorine for industrial uses, was built on **an** appreciation of the difficulties inherent in chemical-by-chemical evaluation and regulation. For example, by 1995 the **US** National Toxicology **Program** had completed assessments for carcinogenicity in around 400 chemicals. Based on the results of these, it was estimated that somewhere around **5%** of the 75,000 chemicals in commercial use (around 3,750 substances) might **be** carcinogenic. These assessments are long and expensive. At present less than 200 have been identified and regulated **as** carcinogens (Steingraber 1997).

The IJC recommendation is intended to be consistent with the "precautionary principle" and **assumes** chlorinated "chemicals **are** bad for the environment and human exposure unless they are specifically proven safe to use or release" (IJC 1996). Several chlorinated chemicals have been found to be toxic, persistent, and bioaccumulative; mix uncontrollably in the environment; and have many health effects (i.e., cancer, endocrine disruption, low birth sizes). Chlorinated chemicals in commercial use, though, are not all equally harmful. Unfortunately, the time and

energy involved examining them all for all of the possible effects is prohibitive. It would take approximately 1 billion laboratories over 130 billion years to understand the synergistic effects of these chemicals (Dorsey 1997). A framework for treating a large number of toxic chemicals at the same time would help to alleviate this problem (IJC 1996).

Despite this, the chemical-by-chemical method is the dominant paradigm in both the US and Canada. In fact, many prestigious organizations support the chemical-by-chemical approach including: the American Chemical Society, American Medical Association (1994), American College of Occupational and Environmental Medicine (1994), and the Society of Toxicology (Holland 1995). They argue that a single chemical property (e.g., contains chlorine) does not adequately determine toxicity (MESB 1994). Furthermore, these experts argue that we can continue using many chlorinated organic chemicals, now and in the future, because we adequately understand their toxicity and environmental affects (Denzel et al 1994). Class-based regulation would unnecessarily and unfairly harm the manufacturers of these compounds and/or their precursors.

### *Is this a ban or a phase-out?*

The IJC recommendation to sunset chlorine as an industrial feedstock is ambiguous. Industry interprets sunset as a ban or immediate halt of chlorine production which would seriously affect their ability to do business (CRA 1993, CRA 1994, Holland 1995). A ban would cause unintended consequences on workers, growers, and sellers (Rosenberg and Levenstein 1995). Because of these unintended consequences, many Non-governmental organizations (NGOs) advocate and interpret "sunset" as a gradual phase-out of all chlorine-based uses (Greenpeace 1992; Thornton 1994; APHA 1994; Great Lakes United 1995). NGOs are commonly misunderstood as advocating an immediate ban. (Thornton 1994).

There are many examples of phaseouts and reductions of products or their application in the US. Examples of successful toxic chemical phase-outs include: mercury in chlor-alkali manufacturing, PCBs in electrical equipment, and lead in gasoline (IJC 1993a). Similarly, in the US, the EPA 33/50 Program has facilities voluntarily set goals to reduce the 1986 base year releases of specific chemicals into the environment by 33% by 1993 and 50% by 1995. Over 1,000 facilities have reduced chemical releases in this program (IJC 1994). In 1997, the US and Canada took steps toward the elimination of toxics in the Great Lakes; the stated goal is the elimination of 5 chlorine-based pesticides, a 90% reduction in PCB, and a 75% reduction in dioxin by the year 2006. Part of the current debate is the question of whether or not it is sufficient or safe to consider each compound separately - a process that, it has been suggested, would take 1 billion laboratories over 130 billion years to complete - or whether it would be prudent to combine all chlorinated chemicals in the same class, with the recommendation for a gradual phaseout of the class. With such a phase-out, the burden of proof would thus be on the potential user or manufacturer of a certain compound to prove it safe for human health and the environment; without this proof each chlorinated compound would be assumed too risky for release into the environment and therefore too risky for use. There are convincing arguments for both sides, as well as conflicting findings.

### *Human Health and Environmental Impact of Chlorine*

The potential for chlorine and chlorinated chemicals to impact human health and the environment is well documented. The World Health Organization reported that 64 organochlorines have "sufficient evidence" and 63 more have "limited evidence" of causing cancer, not including the hundreds of structurally related dioxin compounds (Thornton 1993). Chlorinated chemicals and their derivatives are implicated in a host of cancerous and non-cancerous effects (Agency for Toxic Substances and Disease Registry 1993, EPA 1994, Mackay 1995, MESB 1994) and environmental impacts like depletion of the stratospheric ozone layer (Denzel et al. 1994, EPA 1994, MESB 1994). The IJC (1993) has determined that the adverse effects of toxic chemicals on

wildlife, especially those that feed on fish, can be viewed as a prediction of human population effects. One of these effects on wildlife is disruption of the endocrine system; the same chemicals found in fish and wildlife tissues are being seen in human tissues as well. A correlation has been noted between the amount of toxic chemicals found in human tissue and the amount of fish that person eats. (IJC 1993) Despite this evidence, the largest study to date, reviewing more than 4,000 articles, the *Interpretive Review of the Potential Adverse Effects of Chlorinated Chemicals on Human Health and the Environment* (Delzell et al. 1994), concludes that the fate and toxicity of chlorinated chemicals are now reasonably well understood and their use will not cause adverse effects.

### *Natural versus Human Sources*

Over 2,000 naturally produced chlorinated compounds are documented (Gribble 1994), including chloromethane (methyl chloride) and vinyl chloride monomer (Delzell et al. 1994). Recent information indicates that the contribution of some chlorinated substances from natural sources is significant relative to human sources. Marine algae, volcanic eruptions, and sea salt are major sources of chlorine gas in the atmosphere. For example, the decomposition of chlorides in sea salt by sunlight into chlorine gas ( $Cl_2$ ) results in annual deposition of 2 to 50 kg of chlorine per hectare of land or 2.4 to 60 billion kg globally, most of which reacts immediately. These alternative sources are believed to be ten times higher than human production of elemental chlorine (Delzell et al. 1994). Adding to this debate is the continuing uncertainty in the estimates of dioxin sources. Efforts to account for the source of dioxins known to be in the environment have concluded that from 50 - 80% of all dioxin derives from presently unknown sources. (Carpenter, 1995).

### **History of Chlorine Controversy**

The chlorine controversy emerged against a backdrop of concern about biologically active chemicals in the environment (Carson 1962). Many individual and several groups of chlorinated compounds (and their derivatives) have received varying degrees of attention throughout the last fifty years. While the IJC recommendation to "sunset" chlorine and chlorinated compounds has left its mark, many other prominent events have preceded their recommendation and contributed to the history of chlorine.

### *Early Concern*

Male workers, in 1930, who were chronically exposed to PCBs developed acne-like skin lesions (later known as chloracne) referred to as Cable Haulers Disease. TCDD was identified as causing the occupational skin disease, chloracne in 1957. In 1958 a dioxin, HexaCDD, was responsible for causing millions of chicks to die of chick edema factor. Ten years later in Yusho, Japan, an industrial accident released PCBs into rice bran oil. The oil was consumed by many people causing acute toxicosis (i.e. chloracne, tooth deformities) and generational effects like small birth sizes and lower IQs. In 1969, laboratory studies showed that a pesticide that was mass produced for twenty years (2,4,5-T) was a teratogen causing developmental deformities (Physicians for Social Responsibility et al. 1994).

### *The 1960s and 1970s*

Several major federal and state regulations were passed in the 1960s and 1970s (see Appendix D). The US banned DDT and placed PCB under regulatory control in 1972. Also in 1972, a physician at B.F. Goodrich recognized a connection between the monomer vinyl chloride and cancer in humans. The latency period for this cancer was 26 years. In 1974, TCDD was implicated in the illness of horses (and possibly children) at Times Beach. Later in that same year, a trichlorophenol plant explosion released dioxin and led to children developing chloracne. In 1974, it was discovered that chlorine reacts with organic matter in the drinking water to form organohalides, which are carcinogenic in minute amounts. In 1979, Love Canal hit the front

pages, Vietnam Veterans initiated a class action lawsuit against the federal government for spraying Agent Orange, and rice oil in Taiwan was accidentally contaminated by PCBs. The accidental PCB contamination exposed over 2,000 people. Children of exposed mothers later developed ectodermal dysplasia, and showed developmental delays and abnormal sexual development.

### ***Chlorinated Chemicals in the 1990s***

The IJC (1992), Greenpeace (1992), and the American Public Health Association (1994) asked that chlorine and chlorinated chemicals be treated as a class of chemicals and called for a phase-out of chlorine and chlorinated chemicals. The 15 nation Paris Commission on the North Atlantic held in 1992 and the 21 nation Barcelona Convention held in 1993 agreed that toxic, persistent and bioaccumulative substances particularly organohalogens be eliminated and substituted where possible (Thornton 1994). While the American College of Occupational and Environmental Medicine (1994), American Chemical Society (1994), American Medical Society (1994), and the Society of Toxicology (1994) officially opposed treating chlorine and chlorinated chemicals as a class (Holland 1995).

In 1994, Congress faced a Zero Discharge Act (HR 2898) resolution which included a 5 year phase out of chlorine. The Clinton Administration proposed a Clean Water Act amendment and asked for a task force to study chlorine as a class and requested a national strategy (Thornton 1994).

In November of 1995, the Swedish government passed a resolution to phase out the use of PVC due to associated health risks (EPA 1997). The most recent government action took place on April 7, 1997. On this date, the US and Canada moved to eliminate toxics in the Great Lakes by 2006 including 5 chlorine based pesticides, 90% reduction in PCB, and 75% reduction in dioxin.

### **Chlorine and Dioxins**

Polychlorinated dioxins and furans (hereafter PCDD/F) are highly persistent trace pollutants potentially responsible for many adverse biological and ecological effects, such as endocrine-system disruption, birth defects, developmental and behavioral effects, and cancer. These compounds - believed to be mostly anthropogenic - have been detected all over the globe. The health effects, fate, and sources of PCDD/F are at present highly debated. The following discussion outlines the current debate and knowledge about this class of compounds, and the resultant implications for the industrial use of chlorine and chlorinated products.

#### ***What are "Dioxins"?***

The term "dioxins" refers to two classes of compounds comprised of over two hundred chemically similar molecules: polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF). Structurally, these compounds are tricyclic, planar molecules, where two benzene rings are bridged with either one (PCDF) or two (PCDD) ether (carbon-oxygen-carbon bonds) linkages. On the backbone of this structure is space for up to eight substitutions of chlorine, numbered 1-8.

The result is the possibility for over two hundred positional isomers, each with different toxicological properties. For example, epidemiological studies suggest that the toxicity of one particular isomer may be up to 10,000 times greater than that of another (Rappe 1984). The main health effects due to PCDD/F exposure were initially believed to be carcinogenic, but recent epidemiological studies suggest that these compounds may be more of a concern as hormone disrupting chemicals, where their effects are manifested at much lower concentrations than needed to initiate cancer (Colbom *et al.* 1996; Stone 1994). Toxicologists regard the 2,3,7,8-tetrachloro dibenzo-p-dioxin (or 2,3,7,8-TCDD) as the most toxic of all of the PCDD/F isomers, and in general the most toxic isomers are those with 4-6 chlorine atoms having all lateral positions on the backbone of the molecule (positions 2, 3, 7, and 8) simultaneously substituted with chlorine. Toxicities have been estimated for many individual isomers, and analytical results for PCDD/F loadings are often reported as "toxic equivalents" - or TEQ - to the 2,3,7,8-TCDD isomer. Here,

the quantities and toxicities of the individual PCDD/F isomers are normalized to an equivalent amount of 2,3,7,8-TCDD. Although assessing the toxicity of a particular sample, this method of accounting gives no information on the congener and isomer distributions, making source evaluation difficult.

### *Dioxins in the Environment*

Researchers throughout the world have reported on PCDD/F loadings in a variety of media, such as sediments, air samples, vegetation, and animal tissue and blood serum. PCDD/F are among the most hydrophobic of synthetic organic chemicals found in the environment, and as a result are highly bioaccumulative in nature. For example, when compared to other chlorinated persistent organic pollutants such as PCBs, chlorobenzenes, chlorophenols, and pesticides such as chlordane, toxaphene, mirex, etc., PCDD/F have the highest values for the octanol-water partition coefficient ( $K_{ow}$ ) in the range of  $10^7$  -  $10^8$ . In addition, PCDD/F are characterized as having extremely low water solubilities and are found mostly adsorbed to particulates in water samples. As a result, PCDD/F tend to accumulate in sediments, and the main mode of transport of PCDD/F in water systems is likely governed by the movement of suspended particles. PCDD/F are transported around the globe from their point sources - believed to be primarily combustion processes - by atmospheric mechanisms. Because of their very low vapor pressures and high adsorptive nature, PCDD/F are believed to spend a significant amount of their atmospheric lifetime on particles. Accordingly, depositional processes involving washout of particles are very important to general environmental loadings of PCDD/F. In addition, PCDD/F adsorbed to particles may be shielded from gas-phase atmospheric chemical reactions (Brubaker *et al.* 1997) known to degrade many other organic compounds, helping to make PCDD/F particularly persistent in the environment.

Several studies over the past ten years have attempted to measure temporal trends in PCDD/F loadings in the environment. In a recent excellent review, Alcock and Jones (1996) summarized the available data, some of which was derived from Great Lakes and New York State studies. For example, Smith *et al.* (1992) reported on PCDD/F levels in sediment samples taken from Green Lake in upstate New York. This lake is located in a mostly rural region, and the inputs of PCDD/F are believed to be solely from atmospheric sources. Sediment core samples were collected, dated, and fragmented for PCDD/F analysis. The results are typical of data from sediment cores and archived soil and vegetation samples collected from all over the world: small but measurable quantities of PCDD/F before 1900; a sharp increase in PCDD/F loadings after about 1920; a peak of PCDD/F levels in the 1960s through 1970s; and a leveling or drop to 50-75% of peak levels in the 1990s. The general decreases noticed in the past two decades have been at least partially attributed to improved air pollution control of combustion sources and waste treatment of chemical processes involving chlorophenol and pesticide use and manufacturing. Under debate is whether PCDD/F levels are still dropping from their peak values, or whether they have reached essentially steady-state levels.

### *Dioxins in New York State*

Several studies, such as discussed above, have chronicled the presence of PCDD/F in New York State in a variety of environmental media. Estabrooks *et al.* (1994) conducted a detailed New York State Department of Environmental Conservation (NYS DEC) survey in 1990-1991 of PCDD/F Contamination in Eighteen mile Creek in Niagara County. Eighteen mile Creek flows from the city of Lockport to Lake Ontario and is augmented by water from the Erie Canal, which in turn derives about 90% of its water from the Niagara River. These sites were chosen due to previous studies suggesting unusually high levels of organic chemical contamination in Eighteen mile Creek. At various points along the creek and its tributaries, sediment, water column, macroinvertebrate, and fish samples were collected and analyzed for PCDD/F. Total PCDD/F measured in sediment samples generally ranged from about 1,000-100,000 picograms PCDD/F per gram of sediment (pg/g), or parts-per-trillion (ppt). Converted to 2,3,7,8-TCDD toxic equivalents, the sediment levels ranged from 10-1,000 pg/g TEQ. The United States Environmental Protection Agency (EPA) guidelines for assessing 2,3,7,8-TCDD levels in bottom sediments place a high risk

(TCDD doses expected to cause 50-100% mortality in embryos and young of sensitive species) on sediments containing >25 pg/g. The report concludes that sediments in Eighteen mile Creek contain PCDD/F levels that are of concern. Follow-up studies upstream in 1992 suggested that the majority of the PCDD/F contamination found in Eighteen mile Creek was derived from the Erie Canal. One of these upstream sites, the Petit flume, contained the highest levels of PCDD/F - 16,000,000 pg/g (or 16 ppm) - ever recorded by DEC. This site is located on the Niagara River in the vicinity of the mouth of the Erie Canal, and is known to be near a number of industrial hazardous waste sites. DEC believes that a flux of PCDD/F contaminated sediments from the Niagara River and augmented from various point sources near the Erie Canal (i.e., industrial waste sites) accumulate in Eighteen mile Creek before being slowly flushed into Lake Ontario. Elevated levels of PCDD/F - exceeding the state piscivorous guideline, and approaching the state human consumption guideline - were also noticed in carp and crayfish collected during these studies, and correlated positively with PCDD/F sediment concentrations in the vicinity of their collection. The levels found in Bass filets were well below the state guidelines.

Due to the relatively low atmospheric concentrations of PCDD/F, air sampling for these compounds is a difficult undertaking. Required sampling times are quite long (24-48 hours), and the resultant analytical demands are severe. As a result, data on atmospheric loadings of PCDD/F are not nearly as numerous and comprehensive as those from sediment studies. In New York State, Smith *et al.* (1989; 1990) from the New York State Department of Health have conducted a series of air monitoring studies of PCDD/F levels in a variety of urban areas. Their samples, taken from the cities of Albany, Binghamton, Utica, and Niagara Falls, show atmospheric PCDD/F concentrations in the range of 3-22 pg/m<sup>3</sup>. These results represent the aggregate of particulate and gas phase PCDD/F. Recent air sampling results from a rural region in Chautauqua County about ten miles from the shore of Lake Erie show slightly lower PCDD/F loadings in the range of 2-10 pg/m<sup>3</sup> (Milligan 1997). Based on these preliminary results, there appear to be significant long-range sources of PCDD/F to New York State, separate from the urban point sources, that may make up about half of the total loadings in urban areas.

### **Sources of Dioxins**

Chlorinated dioxins and furans are solely undesired chemical side products derived from a number of different combustion and industrial processes involving chlorine. Many studies in the past few years have attempted to quantify the rate at which PCDD/F are introduced into the global environment from these different sources (Thomas and Spiro 1996; Brzuzy and Hites 1996; Duarte-Davidson *et al.* 1997). These sources of PCDD/F can be classified into two broad categories: chemical and combustion. It is believed that the chemical sources, such as from the manufacturing of pesticides and chlorophenols, wastewater treatment, paper and pulp bleaching, and perhaps other chemical processes involving chlorine, are a minor contributor to environmental loadings of PCDD/F when compared to combustion sources. In addition, chemical sources of PCDD/F may remain a localized problem - such as in the Erie Canal/Eighteen mile Creek study discussed above - resulting in contaminated sediments in the regions near the source, whereas combustion sources provide atmospheric loadings of PCDD/F that can then be transported for long distances. However, it should be noted that the sediment/water and water/vapor interchange dynamics of PCDD/F are poorly understood, and these localized "hot spots" may ultimately be regarded as significant global sources of these compounds.

From a detailed study of known combustion sources from the US, Canada, Japan, Australia, New Zealand, and 12 European countries, Brzuzy and Hites (1997) have estimated that approximately 3,000 kg of PCDD/F are emitted per year from these regions. Unfortunately, little or no data exists for Russia, China, and India, and PCDD/F combustion sources from these countries may be significant. Of the 3,000 kg/yr produced, municipal solid waste incineration (MSWI) is regarded as the major source (1,200 kg/yr), followed by cement kilns (1,000 kg/yr). Cement kilns often employ hazardous waste as a fuel - which can be comprised in part by chlorinated solvents - in their firing processes, and the heterogeneity of the fuel/cement mixture is believed to lead to PCDD/F formation. Behind these two main sources are ferrous metal

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production (steel mills) and biomass combustion, both estimated at about 350 kg/yr. Emissions from steel mills are believed to be a major source of PCDD/F in Europe. Biomass combustion is suspected to produce some PCDD/F, but the source of chlorine is unclear. Here, the chlorine may be derived from natural sources or from pesticide residues. Less important combustion sources are copper smelting processes (80 kg/yr), medical waste incineration (80 kg/yr), and gasoline combustion (12 kg/yr).

It is important to note that combustion sources can only produce PCDD/F if chlorine is present in the fuel. Indeed, it has been proposed that for kinetic and thermodynamic reasons, some PCDD/F - albeit very small amounts - will be formed in any high temperature process involving carbon, oxygen, hydrogen, and chlorine. This pathway has been named the "trace chemistry of fire" theory, or TCOF (Nestrick and Lamparski 1982). As a result, careful control of combustion parameters and novel air pollution treatment processes are required to reduce PCDD/F from combustion sources involving chlorine.

### ***Dioxins from Waste Incineration***

As discussed above, waste incineration is regarded as the most important source of PCDD/F to the environment, but the details and implications of their formation during these combustion processes is often misunderstood. Hazardous waste incineration, even when involving high levels of chlorinated wastes, does not appear to produce much PCDD/F as combustion by-products. In general, hazardous waste incineration involves a carefully controlled combustion of a well-characterized and homogenous waste stream comprised of mainly liquid organic solvents, followed by highly effective emission control devices. Municipal solid waste incineration, on the other hand, involves the combustion of a variable, multi-phase fuel comprised of metals, plastics, liquids, paper, cardboard, etc. Emission factors from MSWI's have been estimated to range from 7-17 µg of PCDD/F formed for every kg of garbage burned (Brzuzy and Hites 1996). Numerous field studies of operating MSWIs have clearly demonstrated that PCDD/F are not formed in the high temperature combustion zone, but instead downstream in the cooler regimes of the process. For example, PCDD/F levels from the exit of the combustion region, where the temperature may be as high as 1,000°C, are often at or below detection limits. Further downstream, as the flue gas stream is passed through a variety of air pollution control devices, such as acid gas scrubbers and particle removal devices such as electrostatic precipitators (ESP), PCDD/F levels are observed to rise.

Municipal waste (garbage) is typically comprised of about 25% non-combustible material, the bulk of which are metals or alloys in pure or oxidized forms. During incineration, most of this fraction ends up essentially unchanged from its original state as bottom ash. However, some of this ash becomes entrained in the flue gas stream during combustion and exits the combustor as residual fly ash. A still smaller proportion is vaporized in the combustion zone, only to cool and condense further downstream as condensation ash. The result is a fly ash consisting of a complex matrix of metals and alloys, metal oxides, metal chlorides, metal sulfates, carbon, etc. The presence of metal-rich and chlorine-rich fly ash in the flue gas stream is instrumental to the formation of PCDD/F during incineration. Although the majority of fly ash is comprised of silica and alumina, many trace transition metals are present - such as iron and copper - that are known to be effective catalysts in many chemical reactions. These catalytic elements in the fly ash are believed to initiate the heterogeneous formation of PCDD/F in the flue gas downstream from the combustion region where the process temperatures are in the range of 250-400°C (Stieglitz and Vogg 1987; Karasek and Dickson 1987; Milligan and Altwicker 1993). The majority of the PCDD/F are adsorbed to the surface of the fly ash particles, and are either collected by particle control devices for ultimate land filling or escape collection and are emitted into the atmosphere from the stack. Gas-phase PCDD/F produced are also likely present, which may be emitted at the stack. The carbon sources for PCDD/F seem to be derived from both residual elemental carbon or soot native to the fly ash, and from gas-phase precursors, such as chlorophenols, formed during the combustion process. The chlorine sources for this downstream formation are unclear but may be due to residual chlorine in the fly ash, or from gas phase HCl and Cl<sub>2</sub> in the flue gas stream.

Polyvinyl chloride (PVC) presents a particular danger when incinerated in house and building fires.. It is also the single largest source of chlorine in incinerators for municipal waste and hospital waste. When burned, the chlorine in PVC is transformed into products such as PCBs and PCDD/Fs which are indisputably hazardous to the environment. (IJC 1993)

Chlorine levels in municipal waste range from a fraction of a percent to as high as 50%, and is found in both organic (such as PVC plastics) and inorganic (such as table salt, or sodium chloride) forms. Most of this chlorine is converted to HCl, and depending on the combustion parameters, trace amounts of Cl<sub>2</sub>. A smaller proportion ends up in the fly ash - as described above - in the range of 1-10% chlorine by weight. In a well controlled incinerator, the nature of the inlet chlorine - organic or inorganic - is irrelevant to the form in which the chlorine exits the combustion zone. There appears to be no memory effect as to the chemical nature of the chlorine in the flue gas stream when compared to its initial form in the feed stream. A recent American Society of Mechanical Engineers (ASME) study also reports that the fractional amount of chlorine in the inlet waste has no statistical correlation to the amount of PCDD/F emitted from the stack of the incinerator (Johnson 1996). In this work, a field study of 107 combustion units showed that incinerators with even less than 1% chlorine in the waste stream can still emit significant amounts of PCDD/F. The explanation for this observation may be related to the complex chemistry involved in the fly ash catalyzed formation of PCDD/F, where only small amounts of chlorine may be required to form these trace pollutants. However, these results have been questioned, and further research is needed for confirmation.

The implications of the above studies are extremely important when drawing conclusions about the role of chlorine in PCDD/F formation in incinerators. Because PCDD/F are formed downstream from the combustion chamber on fly ash particles, the nature of the chlorine in the waste stream does not appear to have an effect on the presence or amount of PCDD/F formed during the incineration process. In addition, the percentage of chlorine in the waste may also not be important to the amount of PCDD/F formed, although this remains a highly debated conclusion. The most important factor in MSWI formation of PCDD/F seems to be the presence of metal catalysts in the waste stream. Japan, which due to lack of landfill space relies heavily on incineration as a municipal waste treatment method, has had some success in reducing PCDD/F levels from their incinerators by carefully removing metal from their feed waste streams. Of course, if there is absolutely no chlorine in the waste stream, no PCDD/F can be formed. However, trace levels of chlorine will always be present, from either natural sources or from inorganic sources in food products and other general household wastes.

### *The Dioxin "Missing Mass"*

One of the many debated issues in the dioxin story involves potential unknown sources of PCDD/F. For example, in the work done by Brzuzy and Hites (1996) discussed above, known sources of PCDD/F resulted in an estimate of about 3,000 kg released into the environment per year from atmospheric point sources. However, data collected from soil samples from around the world by the same team resulted in global deposition estimates of about 13,000 kg/yr - a factor of four disagreement from the known sources. In contrast, a similar study by Thomas and Spiro (1996) concluded that for at least the United States, the balance between known sources and measured loadings to the environment were in fairly good agreement. Both groups agree that the lack of available depositional and loading data for PCDD/F make closing this mass balance difficult. Internal cycling is probably the answer for much of the discrepancy; spacial-temporal averaging has resulted in large errors in data. From these results and others, there is evidence that sources of PCDD/F may exist that have not yet been characterized. Gribble (1994) has proposed that natural sources of chlorinated organic compounds - including PCDD/F - may be derived from microbial processes and forest fires. This hypothesis has been supported by some sediment core studies that show the presence of PCDD/F in sediment layers from pre-industrial revolution years (Juttner et al. 1997). However, these background levels may be due to sample contamination or vertical mixing and diffusion of PCDD/F through the sediment layers. Most researchers believe that all or most of the PCDD/F measured in the environment are anthropogenic in origin, and that natural sources are negligible.

### ***Implications of a Chlorine Ban or Phase-Out to the Presence of Dioxins in the Environment***

Given the current lack of data and understanding associated with the sources and fate of PCDD/F, it is difficult to draw conclusions about the effects that an industrial chlorine ban or phase-out would have on the presence of these compounds in the environment. Even if all anthropogenic sources of PCDD/F were suddenly eliminated, we would still be burdened with the legacy of PCDD/F for decades and perhaps centuries to come. Laboratory and field studies show that these compounds are highly stable thermodynamically, and are resistant to microbial decomposition. As a result, PCDD/F are regarded as one of the most persistent classes of pollutants released into the environment. For comparison, PCBs are still found in often alarming levels in water, sediments, and animal tissue around the globe, even though their production was banned in the 1970s. We might expect the same behavior from PCDD/F, which are more resistant to environmental degradation than PCBs.

PCDD/F are formed as trace, undesired chemical byproducts from a variety of different chemical and thermal processes, such as chlorophenol and pesticide production, bleaching processes, and waste incineration. Laboratory and field studies suggest that the level of chlorine in a process or waste stream is not well-correlated with the amount of PCDD/F produced. The chemical mechanisms describing PCDD/F formation are complicated, and do not depend strongly on chlorine concentration. These results imply that even a significant reduction of chlorine levels in these process or waste streams may not result in a proportional decrease in PCDD/F formation. In addition, the chemical nature of the chlorine (organic versus inorganic) in a process does not seem to be an important factor in resultant PCDD/F formation, particularly in waste incineration. As a result, the presence of even small amounts of inorganic chlorides - ubiquitous in nature - may still result in PCDD/F formation. We should emphasize that the chemistry of PCDD/F formation is not well understood, and further research is needed to have confidence in what a chlorine ban or phase-out would mean to PCDD/F releases to the environment.

### ***Dioxin in Summary***

Chlorinated dioxins and furans (PCDD/F) have spread all over the globe from their sources by the transport of contaminated sediments and atmospheric processes involving gas phase and particulate bound PCDD/F. These compounds are highly persistent, are resistant to microbial degradation, have low water solubilities, and are highly bioaccumulative. PCDD/F are found in sediment and air samples from New York State, both from local and long distance sources. PCDD/F levels found in some highly contaminated sediments of New York State are of high concern. Sampling data from sediment cores and archived soil samples suggest that PCDD/F loadings to the environment have leveled or dropped from their peak values in the 1970s.

Combustion processes are likely the main sources of PCDD/F - particularly solid waste (garbage) incineration. Hazardous waste incineration is likely a minor or negligible source. PCDD/F are also derived from other chemical processes, such as pesticide manufacturing, chlorophenol manufacturing, and pulp bleaching. However, these sources may be a minor contributor to the overall loadings of PCDD/F in the environment. In solid waste incineration, the chemical nature and concentration of chlorine in the waste feed stream may be a relatively unimportant factor to the amount of PCDD/F emitted from the stack. Thus, PCDD/F can be formed whether the chlorine enters the waste stream as either a plastic such as PVC or as table salt. Unless chlorine is completely eliminated from the waste stream - a difficult task given the presence of natural chlorine sources - the potential exists for the formation of PCDD/F.

Data on depositional rates and environmental loadings of PCDD/F throughout the globe are sparse. Unknown sources of PCDD/F - either anthropogenic or natural - may exist. It is also likely that a portion of the measured deposition is PCDD/F that was emitted historically and is still cycling within the environment. Further work is needed to better measure PCDD/F loadings and to identify unexpected sources and environmental cycling.

## Section Two: Economic Impact

The goal of this section is to survey existing information and point out data gaps in our understanding of chlorine and the New York State chlorine economy. In accomplishing this goal, a literature review and examination of relevant databases that pertain to the chlorine industry are necessary. A wide diversity of sources are drawn upon in order to better understand and evaluate the socio-economic implications of a chlorine phase out in New York. This section does not collect primary socio-economic data. However, a limited analysis of primary data collected by the US Department of Commerce was undertaken.

### Chlorine in Commerce

#### *How much chlorine is produced?*

In the United States, there are 18 producers producing over 12 million short tons of chlorine at 36 facilities. Three of these facilities (DuPont, Niachlor, and Occidental Chemical) are based in New York, all in the city of Niagara Falls (see Table 1). The projected 1997 production and capacity levels are 200% higher than 1965 levels. It is also important to note that chlorine output is usually consumed relatively quickly after it is made, because chlorine is difficult to store (Mannsville 1995).

**Table 1. New York Producers of Chlorine\***

Location	Company	Plant Capacity**
Niagara Falls, NY	DuPont	85,000
Niagara Falls, NY	Niachlor	240,000
Niagara Falls, NY	Occidental Chemical	330,000

\*Mannsville 1995

\*\* Short tons

### Socio-economic Evaluation

#### *US Socio-economic Evaluation*

The US chlorine industry is the subject of only a few major economic analyses. These reports exclude the benefits that are associated with phasing out chlorine and do not look at Full Cost Accounting (Charles River Associates 1993). Whether or not a report considers full cost accounting is the heart of many economic disagreements between proponents and opponents of a chlorine phase-out policy. Full cost accounting is inclusive of "avoided costs as well as direct and indirect subsidies provided to polluters through preferential pricing of energy and resource inputs, tax incentives, limited liability, and external costs (such as damage and cleanup costs) born by society" (LJC 1993a). The Charles River Associates (1993) report is cited most often and is therefore used quite often in the following section on economic impacts.

Charles River Associates (1993) reports that in the US in 1991, 370,000 jobs were directly dependent on chlorine, and 950,000 additional jobs were created by these employees spending their earnings. Almost half of the 370,000 jobs were workers in PVC plants. The Charles River Associates 1993 report also only considers job loss to the chlorine industry not job gain to the chlorine-free alternative industries. In doing so the Charles River Associates calculation of \$33 billion per year is suspect. According to the LJC(1993), the employment impacts "are likely to be positive, both in terms of number and quality of jobs."

The loss to the US economy, based on **1991**, is projected to be **\$102 billion** per year (Charles River Associates **1993**). The costs are the result of predicted job losses, expensive alternatives and high start up costs for new facilities. However, others estimate that “**97.6 percent** of the chlorine could be phased-out for less than **\$22 billion** per year...[or] ...over half of all chlorine use examined could be phased out for only about **\$4 billion**” (Thornton **1994**). The costs associated with an instantaneous implementation of expensive and inferior alternatives **as well as** a focus on the benefits and savings of the chlor-alkali industry are credited for “industry’s inflated cost estimates” (Thornton **1994**).

There are many projected savings in a chlorine-free economy. For example, Thornton (**1994**) argues that **TCF** (totally chlorine free) pulp bleaching would **be** cheaper than current chlorine-bleached pulp. The argument is based on reduced chemical purchases (**\$5 to \$10** per ton or at least **\$185 million** per year in savings), less energy to run the mills (at least **2.4 billion** kilowatt-hours per year and a savings of **\$108 million** per year), reduced water use, effluent treatment, disposal of contaminated sludge, and elimination of organochlorine contamination lawsuits (which have been **as high as \$10 billion** in the US for a single lawsuit) (Thornton **1994**). Closed-loop bleaching mills are estimated to save **\$1.4 billion** per year if the entire US (and Canadian) industry converted (Thornton **1994**).

In addition, the EPA estimates that switching from to a solvent free dry-cleaning method would require **42%** less capital investment to install, generate a **78%** better **return** on investment, **results** in almost equal operating costs due to reductions in chemical procurement and chemical disposal, **5%** increase in profit, and a **38%** increase in wages (Thornton **1994**). The most notable change in a chlorine free economy is decrease in health care costs, which the IJC estimates to be around **\$100 to \$200 billion** per year (IJC **1993b**).

A comparison between the US and New York chlorine economy reveals that New York significantly contributes to US chlorine-based industries (see Table 2).

Table 2. Value of Chlorine Chemistry - United States\* vs. New York\*\*

Economic contributors***	US	New York
Direct Employment	\$366,700	\$27,515
Indirect Employment	\$948,300	\$50,996
Direct Payroll	\$9,900,000,000	\$636,447,000
Indirect Payroll	\$21,400,000,000	\$1,352,093
Annual Sales	\$71,400,000,000	\$2,663,038,000

\*Sources: Charles River Associates **1993**

\*\* Sources: Charles River Associates **1995**.

\*\*\* Reported in Millions (000)

### New York Socio-economic Evaluation

Only one report examines the use of chlorine in New York. The New York report is brief and examines eight industries (see Table 3). A total of **27,515** New York residents, with a **total** payroll of **\$636 million** per year, are employed at the **5,085** New York facilities that directly use chlorine. If indirect users of chlorine are included, the employment total rises to **78,511** and the payroll to **\$1,989 million** per year. In addition, over **16.2 million** New York residents **drank** chlorinated water (Charles River Associates **1996**). Assumptions **are** not given so many of the figures are suspect.

**Table 3.** Economic Benefits of Chlorine in New York\*

	Drinking Water	Waste Water	Pulp Mills	PVC	Health Care	Chlorine Using / Chlorine Producing	Farming	Dry Cleaning
Number of facilities	959	243	2	119		20/3	32,306	3,739
Number of employees			64	4,723		7,154	66,082	15,575
Annual Payroll			\$3 Million	\$181 Million		\$325 Million		\$128 Million
Annual Sales				\$553 Million			\$2,622 Million	\$673 Million
Fixed Assets	\$4,206 Million		\$38 Million	\$357 Million		\$2,382 Million		\$193 Million
Values Added			\$11 Million	\$336 Million		\$1,753 Million		\$563 Million
Cost Increase without Chlorine	\$1,125 Million (plant changes)	\$183 Million (new plants & equip.)			\$3,553 Million		\$259 Million	

\*Source: Charles River Associates 1996; blank spaces indicate there is no data given.

### Summary of Chlorine Economy Findings

There are many data access barriers and data collection gaps for the New York “chlorine industry.” Therefore, this section relies on revenues listed in several industry based articles as a surrogate for access to actual revenues. Also missing from publicly available databases are figures on chlorine and chlorinated chemical production in New York. While US production information for each industry is provided in the US Department of Commerce’s *Current Industrial Reports* (1993), there is no New York equivalent. Again this section relies, where available, on the information that exists in the literature. Information pertaining to alternatives is available for some industries in the literature. Where available revenues, costs and production figures are listed for alternatives to the chlorine industry. Salary, range of employees and number of establishments, for New York State, are listed in the US Department of Commerce’s *County Business Patterns* (1993).

#### Socio-economic Databases

There are several socio-economic databases in New York and the US. The US Department of Commerce is responsible for publishing *County Business Patterns* (1993) and *Current Industrial Reports* (1993). The *Current Industrial Reports* carry production data for all US industry sectors (national level), whereas the *County Business Patterns* holds the number of employees, payroll, and the number of establishments per industry sector (down to the county level).

The New York Department of Economic Development databases contain information on the number of facilities, employment information, revenues per industry sector and the Gross State Product (GSP). Other types of socio-economic data are collected by the New York Department of Environmental Conservation under the Toxic Release Inventory (TRI) program. The TRI program requires each facility in New York, with at least 10 employees and releasing any of the more than 600 chemicals (above specified threshold levels), to file a Form R report. The socio-economic data that is collected by the Form R includes: facility location, chemicals used, and whether they are manufacturing or producing the chemical.

## Literature Review

An enormous quantity of publications surround the chlorine debate. The debate is inclusive of, but not limited to, socio-economic issues. While our attempt is to review **all** relevant articles and reports, due to the enormous volume of publications, there is a likelihood of omitting some.

### Environmental and Health Databases

There are many databases that include information pertaining to chlorine and chlorinated chemicals (see Appendix A), however these are largely environmental and human health based (Alston 1991). Where appropriate, information from these databases are included in this section.

### Alternatives to the Chlorine Industry

There are alternatives available for most of the current uses of chlorine. Replacements for PVC include wood, metal, paper, and ABS (acrylonitrile-butadiene-styrene), a non-chlorinated plastic. In the Pulp and Paper industry, where chlorine is used in the bleaching process, steps have already been taken to reduce the amount of chlorine used. Alternatives include using more off-white paper, as well as Oxygen-based bleaching. Chlorinated solvents, used for cleaning, are being replaced by water-based methods, such as steam-cleaning in the **Dry** Cleaning industry. Chlorinated pesticides are being replaced by biological pesticides in addition to changes in farming methods. Alternatives to chlorine in the disinfection of water, such as the use of Ozone and Ultraviolet (UV) treatments, have met with success. (IJC 1993)

The issue is not whether options for chlorine and chlorine containing chemicals exist but how well those alternatives would perform if chlorine is phased out. The Netherlands Scientific Council for the Government (1995) states that there are already alternatives which would be perfectly capable of meeting the economic and technical requirements either now or after a certain amount of further development in the near future. CHEMinfo (1997) also reports that there are several alternatives to chlorine and chlorine-based products that do and are meeting both economic and technical requirements. In the Canadian economy, market shares are higher for many of the alternatives to chlorine-based products (see Table 4). Although the CHEMinfo (1997) report deals solely with the Canadian economy, the generalizations may be applied to both the US and New York economies because of similar chlorine uses and alternatives.

**Table 4.** Market Shares for Chlorinated Substances and Alternatives\*

Chlorine-Based Product	Market Share (Cl)	Alternative Product	Market Share (Alt)
<i>PVC:</i>			
Drainage Pipe	Low	HDPE	High
Flooring	Low	Carpet	Medium
Drain, Waste, Vent pipe	Low	ABS	High
Flexible sheet, vehicle trim	Low	Fabric	High
Plastic Bottles	Low	PET	High
<i>Other Chlorinated Substances:</i>			
Trichloroethylene	Low	Hydrocarbon solvents	High
Flame Retardants	Low	Aluminum trihydrate	Medium

\* Source: CHEMinfo 1996; based on Canadian market only.

However, the Charles River Associates (1993) report assumes that "chlorine-free alternatives can be provided by returning to older products or technologies that have been displaced by more efficient chlorine-based ones, or by developing new, chlorine-free technologies." The alternatives that are selected by the Charles River Associates report are often criticized as "frequently ones that perform poorly, that are unreasonably expensive, or are not those the marketplace would select" (Thornton 1994). For example, while the Charles River Associates

report selects the Stoddard solvent, over perchloroethylene, the marketplace would not have because of toxicity, flammability and high equipment replacement costs (Thornton 1994). Another example is chlorine free bleaching which saves \$5 to \$10 per ton and requires half the energy (national level, not site specific) of a traditional plant (Patrick 1993). The Charles River Associates report also overlooks alternative pest management strategies and determines a \$24 billion per year cost and “20 to 70 percent decline in agricultural yields and the forced cultivation of tens of millions of additional acres to offset massive crop loss” (Thornton 1994). Further, the Charles River Associates report estimates regarding pharmaceuticals are flawed for three reasons: 1) all proposals have included provisions to exempt minor uses of chlorine where no alternatives exist, 2) many of these [pharmaceuticals] would not be affected by a chlorine phase-out policy” because only 20% actually contain chlorine, and 3) “the majority of pharmaceuticals could be produced through alternative means” (Thornton 1994).

Thornton (1994) suggests a prioritized plan that would select the weakest chlorine-based industry sector first (see Table 5). It appears that some industrial solvents, at \$180 million per year, are the least costly to replace, while pharmaceuticals, at \$53,600 million per year, are the most costly to convert to chlorine-free.

Other aspects to consider when looking at the “impact” of an alternative to a chlorine-based product or process, include: costs of substitution, facility dislocation, employment net changes, technical requirements, human health and environmental considerations.

Table 5. Alternative Prioritization\*

Rank	Industry Sector	Chlorine used (kt/yr)	Cost of phase out (\$million/yr)	% of Chlorine use	Cost (\$/ton)
<i>Least Costly to Convert:</i>					
1	Industrial Solvents	1,100	\$180	9.2	\$162
2	Propylene oxide	930	\$190	7.7	\$204
3	HCl - other than steel	690	\$160	5.7	\$232
<i>Most Costly to Convert:</i>					
1	Pharmaceuticals	160	\$53,600	1.3	\$335,000
2	Pesticides	130	\$24,300	1.1	\$186,923
3	Drinking Water	154	\$3,500	1.3	\$22,727

\* Sources: Thornton 1994; based on Charles River Associates 1993.

### A Time-series Appraisal of the Contributions of Chlorine-related Industries to the New York State Economy (1977-1991): Implications for the Chlorine Phase-Out Debate.

The chemical industry has responded to the calls for a chlorine phase-out by arguing that such a move will result in exorbitant costs for the US economy as a whole, about \$100 billion/year, (Charles River Associates 1993) together with massive job losses in the US and Canada. The industry’s scenario, however, appears to be based upon invalid assumptions that drastically overestimate the costs and underestimate the benefits of a well planned transition from chlorine-based processes to clean [chlorine-free] production (Thornton & Weinberg 1994).

There is no doubt that phasing-out chlorine will require substantial technological conversion. Based on Canadian industry estimates, the investment in new technology would itself stimulate the creation of about 925,000 job-years of employment (CHEMinfo Services 1997). But while the net economic effect is expected to be positive, a real disruption for some sectors — specifically those involved in the production of chlorine and chlorinated chemicals also has to be acknowledged.

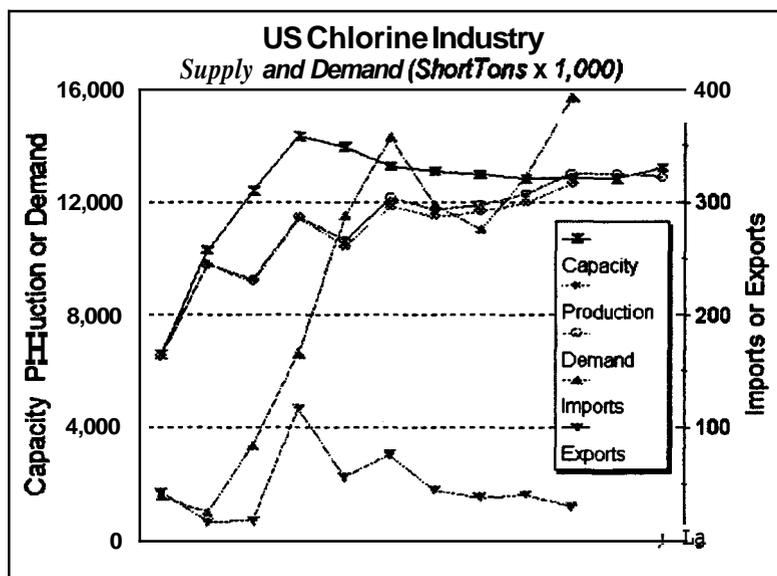


Figure 4. Trends of production capacity, supply, demand and trade of chlorine in the United States (1965-1996).

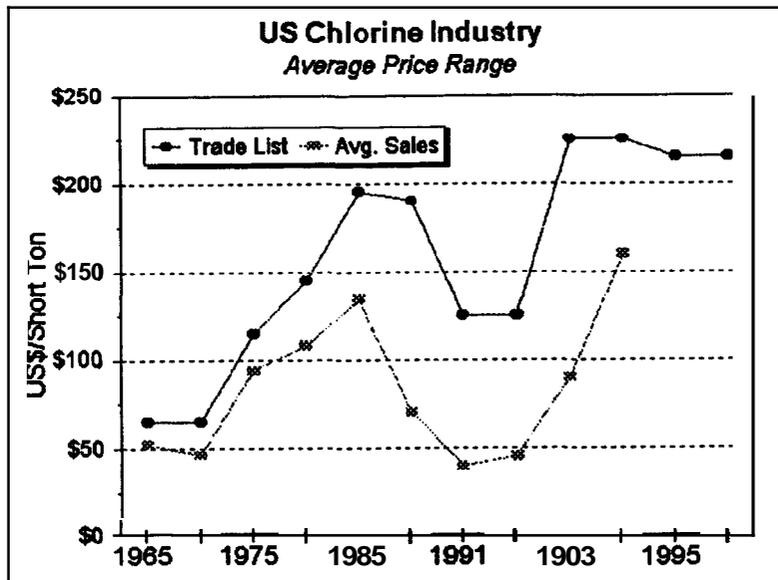


Figure 5. Chlorine price fluctuations ranged from trade list and average sales in the United States (1965-1996).

Only 3 chlorine producing plants are located in New York State Great Lakes Basin, barely contributing 5% of the total US production capacity (i.e., 655,000 short tons). Furthermore, within New York State, the manufacturing sector — for which most of the chlorine-related industries were retrieved according to their SIC codes, has been decreasing its contribution to the NYGSP steadily from 18.3% down to less than 15% from 1977 to 1992 (Figure 6: Mnf/GSP).

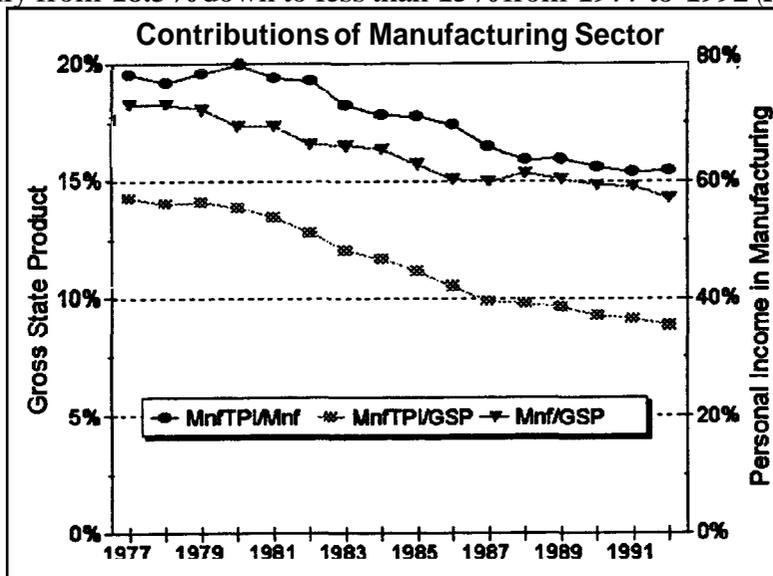
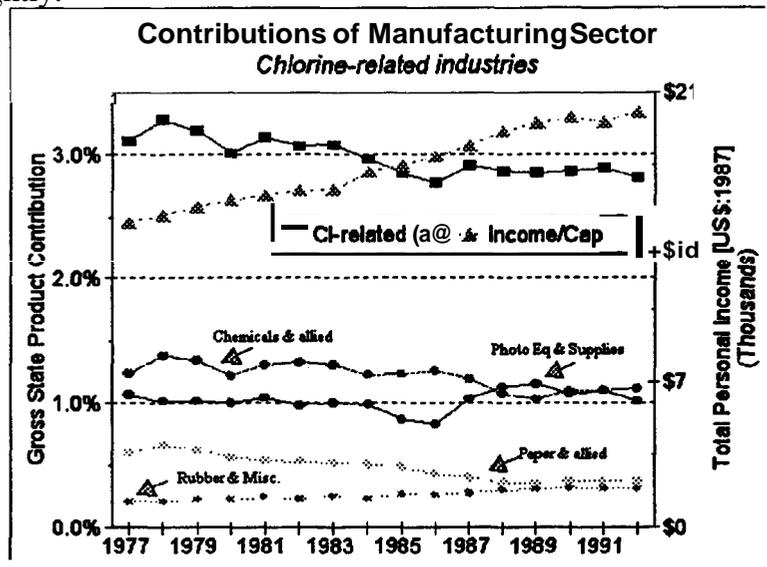


Figure 6. Contributions of the manufacturing sector (Mnf) to the New York State economy (GSP=Gross State Product, TPI=Total Personal Income) from 1977 to 1992.

The decreasing trend of the TPI fraction within the manufacturing sector itself decreased accordingly from close to 78% —peaking up to 80% in 1980, down to 62.5% (Figure 6: MnfTPI/Mnf), and relative to NYGSP from 14.2% down to 9% during the same period (Figure 6: MnfTPI/GSP).

The total contribution of chlorine-related industries of the manufacturing sector to the NYGSP has barely exceeded 3%, and has stabilized itself slightly below that percentage since 1987, following the highest observed prices at the peak-importing year (Figure 7). The dollar equivalent of this percentage is not negligible, though (i.e., \$9.5 billion), being the *chemicals and allied* industries the ones marking this trend (i.e., \$4.45 billion). Chlorine use in pulp bleaching has declined to stabilization since 1988, and its use within the plastic *materials* and resins industry (i.e., ethylene dichloride as intermediate for PVC production) has remained to some extent stable, increasing slightly.



**Figure 7.** Contributions of chlorine-related industries to the New York State economy (1977-1992).

In opposition to these decreasing contributions to NYGSP, both NYGSP and TPI per capita have increased in *real terms* (Figure 8), notwithstanding significant demand-driven inflationary year-to-year fluctuations linked to an increasing trend in the number of New Yorkers (Figure 9).

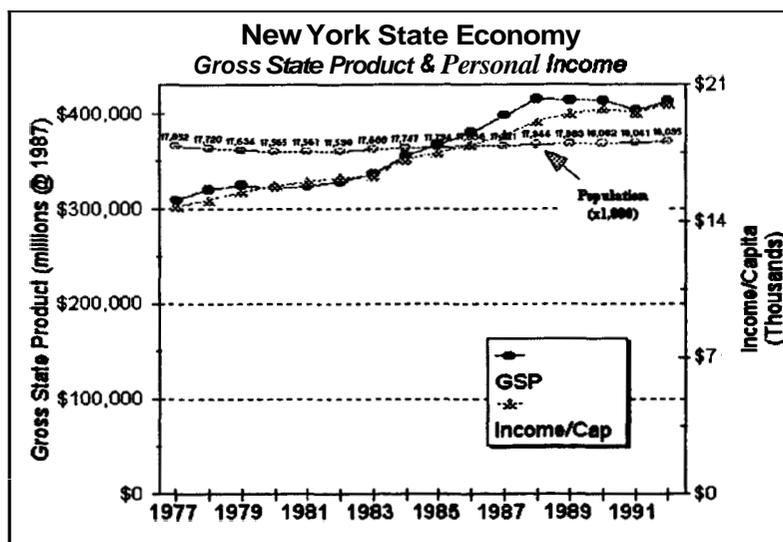


Figure 8. Trends of the New York State economy and its population (1977-1992).

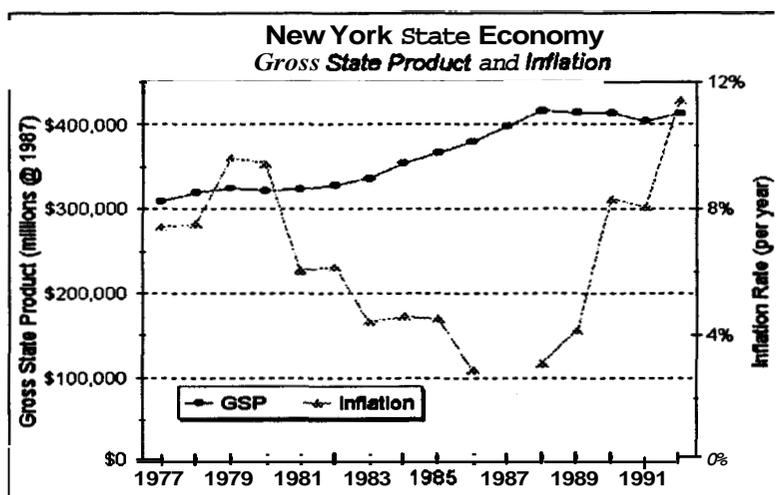


Figure 9. Inflationary trends of the New York State economy (1977-1992).

### Discussion

The use of ethylene dichloride as intermediate for PVC production, within the plastic materials and resins industry (SIC 2821), and its production along with propylene oxide, chlorinated ethanes and methanes, and other industrial organic chemicals (SIC 2869), while being used in several other industries, are very difficult to trace by SIC code. In contrast, its use in pulp and paper (SIC 2621) and alkalis and chlorine (SIC 2812) production, was rather a straight-forward situation.

While the New York County Business Patterns data source, excludes most government employees, railroad employees, and self-employed persons, or 55% of the total personal income balance for the State, it is remarkable that 51,650 people were employed in the chlorine-related industrial sector — as identified above, just in 1993. The payroll equivalent of this manufacture force exceeded \$500 million (excluding the payrolls of the alkali & chloride, and plastics & resins industries which are not disclosed in these public-access databases), which means that a significant portion of the contribution of these industries to NYGSP (i.e., value added) relies significantly on the wholesale trade of paper production, and chemicals & allied industries, adding 20.6 thousand

and 8.5 thousand workers, and \$621 and \$381 million, respectively, to most of the whole chlorine-related sector (circa 1993) we were able to identify. Still close to \$8 billion of the revenues implicit in our estimates at the NYGSP scale, are difficult to explain without a comprehensive understanding of the economics involved in an evaluation of this nature.

The important finding of this section, though, is that at the scale of the whole New York State economy, there seems to be an independent trend of economic growth in both NYGSP and TPI, notwithstanding the decreasing contribution of chlorine-related industries to NYGSP —which also appears to be independent of price fluctuations, production or demand of chlorine at a national level. This observation is still significant but apparently unrelated to other major non-chlorine related economic activities. On its own this decreasing trend seems to be related to another observed decreasing trend in the discharge of regulated chlorinated compounds into New York's share of the Great Lakes Basin (see Section Three).

The magnitude of this growing economic trend is certainly encouraged by the continual process of growth of new markets and industries, and the disappearance of old ones. Innovation, trade, and government regulation are the market forces by which the proposed phase-out of chlorine might already be occurring. Both further automation in the manufacturing sector, and a shift to the retail and services sector of the New York State working force, might be buffering any negative effect of this virtual phase-out, which effect was being barely noticed in the TPI per capita of 17 million New Yorkers of whom hardly 100,000 were somehow directly employed by chlorine-related industries in 1993. These opposing trends seem to continue operating.

## Section Three: Chlorinated Compound Data

This Section is intended to be a review, evaluation, and interpretation of available chlorinated compound release data. To this end, available sources of chlorinated loading data for the Lake Ontario basin are described below along with a presentation of loading trends and amounts for each of these sources. A numerical model was also used to demonstrate the behavior of a number of chlorinated compounds in Lake Ontario for various loading scenarios and these results are presented. Finally, a discussion of the implications of the results with regard to the sunsetting of chlorine for New York State is given.

### Review and Evaluation of Available Data

#### *Review of Databases Useful in Quantifying the Releases of Chlorinated Compounds to the Great Lakes Basin from New York State*

The ability to assess the impacts on water quality in New York State that would be produced by a chlorine sunsetting in the Great Lakes basin is largely governed by the availability of reliable loading data. Presently, releases of toxic compounds are inventoried by way of several database efforts maintained at both the Federal and State level. Though records of toxic releases to the environment are maintained more thoroughly than ever before, it is safe to say that many releases go untracked or are not accounted for accurately by current inventory mechanisms. It is with full acknowledgment of these limitations that any release amounts are reported or used in this paper. Despite these limitations, current data sets can be useful in the effort to begin to evaluate in a specific manner the environmental consequences that may be incurred by a sunsetting of chlorine. What follows is an overview of the main data sources available to quantify chlorinated loadings to Lake Ontario from New York State.

#### *Toxic Release Inventory (TRI)*

The Toxic Release Inventory is a database maintained by the US EPA to provide information to the public regarding release of toxics to the environment from manufacturing facilities. Facilities must report estimates of releases to air, surface water, land, or subsurface wells if they conduct manufacturing processes within Standard Industrial Codes 20 through 39 and have 10 or more full time employees, or if they manufacture or process more than 25,000 pounds of any listed chemical throughout the calendar year. Also, facilities that use more than 10,000 pounds of any listed chemicals during the calendar year must report estimates of release amounts.

In 1994, 4.9 million kilograms of chlorinated compounds were released to the environment from New York State according to the TRI. Of this, 2.8 million kilograms were released from within the Lake Ontario basin. A year by year trend for total chlorinated compound releases is illustrated in Figure 10, where total release amounts are plotted versus year for statewide releases and basin releases. From this figure, it can be seen that chlorinated releases have been dropping each year since 1988 in both the state and the Lake Ontario basin.

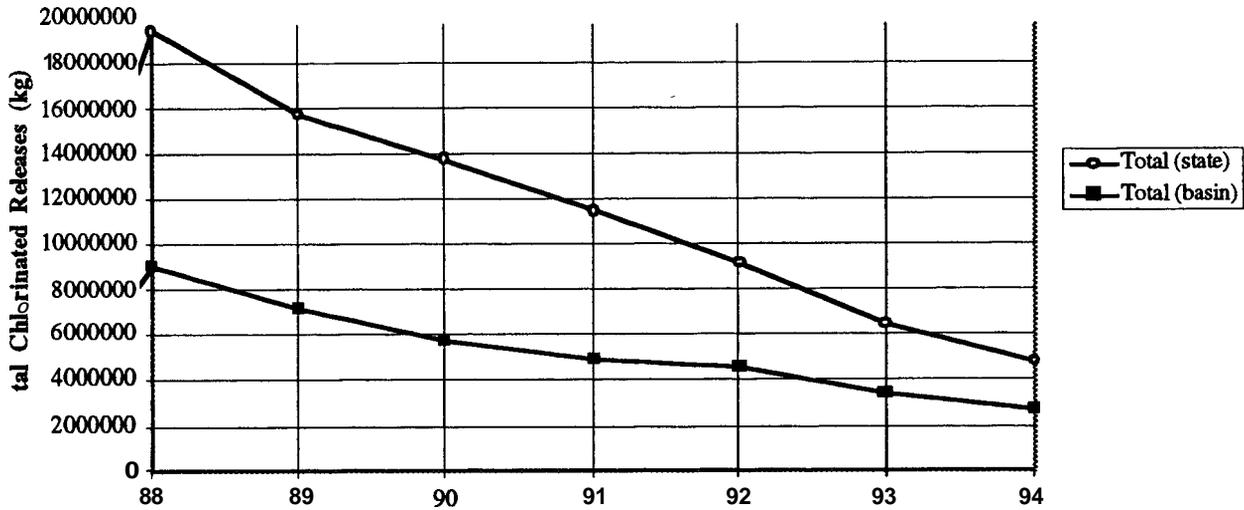


Figure 10. New York State TRI: Total Chlorinated Releases (1988-1994)

There were **379** facilities releasing chlorinated compounds in **1994** according to the TRI and **87** of these were located within the Lake Ontario basin. The number of facilities releasing chlorinated compounds is plotted as a function of year in Figure 11 for both the entire state and Lake Ontario basin. Here, as with the total release amounts, the number of facilities reporting releases of chlorinated compounds to the TRI has been decreasing each year since **1988**, though this number has decreased more slowly for facilities located within the basin.

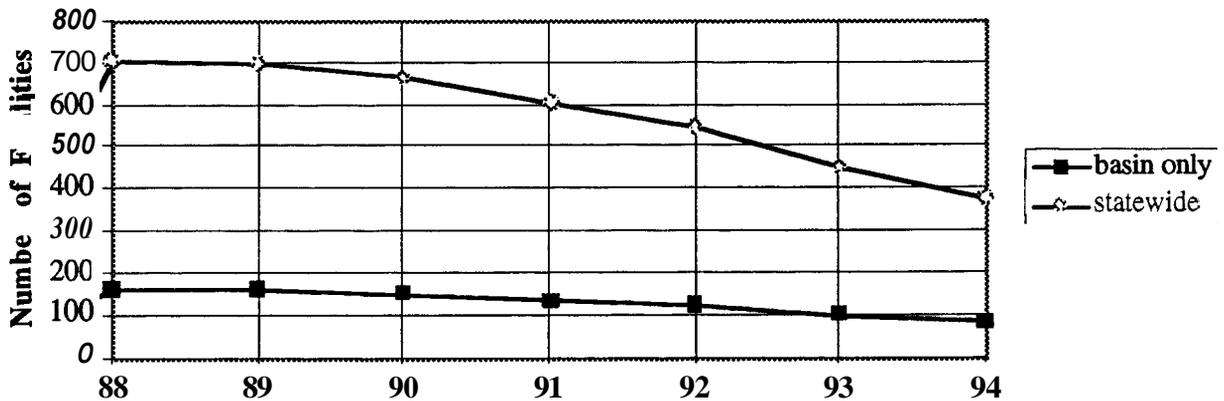


Figure 11. New York State TRI: Number of Facilities Releasing Chlorinated Compounds (1988-1994)

A breakdown of the medium to which these releases have been discharged to is given in Figure 12 where it is shown that **65%** of chlorinated releases tracked by the TRI have been to air

by way of stack emissions for the period 1988-1994. Stack emissions to the air encompass any release to the environment from stacks, vents, ducts, pipes, or other confined air streams. Fugitive emissions have accounted for 33% of TRI chlorinated emissions in New York State. These emissions consist of any releases to the air that do not originate from the sources characterizing stack emissions. This includes leaks in piping systems and evaporative losses. Also, it is shown in Figure 12 that direct releases of chlorinated compounds to water and publicly-owned treatment works (POTWs) have occurred in much lower amounts relative to air releases. The year by year trends of chlorinated releases to each medium from the TRI are shown in Figures 13a - 13c for both releases from the entire state and releases from within the Lake Ontario basin. Fugitive and Stack emissions are shown in Figure 13a, releases to POTWs are shown in Figure 13b, and releases to surface water are shown in Figure 13c. For each of these media, chlorinated compound releases tracked by the TRI have generally decreased.

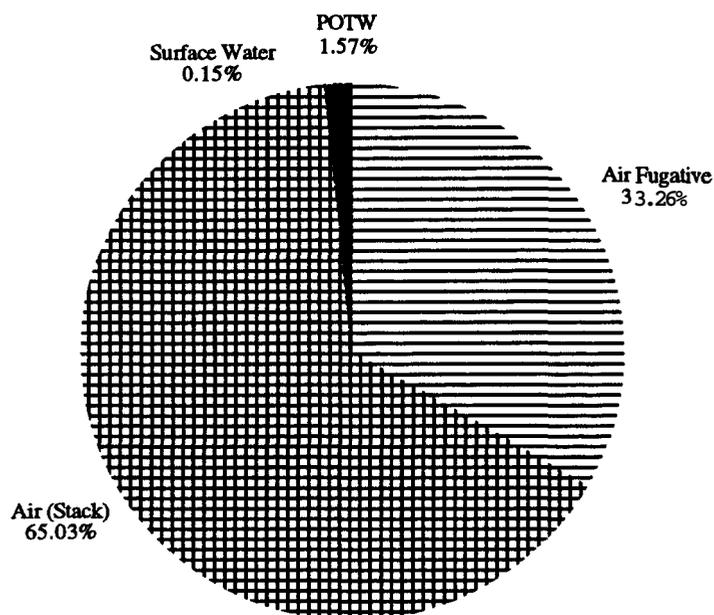


Figure 12. New York State TRI: Chlorinated Releases (1988-1994) by Medium

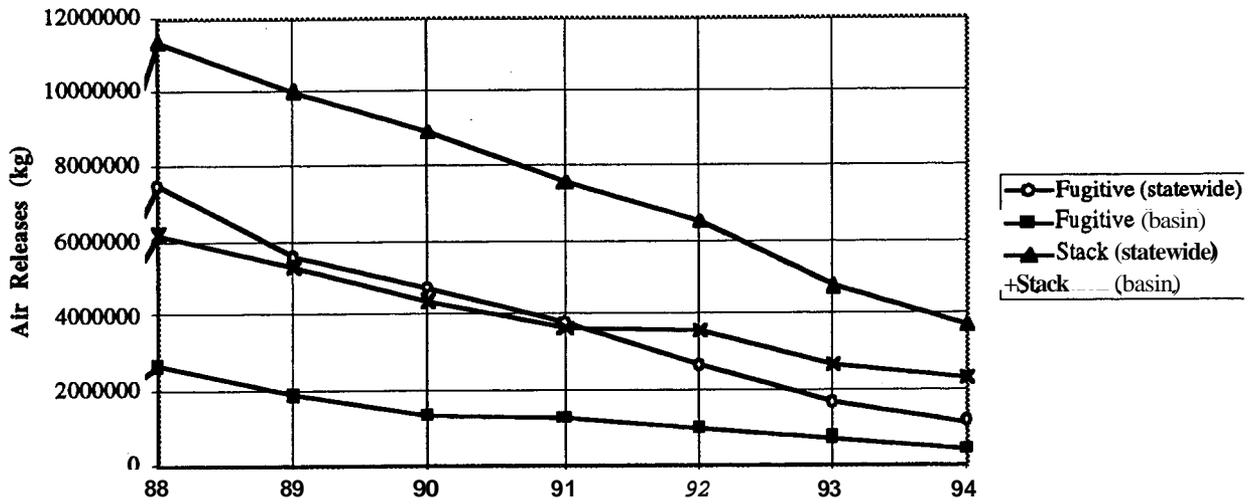


Figure 13a. New York State TRI: Chlorinated Releases to Air, Fugitive and stack (1988-1994)

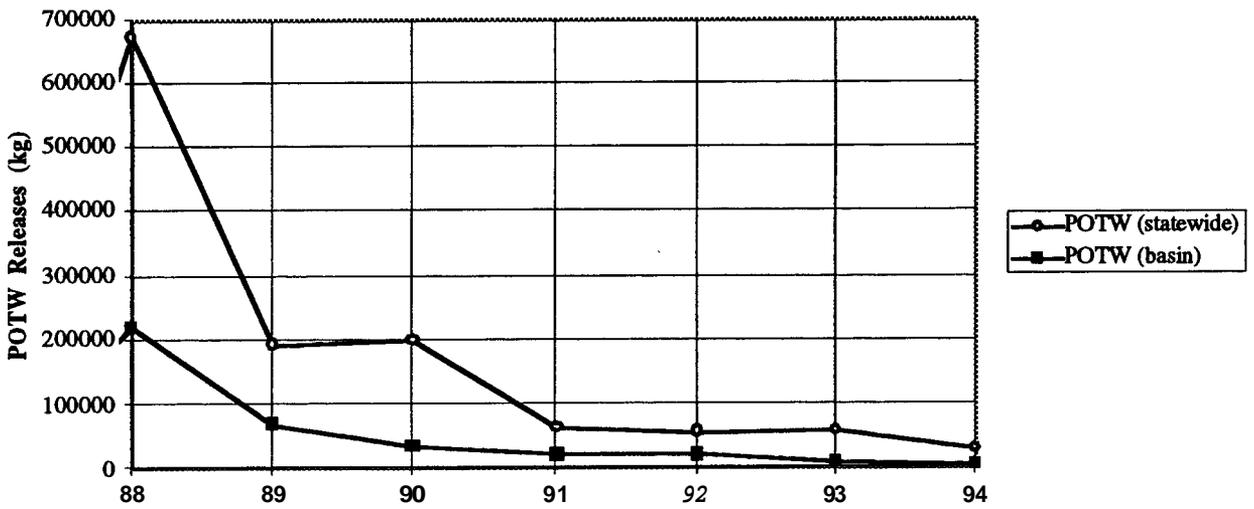


Figure 13b. New York State TRI: Chlorinated Releases to POTWs (1988-1994)

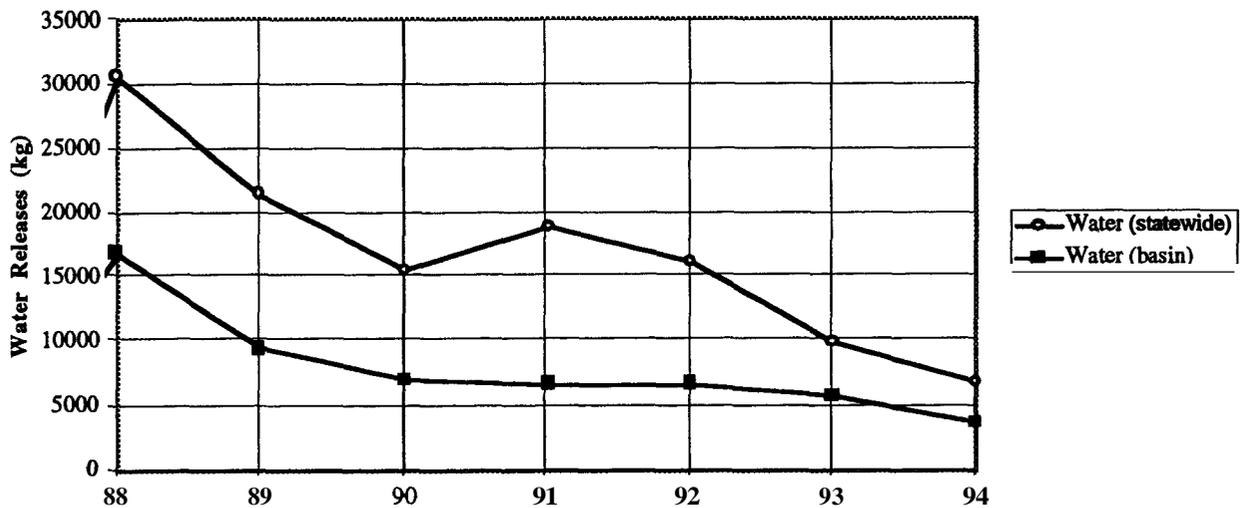


Figure 13c. New York State TRI: Chlorinated Releases to Water (1988-1994)

The ten chlorinated compounds which were released in the highest amounts to air from stack emissions and fugitive emissions are shown in Table 6. Similarly, the ten chlorinated compounds most released to POTWs and to surface water are given in Tables 7 and 8. For each of these mediums, methylene chloride was released in either the highest or next to highest amounts. Also, for the cases of POTWs and surface water releases, an associated table is provided in which the highest released chlorinated compounds in the Lake Ontario basin are singled out. The compounds appearing in each of these basin-specific tables are generally similar to their state-wide counterparts.

**Table 6: New York State TRI: Listing of Ten Most Released Chlorinated Compounds to Air (Stack) and Air (Fugitive), 1988-1994**

Compound	Air (Stack) Amount (kg)	Air (Fugitive) Amount (kg)
Methylene Chloride (Dichloromethane)	18,765,502	8,183,915
Hydrogen Chloride Gas/Hydrochloric Acid	14,121,069	326,973
1,1,1-Trichloroethane	9,631,067	5,737,198
Freon 113 (1,1,2-Trichloro-1,2,2-Trifluoroethane)	1,474,855	6,116,403
Trichloroethylene	4,252,480	3,308,692
Tetrachloroethylene	2,524,301	2,050,167
1,2-Dichloro- Propane	852,753	245,393
Dichlorodifluoromethane (CFC-12)	---	553,957
Chlorine Gas	443,412	---
Chlorine Dioxide	194,583	---
Vinyl Chloride	167,241	---
Chloroform	---	117,694
Chlorodifluoromethane (HCFC-22)	---	74,038

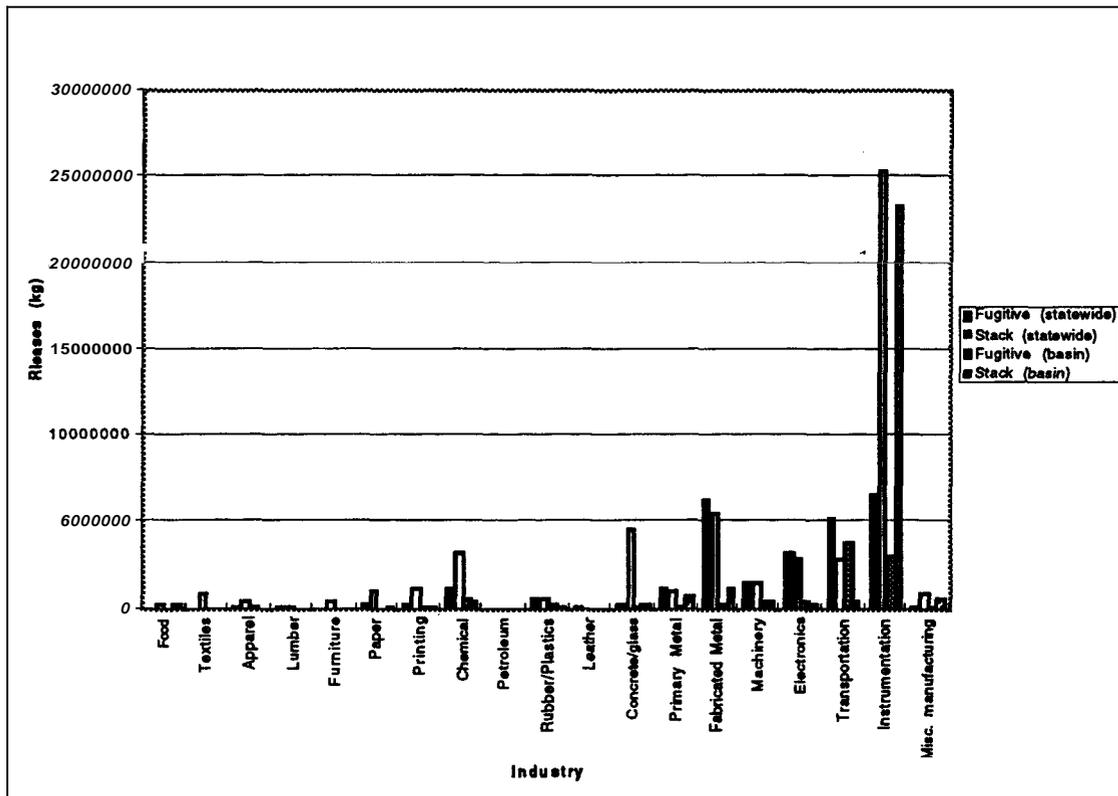
**Table 7: New York State TRI: Listing of Ten Most Released Chlorinated Compounds to POTWs for Entire State and Lake Ontario Basin: 1988-1994**

Compound	Entire State Amount (kg)	Lake Ontario Basin Amount (kg)
Hydrogen Chloride Gas/Hydrochloric Acid	945,940	146,604
Methylene Chloride (Dichloromethane)	255,302	235,074
Chlorine Gas	44,828	1,405
1,2-Dichloro-Ethane	10,781	262
Trichloroethylene	5,499	336
1,1,1-Trichloroethane	5,131	552
Tetrachloroethylene	2,510	---
Chlorine Dioxide	1,815	---
Vinyl Chloride	1,085	---
Chloroform	958	958
Carbon Tetrachloride	---	339
Chlorobenzene	---	259
Freon 113 (1,1,2-Trichloro-1,2,2-Trifluoroethane)	---	124

**Table 8: New York State TRI: Listing of Ten Most Released Chlorinated Compounds to Surface Water for Entire State and Lake Ontario Basin: 1988-1994**

Compound	Entire State Amount (kg)	Lake Ontario Basin Amount (kg)
Chlorine	49,383	1,645
Methylene Chloride (Dichloromethane)	27,087	26,820
1,2-Dichloro- Propane	13,245	13,245
Hydrogen Chloride Gas/Hydrochloric Acid	6,416	2,296
Chloroform	5,899	907
1,2-Dichloro-Ethane	4,893	4,885
Methyl Chloride	2,663	---
1,1,1-Trichloroethane	2,038	1,651
Tetrachloroethylene	1,972	---
Trichloroethylene	1,950	1,423
1,1,2-Trichloro-Ethane	---	1,882
Freon 113 (1,1,2-Trichloro-1,2,2-Trifluoroethane)	---	517

A breakdown of chlorinated releases by industry to air, POTWs, and to surface water is provided in Figures 14- 16. The instrumentation/photographic industry (SIC category 38) has been the largest releaser of chlorinated stack and fugitive emissions, as well as to surface water throughout the seven year period. The chemical industry has released the largest quantities of chlorinated compounds to POTWs.



**Figure 14. New York State TRI: Chlorinated Releases to Air, Fugitive and Stack, by Industry (1987-1994)**

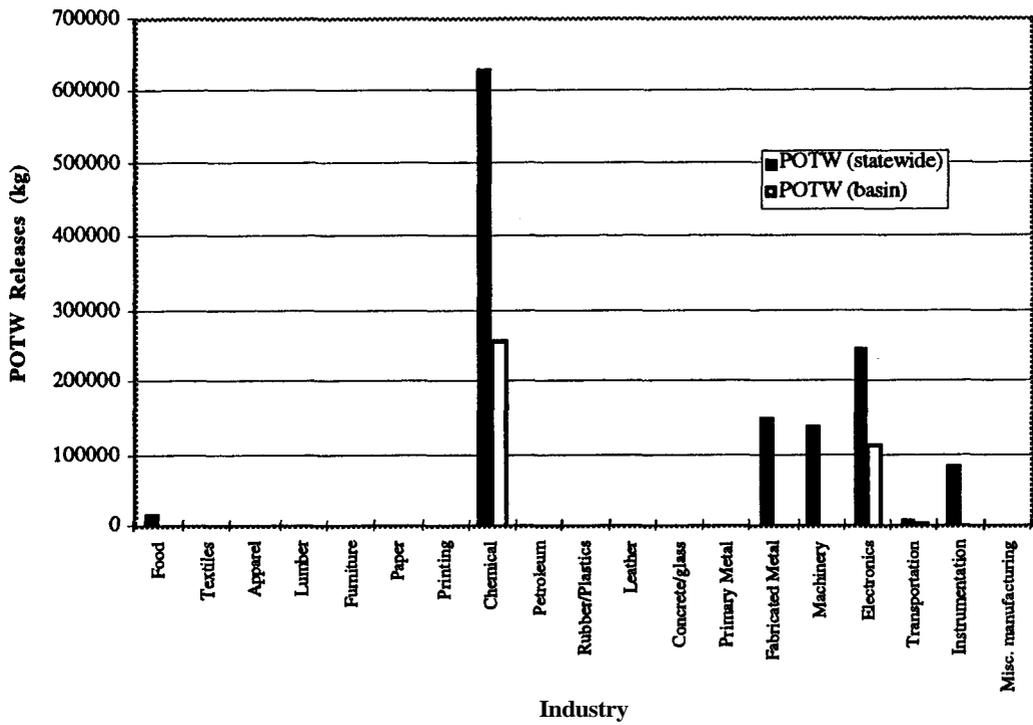


Figure 15. New York State TRI: Chlorinated Releases to POTWs by Industry (1988-1994)

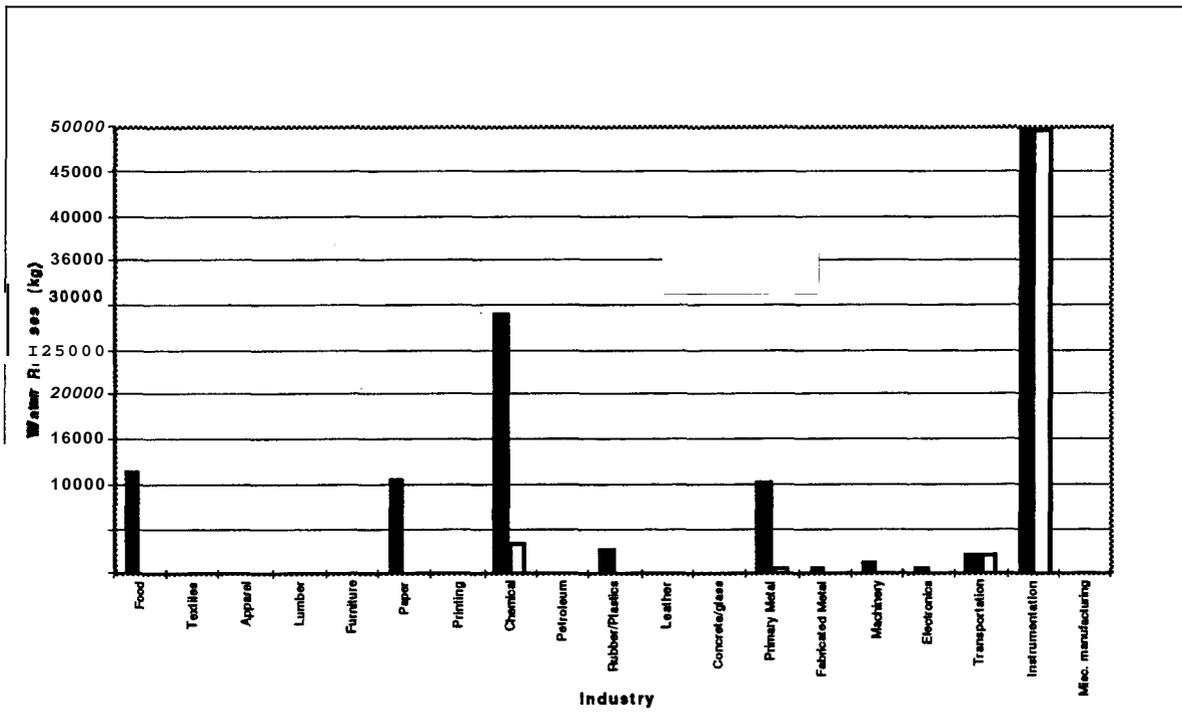


Figure 16. New York State TRI: Chlorinated Releases to Water by Industry (1988-1994)

### Niagara River Upstream/Downstream Data

Loading amounts to Lake Ontario from the Niagara River are calculated in annual reports sponsored by Environment Canada, EPA, Ontario Ministry of Environment, and NYSDEC. Concentrations of a variety of compounds are measured in weekly samples taken at the upstream end of the Niagara River (Fort Erie) and at the downstream end (Niagara on the Lake). The portion of a contaminant present in the dissolved form and the portion attached to suspended solids are measured. Loading values for each of the compounds are calculated using an algorithm which incorporates sampled concentrations, flowrate data from the river, as well as the number of samples for the year which yielded concentrations below the detection limit. Of the 78 compounds presently being sampled, 53 are chlorinated. Data from the years 1986-1992 were used in this section. The loading amounts of chlorinated compounds from this data set are shown in Figure 17. Data from the year 1989 have not been included in this plot due to an exceptionally high loading of methylene chloride that occurred in that year. Also, the ten compounds from this data set having the highest average loadings to Lake Ontario are shown in Table 9. As was the case for the TRI data, methylene chloride is the compound with the highest load.

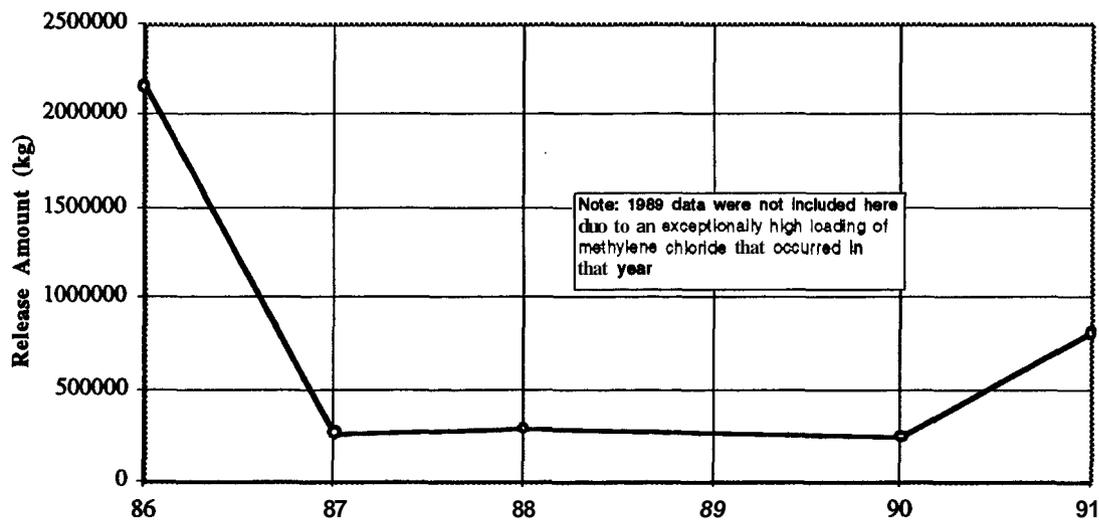


Figure 17. Niagara River Chlorinated Releases to Lake Ontario (1986-1991)

**Table 9. Niagara River Data: Ten Compounds with Highest Loadings to Lake Ontario (1986-1992)**

<b>Compound</b>	<b>Amount (kg/yr)</b>
Methylene Chloride	10,800.174
Tetrachloroethylene	31,964
Atrazine	6,716
Chloroform	2,646
Metolachlor	2,459
1,4-Dichlorobenzene	545
PCB	405
Alpha Bhc	389
1,2-Dichlorobenzene	356
Pentachlorophenol	351

### *Permit Compliance Database for New York State*

Releases of constituents of concern to the quality of New York's waters are regulated by National Pollutant Discharge Elimination System (NPDES) permits. These are issued to industries and POTWs to establish maximum concentrations or maximum loadings of a compound that may be discharged into a given waterbody. This program is administered in New York by the Department of Environmental Conservation. Permits generally require that sampling of permitted waste streams be performed at a set interval (i.e. every week, every month, etc.). The results of these samplings are tracked through a database known as the Permit Compliance System (PCS) which was set up to flag cases where effluent levels exceed permitted amounts. Though the database was primarily constructed for this purpose, it has been modified by the EPA to convert sample concentrations into loading amounts by considering the average effluent flowrates of each permitted location. Loadings amounts of chlorinated compounds from this database were obtained from NYSDEC for the years 1993-1995. The total chlorinated loadings inventoried by this system for the entire state and the Lake Ontario basin are shown in Figure 18 where it is shown that these amounts have decreased each year in this period while the number of permitted releases has remained nearly constant as shown in Figure 19. The most released compounds during 1993-1995 according to the PCS are shown in Table 10 with chloride and chlorine being the highest for both the entire state and for the Lake Ontario basin. Methylene chloride appears in the highest amounts after chloride and chlorine.

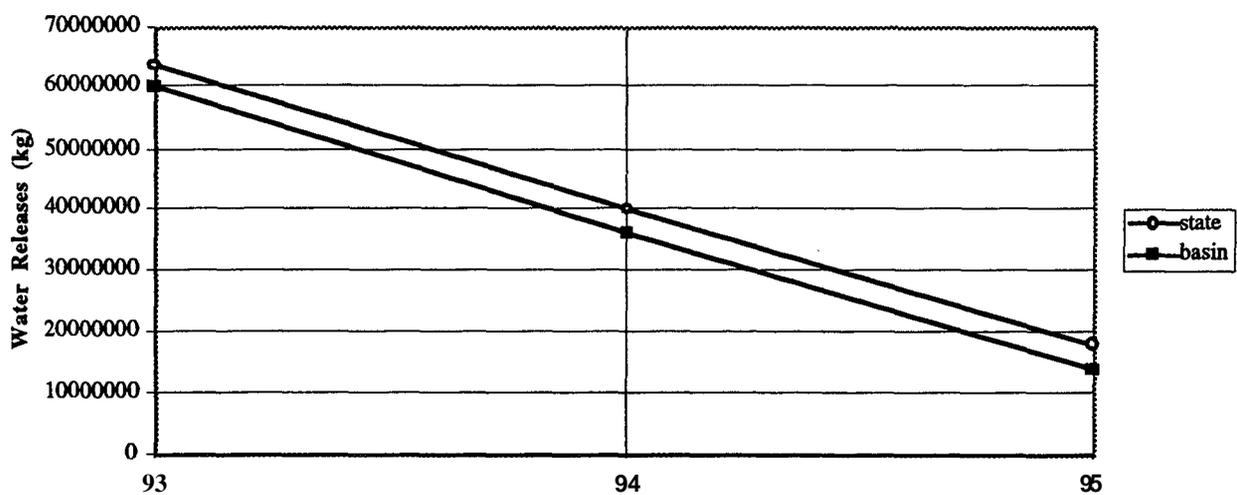


Figure 18. New York State PCS: Chlorinated Releases to Water (1993-1995)

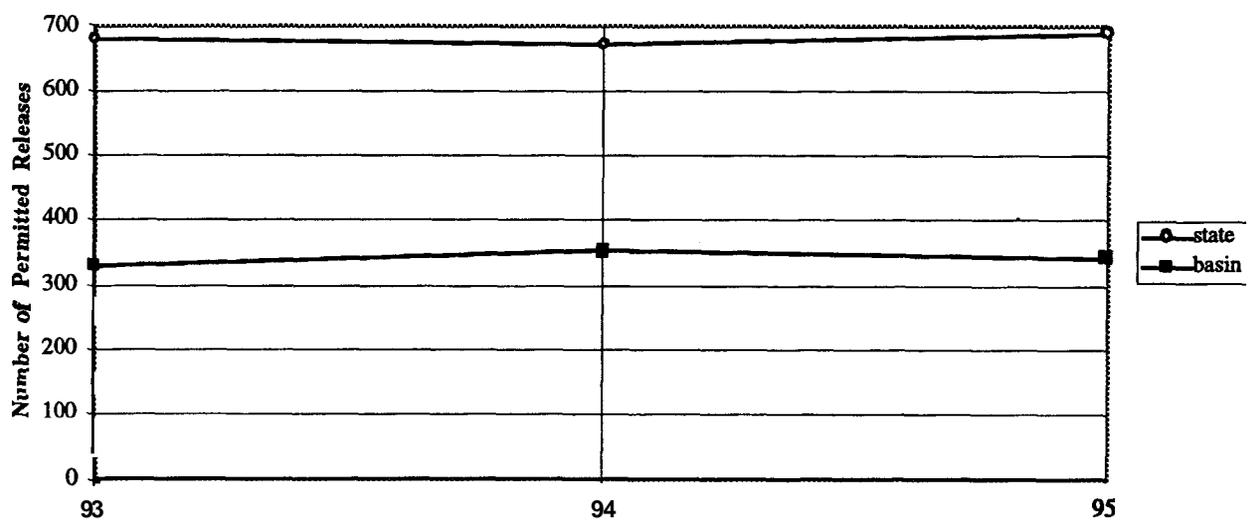
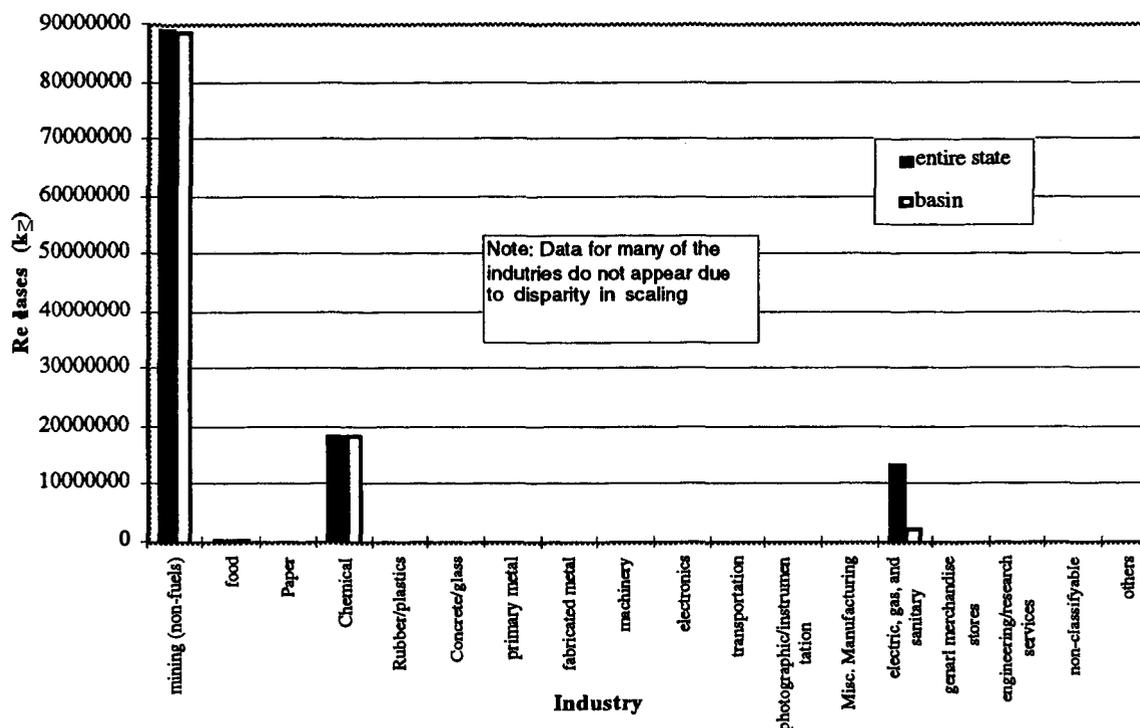


Figure 19. New York State PCS: Number of Permitted Releases (1993-1995)

**Table 10. New York State PCS: Ten Compounds having the Highest Release Amounts for Entire State and Lake Ontario (1993-1995)**

Compound	Entire State Amount (kg)	Lake Ontario Amount (kg)
Chloride (as Cl)	1.09E+08	1.08E+08
Chlorine, Total Residual	12,706,326	2,032,066
Chlorine, Free Available	92,641.26	92,637.99
Methylene Chloride	3 11648.66	28,564.32
1,1-Dichloroethylene	22,943.43	22,764.59
Dichloromethane	19,219.94	19,219.94
Chloroform	101794.26	5,13 1.377
1,2-Dichloroethane	7,054.3 1	7,054.241
1,2-Dichloropropane	6,429.3 16	6,429.3 16
Tetrachloroethylene	4,592.35	2,644.47 1
Trichloroethylene	3,338.549	--

The release amounts of chlorinated compounds to water as tracked by the PCS are plotted according to the industry from which they are released in Figure 20. The mining industry (non-fuel) contributed the largest amount of permitted chlorinated discharges, both for the whole state and for the Lake Ontario basin. Figure 21 also shows chlorinated release amounts from the PCS but with chlorine and chloride excluded. In this case, the photographic/instrumentation industries released the largest amounts of chlorinated compounds for the period 1993-1995.



**Figure 20. New York State PCS: Releases by Industry (1993-1995)**

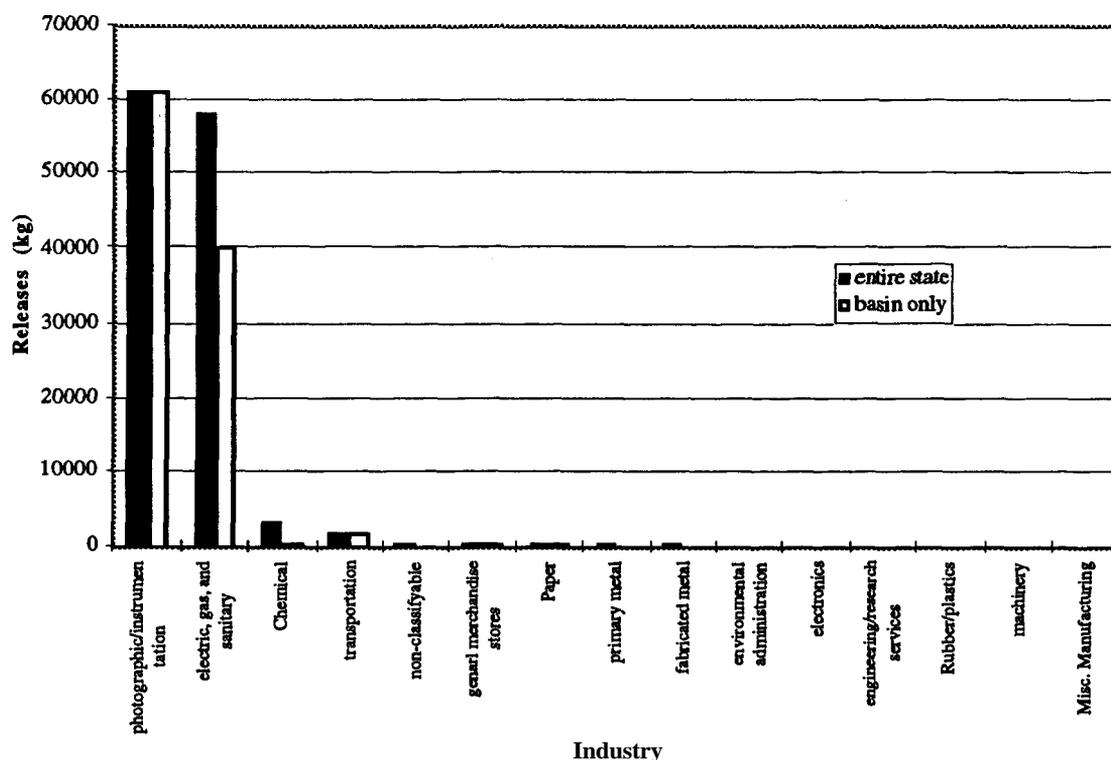


Figure 21. New York State PCS: Chlorinated Releases by Industry (1993-1995) Chlorine and Chloride Releases not Included

### National Pollutant Release Inventory (Canada)

Releases of chlorinated compounds as well as others are currently being inventoried in Canada by way of the National Pollutant Release Inventory (NPRI). This program has thus far issued data for year 1993 and is similar in scope and purpose to the Toxic Release Inventory. A broad characterization of the 1993 data with regard to chlorinated compounds is shown in Figure 22 where releases to water, air, and POTWs are shown as percentages of the total releases for the province of Ontario. Similar to TRI release amounts, the greatest discharges of chlorinated compounds are to air, followed by POTWs and water.

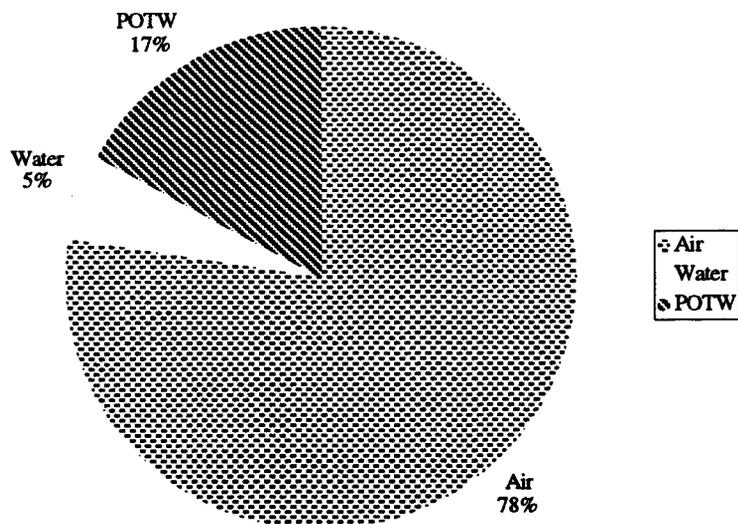


Figure 22. NPRI: Ontario releases of Chlorinated Compounds (1993) Total Releases = 7,259,058 kg

*Presentation of Loading Amounts of Chlorinated Compounds*

Of the thousands of chlorinated compounds that exist, a number of them have been singled out on priority pollutant lists by various agencies as being of special concern due to their toxicity, persistence, or a combination of both. These lists include:

*The priority pollutant list from the Clean Water Act*

*The priority pollutant list from the Clean Air Act*

*The Bioaccumulative Chemical of Concern (BCC) List from the Great Lakes Initiative (GLI)*

*Priority pollutants of concern other than BCC compounds listed in the GLI*

*Level I, Level II, and Critical pollutant lists from the International Joint Commission (IJC)*

Each of these lists contains both chlorinated and non-chlorinated compounds. A combined listing of the chlorinated compounds contained on these lists is shown in Appendix E, Table E1. The release amounts to air and water given by the New York State TRI and PCS, along with Niagara River loading amounts, are shown in Appendix E, Table E2. Each of the loading amounts shown in Table E2 were averaged over the aforementioned time frame for each respective database. In addition, zero values and below detection limit values were given equal weight in this averaging. It should be noted that in the case of the Niagara River data, the averaging of below detection values as zero values will result in loading numbers that are more than likely less than the actual loading amounts since some quantity of chemical is apt to be present even if this amount is not detectable.

## Modeling of the Bioaccumulative Compounds of Concern (BCC) for Lake Ontario

Numerical water quality models can be used to simulate the concentrations of a compound within a waterbody for varying loading amounts. These models are derived from mathematical conceptualizations of the various physical, chemical, and biological processes that a contaminant undergoes in a water system. These formulations result in a series of equations that describe the rate of change of contaminant mass with respect to time as a function of the contaminant's chemical properties, loadings, and the waterbody's morphology. Water quality models are useful tools in assessing the manner in which concentrations of a compound will change when inputs of the compound to the waterbody are varied. In an effort to illustrate the varying relationships between loadings and concentrations that exist among chlorinated compounds, a numerical model of Lake Ontario has been applied for the chlorinated BCC compounds. Some of the specific aspects of this model are discussed in the following sections along with a presentation and interpretation of the results.

### *The LTI Toxics Model*

The LTI Toxics Model was used to establish the relationships between loadings of the chlorinated BCC's and the resulting concentration of these chemicals in Lake Ontario (IJC, 1988). This model was formulated in 1988 as part of a report to the Great Lakes Water Quality Board of the IJC focused on the numerical modeling of PCBs in Lake Ontario. Though the model was used in that report for PCBs, its framework was able to be adapted to accommodate the modeling of other toxics as well. The LTI model is termed a mass balance model in the sense that it calculates concentrations within the lake according to the conservation of mass equation for the water column. In words, this equation may be stated as follows:

The rate of accumulation of a substance within a system	=	The rate at which the substance enters the system	•	The rate at which the substance exits the system	±	The rate of generation or decomposition of the substance.
---	---	---	---	--	---	---

It is assumed in the model framework that the water column of the lake is completely mixed and that a contaminant may exit the system by being flushed out via the Saint Lawrence River or may be removed through a degradation process such as hydrolysis, photolysis, or biodegradation. Also, a compound may be removed from the lake by being volatilized into the atmosphere or buried into the sediments by way of settling. Conversely, a compound may be introduced into the lake from the atmosphere or sediments if the concentration in one of these compartments is higher than that in the water column. Bulk contaminant concentrations within the water column are considered to exist in three phases: the dissolved phase, attached to abiotic suspended solids, and attached to biotic suspended solids. The partitioning of a compound among these phases is a function of the suspended solids concentration, the percent of organic carbon found in the suspended solids, and the affinity of a compound for particulate matter.

Given the assumptions discussed above, the mass balance statement may be represented in greater detail by the input-output diagram shown in Figure 23. Here, the boundaries of the lake are shown as a shaded, dashed box and the various inputs and outputs of the contaminant from the lake are shown as arrows. Notice that exchange of contaminant to the water column from the air or sediments is represented as being either an input or an output as mentioned above. A development of the model equations, along with a listing of the contaminant and lake parameters used in the model for the BCCs may be found in Appendix B.

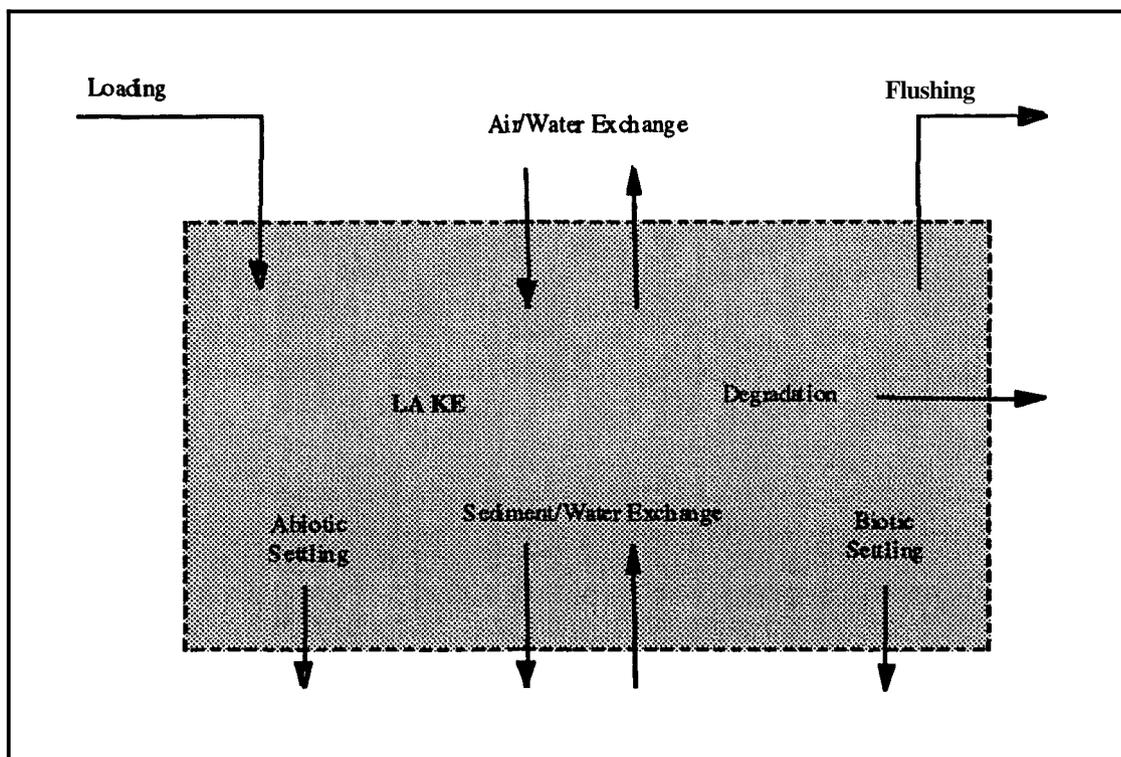


Figure 23. Input-Output Diagram for Contaminants in a Completely Mixed Lake

### *Results of the Model*

The LTI model for Lake Ontario was applied to 17 chlorinated Bioaccumulative Compounds of Concern as defined in the Great Lakes Initiative. These are listed in Table 11 below. The BCC compounds are generally considered to be the most threatening to wildlife and human health of the chlorinated compounds. Their threat lies not only in their toxicity but also in their propensity for concentrations of these compounds to become magnified in the tissues of fish which reside at higher levels on the food chain. Thus, exposure to high concentrations of these compounds becomes more likely through the consumption of fish.

**Table 11. BCC Compounds which were modeled**

Chemical Name	CAS no.
1,2,3,4 Tetrachlorobenzene	634662
1,2,4,5 Tetrachlorobenzene	95943
BHC - Alpha	319846
BHC - Beta	319857
BHC - Delta	319868
chlordan	57749
DDD	72548
DDE	72559
DDT	50293
Dieldrin	60571
Hexachlorobenzene	118741
Hexachlorobutadiene	87683
Lindane	58899
Mirex	2385855
PCBs	1336363
Pentachlorobenzene	608935
TCDD	1746016

### Steady State Results

Several modeling scenarios were considered for the list of compounds shown in Table 12. Since the focus of the effort was to begin to illustrate the varying nature of the relationships between chlorinated compound's concentration and its loading, the use of the LTI model for *steady-state* conditions was chosen to be a suitable approach. The steady-state condition refers to the case where there is no variation in time of any loadings, chemical properties, or concentrations within the system. In other words, the steady-state of a system is achieved after a long enough period of time has passed so that, given a constant loading rate, contaminant concentrations are no longer varying with time. The results of the steady-state modeling of the chlorinated BCC compounds with a uniform loading of 1000 kg/yr non atmospheric load are shown in Figure 24. Here, two cases are demonstrated. The first case consisted of setting the atmospheric concentration of each compound equal to zero, and the second involved setting the atmospheric concentration in the model equal to measured values. A summary of each of the measured atmospheric concentrations and their corresponding data sources is shown in Table 12. It can be seen in Figure 24, that the steady-state concentrations vary from compound to compound even when the same loading is applied and the same atmospheric concentration is present for each. The cause of this can be attributed to the fact that each compound has varying rates of degradation, volatilization, and varying affinity for solid particles. Compounds with high degradation or volatilization rates will be removed from the system quickly, resulting in lower steady-state concentrations. Also, compounds with high affinity to be bound to particulate matter in the water column will experience higher removal via settling than those that remain primarily in the dissolved phase, thereby causing lower steady-state concentrations as well. For example, the steady-state concentration for DDD was much higher than that for DDE. In this case, the disparity is largely attributable to the differences in degradation rates between the two compounds. In Table 12, it is shown that the half-lives for these two compounds differ greatly with DDD having a half-life in water of 78760 hours (9 years) and DDE having a half-life of only 80.5 hours (3.4 days). Thus, it is reasonable for the model to yield a high steady-state concentration for DDD and a low steady-state concentration for DDE.

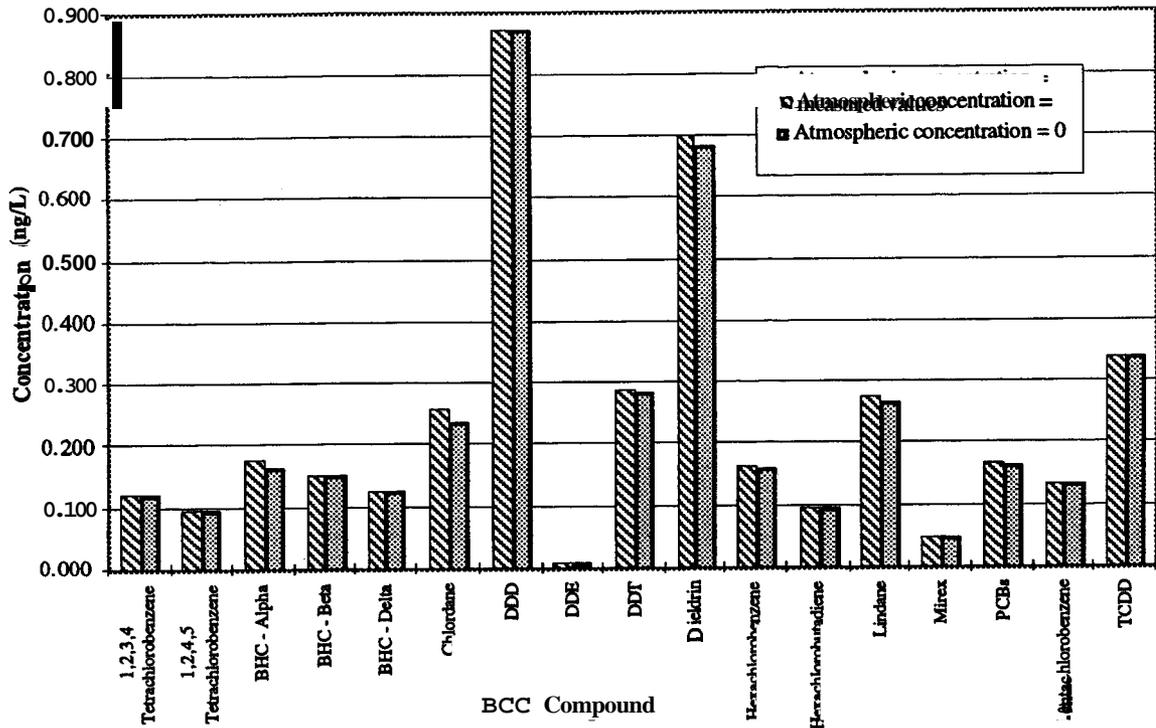


Figure 24. Steady-State Concentrations for *Lake Ontario* Loading = 1000 kg/year

**Table II. BCC Compounds which were modeled**

<b>Chemical Name</b>	<b>CAS no.</b>
1,2,3,4 Tetrachlorobenzene	634662
1,2,4,5 Tetrachlorobenzene	95943
BHC - Alpha	319846
BHC - Beta	319857
BHC - Delta	319868
chlordan	57749
DDD	72548
DDE	72559
<b>DDT</b>	<b>50293</b>
Dieldrin	60571
Hexachlorobenzene	118741
<b>Hexachlorobutadiene</b>	<b>87683</b>
Lindane	58899
<b>Mirex</b>	<b>2385855</b>
PCBs	1336363
Pentachlorobenzene	608935
TCDD	1746016

### *Steady State Results*

Several modeling scenarios were considered for the list of compounds shown in Table 12. Since the focus of the effort was to begin to illustrate the varying nature of the relationships between chlorinated compound's concentration and its loading, the use of the LIT model for *steady-state* conditions was chosen to be a suitable approach. The steady-state condition refers to the case where there is no variation in time of any loadings, chemical properties, or concentrations within the system. In other words, the steady-state of a system is achieved after a long enough period of time has passed so that, given a constant loading rate, contaminant concentrations are no longer varying with time. The results of the steady-state modeling of the chlorinated BCC compounds with a uniform loading of 1000 kg/yr non atmospheric load are shown in Figure 24. Here, two cases are demonstrated. The first case consisted of setting the atmospheric concentration of each compound equal to zero, and the second involved setting the atmospheric concentration in the model equal to measured values. A summary of each of the measured atmospheric concentrations and their corresponding data sources is shown in Table 12. It can be seen in Figure 24, that the steady-state concentrations vary from compound to compound even when the same loading is applied and the same atmospheric concentration is present for each. The cause of this can be attributed to the fact that each compound has varying rates of degradation, volatilization, and varying affinity for solid particles. Compounds with high degradation or volatilization rates will be removed from the system quickly, resulting in lower steady-state concentrations. Also, compounds with high affinity to be bound to particulate matter in the water column will experience higher removal via settling than those that remain primarily in the dissolved phase, thereby causing lower steady-state concentrations as well. For example, the steady-state concentration for DDD was much higher than that for DDE. In this case, the disparity is largely attributable to the differences in degradation rates between the two compounds. In Table 12, it is shown that the half-lives for these two compounds differ greatly with DDD having a half-life in water of 78760 hours (9 years) and DDE having a half-life of only 80.5 hours (3.4 days). Thus, it is reasonable for the model to yield a high steady-state concentration for DDD and a low steady-state concentration for DDE.

**Table 12. Measured Atmospheric Concentrations and Half-Lives for Modeled Compounds**

Chemical Name	Atmospheric Gas Phase Concentration (pg/m <sup>3</sup> )	Source	Half-Life (hours)
1,2,3,4 Tetrachlorobenzene	5.3	b	5,500
1,2,4,5 Tetrachlorobenzene	1.0	d	2,496
BHC - Alpha	79.0	c	1,785
BHC - Beta	1.8	b	1,653
BHC - Delta	1.0	d	1,365
Chlordane	82.0	b	4,488
DDD	2.3	c	78,760
DDE	16.0	c	81
DDT	11.5	a	4,284
Dieldrin	23.0	c	15,060
Hexachlorobenzene	130.0	c	36,696
Hexachlorobutadiene	1.0	d	2,496
Lindane	27.0	c	3,048
Mirex	1.0	d	665
PCBs	170.0	c	55,000
Pentachlorobenzene	8.0	b	6,468
TCDD	1.0	d	12,096

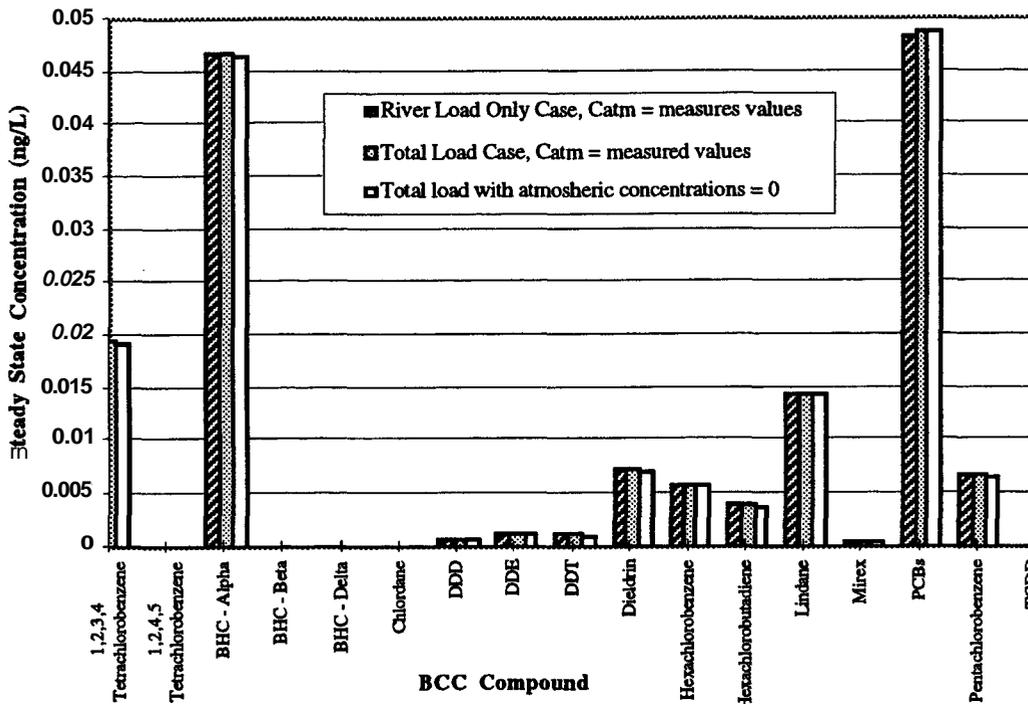
Key to atmospheric concentration sources:

- a: From Illinois State Water Survey publication 158 (IADN Data), average of vapor phase concentrations for 1991 and 1992 at Pt. Petre, Ontario.
- b: From ES&T article by Hoff *et al.* 1992, 26, 266-275
- c: A 1994 update of the Atmospheric Dep to the great lakes by Hoff *et al.*
- d: Assumed value

The effect of atmospheric concentrations on the steady-state results is also shown in Figure 24 where the inclusion of measured air concentrations resulted in slightly increased values relative to the case where air concentrations were set to equal zero. This illustrates the concept that the amount of mass transfer of a contaminant between water and air is dependent on the magnitude of the difference in concentrations between these two mediums.

Another modeling scenario that was considered was the case where actual inventoried loadings were applied to the model. The loadings used for this case are summarized in Appendix E and were obtained from the same data sources discussed earlier. Two actual loading groups were modeled. These were, namely, the average loadings to Lake Ontario from the Niagara River and a 'total loading' scenario which was comprised of the Niagara River loads plus the greater of the average loads from the permit compliance database or the TRI. For each compound, the average loads from the TRI and permit compliance database were not both included because it is conceivable that one of these databases may be a subset of the other since both may include the same discharges. The results from these loadings are shown in Figure 25. The lack of loading data for compounds such as 1,2,4,5 tetrachlorobenzene, BHC -beta, BHC - delta, chlordane, and 2,3,7,8 TCDD has resulted in concentrations for these that are equal to zero when the atmospheric concentrations were set equal to zero. This occurs, of course, because there are no inputs of these compounds to the system. It can also be seen in this figure that concentrations from the total loading case are nearly identical to those river loading case. This is consistent with the fact that the contribution from non-river databases to the total loading is very small. If these loading values were considered to be an accurate representation of the actual loading amounts of these compounds

to the lake, it could be concluded that the presence of these compounds in Lake Ontario is mainly due to sources outside of the lake's drainage area. That being said, it should be emphasized that it is very unlikely that the inventoried amounts of these chemicals truly represent the actual magnitudes of loadings to Lake Ontario due to the difficulties associated with accounting for all loading sources of a contaminant.



**Figure 25. Steady State Concentrations for BCC Compounds in Lake Ontario. River Load = Niagara River. Load Only. Total Load = Niagara River Load + Greater of SPDES Load or TRI Load**

Concentrations from several of the loading scenarios described above are compared to recommended standards from the Great lakes Initiative in Figure 26 for cases where explicit concentration based standards are stated in that document. The GLI standards and are listed in Table 12.

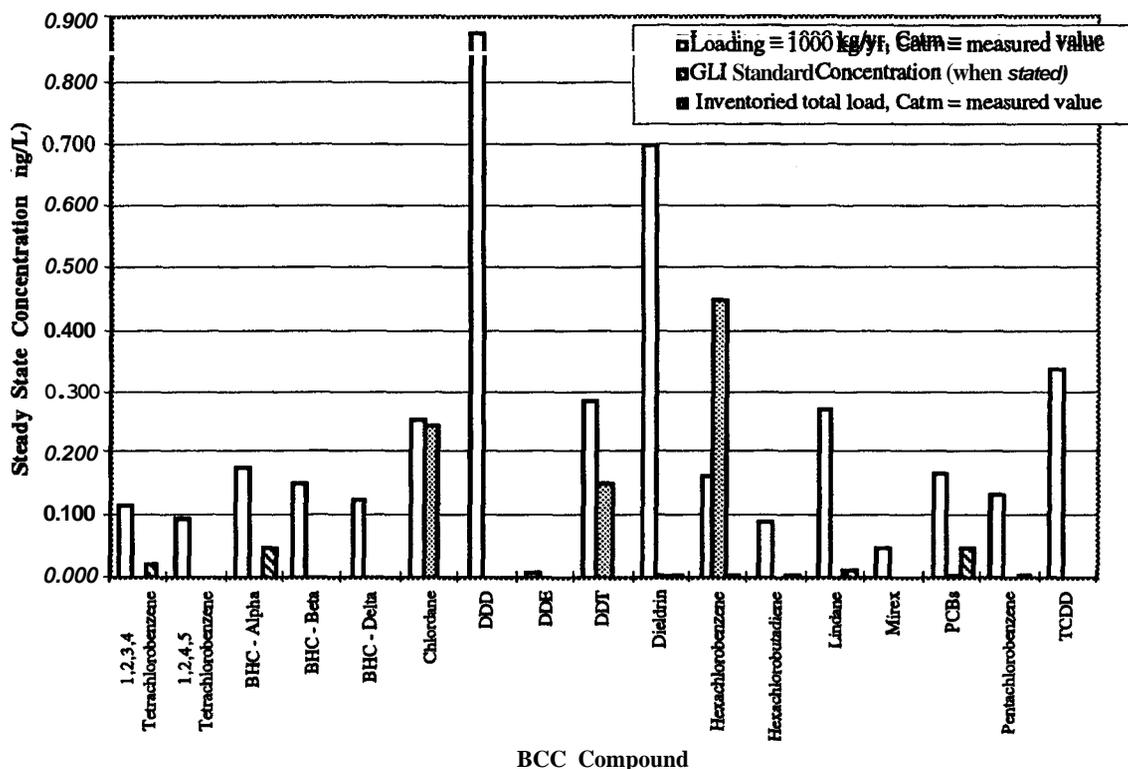


Figure 26. Steady State Concentrations for BCC Compounds standards also shown for compounds where standard is stated in the GLI

It should be re-stated that all of the above results were produced using the steady-state assumption. Though this assumption is useful for comparing the general behavior of toxics in Lake Ontario, it does not allow for any analysis of how the lake would respond to loadings that vary with time, as all actual loadings do. The manner in which a waterbody would respond to a transient loading could be modeled but this type of analysis would require some reliable source of time variable loading data. The concept of a waterbody's response time is, however, a practical way of assessing the time frame it will take for a contaminant to be removed from a system. This concept is discussed in the next section.

### Response Times

The response time of a contaminant within a lake may be defined as the time required for the lake to complete a fixed percentage of its recovery (Chapra, 1997). For example, the 95% response time for a contaminant in Lake Ontario would indicate the period required (from the time that all loadings have ceased) for 95% of the contaminant mass present in the lake to be removed via its various output mechanisms. The 95% response times of the chlorinated BCC compounds under consideration are depicted in Figure 27. Here, it can be seen that the response times of the lake for these compounds vary from less than half a year for DDE to almost 4.5 years for DDD. It should also be noted that the steady-state concentrations shown in Figure 24 are well related to the 95% response times for each the compounds. As stated above, it is implicit in the concept of a system's response time that all loadings have ceased. This includes loadings from direct sources as well as atmospheric loadings. Given the absence of any loadings, a contaminant will be removed from the lake through flushing, degradation, volatilization, and by settling (for the fraction attached to particulate matter). The rates of degradation and settling will vary from compound to compound, whereas the influence of removal by flushing will be the same for all

compounds. It is of interest to consider the response time in Lake Ontario for a conservative substance such as chloride which does not undergo any appreciable removal from settling, degradation, or volatilization. For such a substance, removal will occur by flushing only and the 95% response time for the lake is equal to 24 years. This 95% response time can be considered as an upper bound value for any contaminant in Lake Ontario. The relationship between concentration and time is shown in Figure 28 for Dieldrin, Lindane, and Chloride for Lake Ontario under the assumptions that each was present in same concentration and that loadings for each had ceased at time = 0 years. It is evident in this figure that Lindane, having the smallest response time of the three is removed from the lake most rapidly, while chloride is removed at a considerably slower rate. Based on these types of transient and steady-state analyses it may be concluded that not only will different compounds experience varying steady-state concentrations in Lake Ontario but also that each will exhibit different rates of removal as characterized by their varying response times.

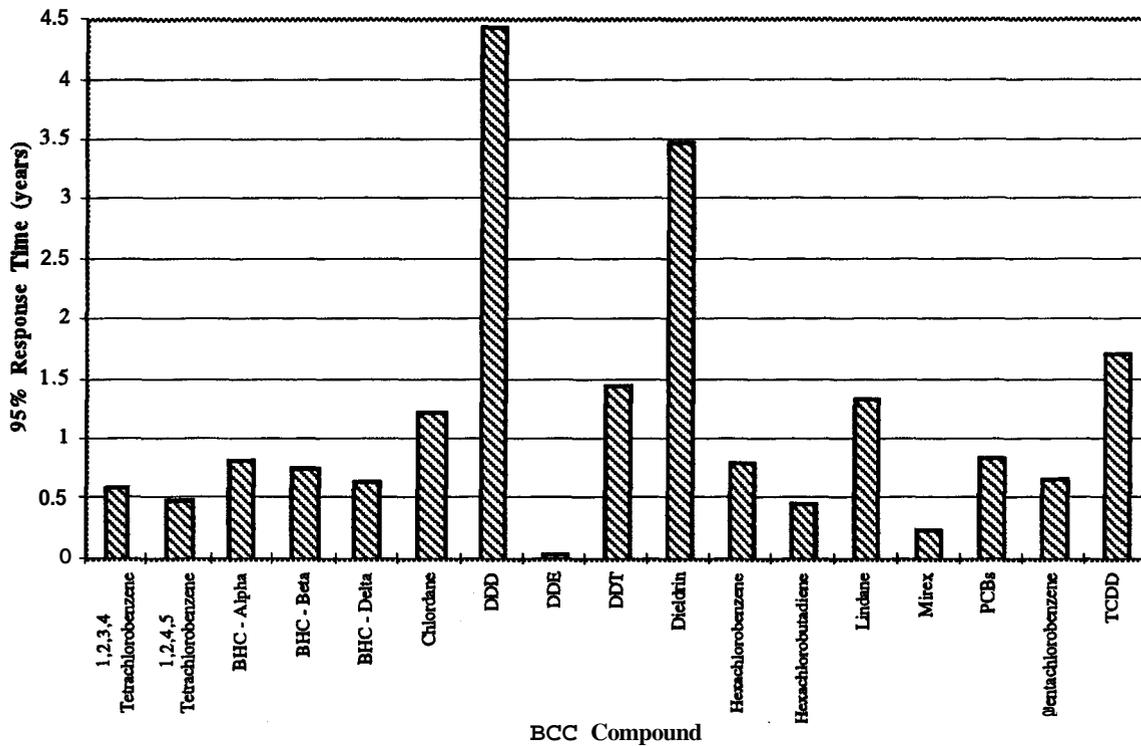


Figure 27.95% Response Time in Lake Ontario for BCC Compounds

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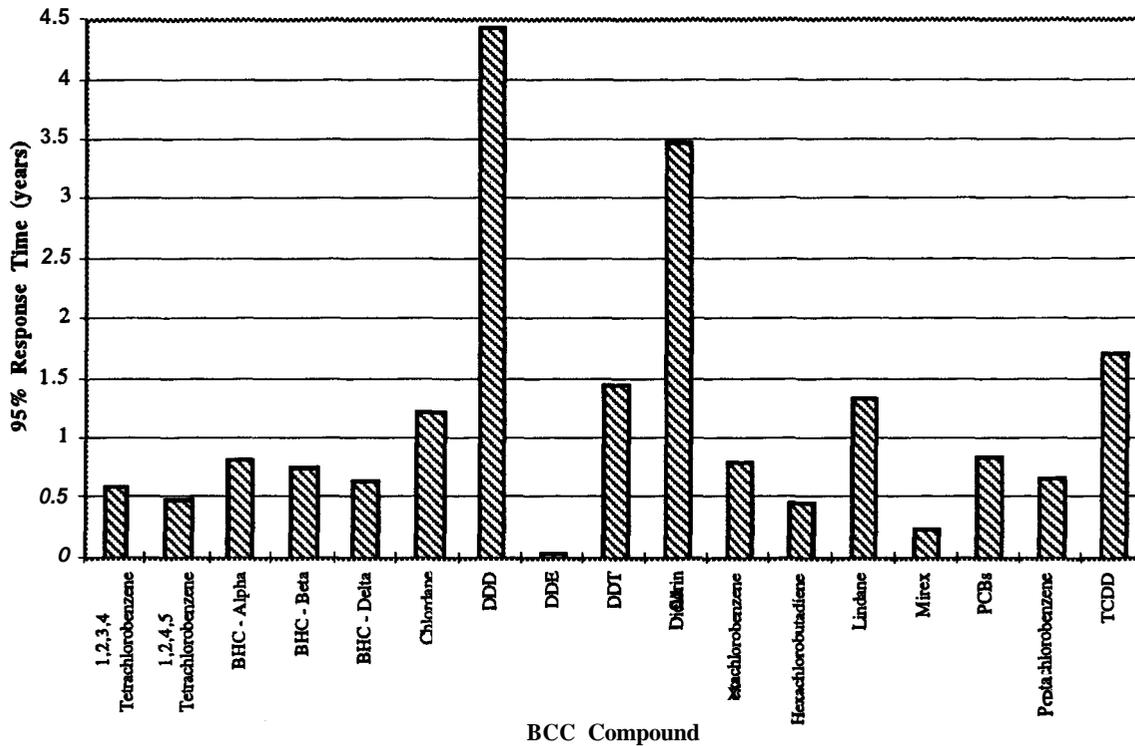


Figure 27.95% Response Time in Lake Ontario for BCC Compounds

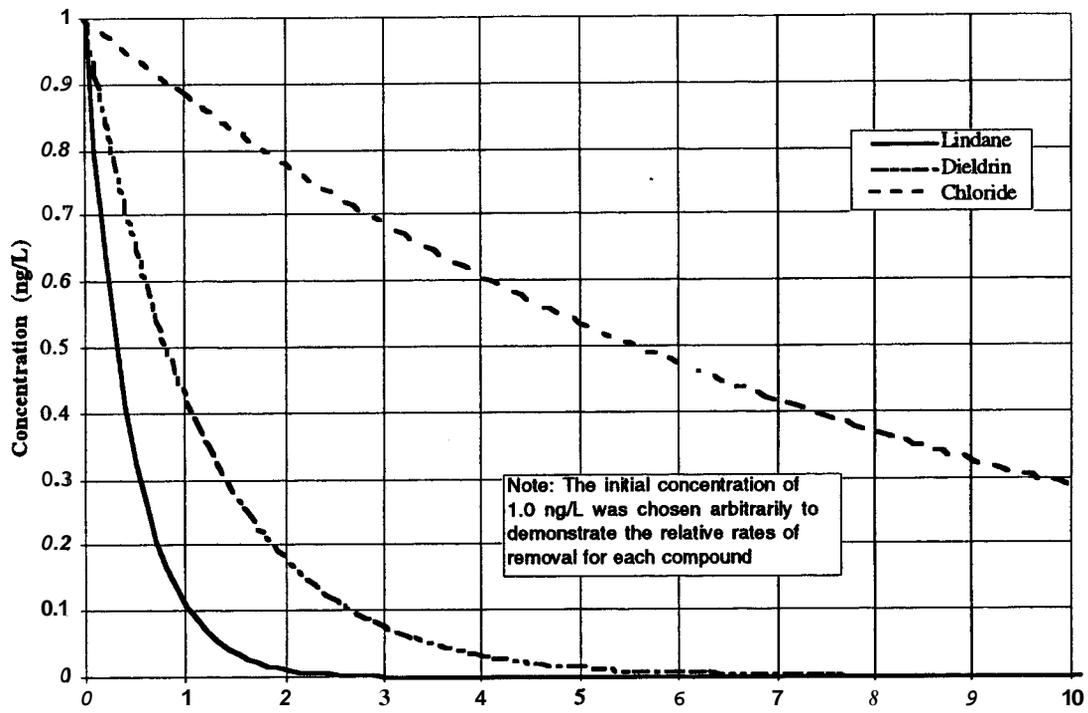


Figure 28. Comparison of Removal Rates for Dieldrin, Lindane, and Chloride in Lake Ontario

## Conclusion

With the limited data we have had to work with the following conclusions can be drawn:

1) A complete ban on **all** Chlorine use and the production of **all** chlorinated compounds within the Great Lakes basin is neither politically feasible nor scientifically supportable. Most proponents of the Chlorine sunseting argue instead for a phased and selective sunseting of the use of chlorine and chlorine containing compounds as industrial feedstocks and the reduction and elimination of other uses where alternatives are available or could be available soon if market forces were supportive. New York State should focus policy attention on supporting the transition away from Chlorine use in those instances in which alternative processes or substitute materials are available.

2) The economic impact of a phased and selective **sunseting**, if carried out on an international or regional basis would not likely have dramatic negative economic consequences for the economy of New York State and might have some net positive benefit.

3) The development of methods **to** supplement the chemical-by-chemical approach to evaluating the toxicity and potential environmental impacts of the thousands of industrial chemicals currently manufactured or inadvertently formed is warranted. New York should explore scientifically justifiable classification approaches for environmentally significant xenobiotics to determine which if any classes of compounds could form the basis for such a supplementary approach. It is not likely that a single characteristic (Chlorine-containing) would be a useful classification scheme.

4) Given existing approaches New York State is already accomplishing a significant emission reduction of chlorinated compounds without the institution of a chlorine sunseting plan. According to the **1994 TRI**, there are **379** facilities in New York releasing **49** million kilograms of chlorine or chlorinated organic compounds, of which **87** facilities releasing **28** million kilograms are located within the Lake Ontario drainage basin. Releases of chlorinated compounds from New York facilities have declined considerably from **1988-1994** (approximately **75%** reduction). Releases to POTWs and directly to receiving waters have also dropped precipitously during the period of record. The vast majority of the statewide releases (**98%**) are to the air (either via stack (**65%**) or as fugitive air emissions (**33%**)). The **instrumentation/photographic** industry (SIC #38) has been the largest emitter of chlorinated stack and fugitive gas emissions, while the chemical industry has discharged the largest quantities to POTWs. These discharge inventories and their trends suggest that a considerable reduction of chlorinated compound emissions has occurred in New York, even in the absence of a chlorine sunseting.

5) Because most of the chlorinated compound releases from New York **are** into the atmosphere and because there is a general lack of release tracking data, it is virtually impossible to determine the relative impact that New York releases or their abatement **are** having on a Great Lake like Lake Ontario. Using chlorinated organics measured in the Niagara River (**85%** of the water inflow and **>50%** of the load of most chlorinated organics) **as** an indicator of what is occurring basin-wide, we have seen a reduction in loadings to the lake that is consistent with the statewide release inventories. Recent progress reports of the Niagara River Toxics Management Plan (Niagara River Secretariat, **1996; 1998**) have documented significant reductions of most of the chlorinated organics in their monitoring program (including such compounds as PCB congeners, hexachlorobenzene, dieldrin, octochlorostyrene, and mirex). **While** difficult to quantify the exact contribution, it is safe to say that reductions in New York releases of chlorinated organic compounds have contributed to reductions in loadings of these compounds to Lake Ontario. It is

not clear that a new program of phased chlorine sunseting would significantly accelerate what is already happening under existing programs. With the development and implementation of the Lake Ontario LaMP and the Canada-US. Binational Virtual Elimination Strategy, it is likely that even further emission reductions can be expected in the future.

6) For some chemicals, further emission reductions will lead to measurable improvements in Great Lakes waters, but for others these emission reductions will not produce measurable decreases in receiving water body concentrations. Also, chlorinated compounds represent an extremely wide range of fate and transport behavior, persistence, bioaccumulative potential, and ecological and human effects. Many of these chlorinated compounds and compounds derived from the use of chlorine as an oxidant have very high economic and social value. Many of the most troublesome contaminants are global pollutants.

7) For those chemicals or chemical mixtures that prove to be most persistent, bioaccumulative and toxic, we need to investigate risk management options beyond emission limits and best available technologies, including voluntary agreements, economic instruments, and more severe options such as bans, replacements, and phase-outs. Although continued reductions in the **NY** State portion of the Great Lakes basin is likely given current trends, the achievement of the Great Lakes Water Quality Agreement goal of virtual elimination of persistent toxic substances is unlikely to occur without new and innovative public policies directed at pollution prevention rather than discharge control. If the IJC's 1992 recommendation helps to stimulate debate and experimentation on such alternatives it would have been valuable indeed.

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## Appendix A

**Table A1. Databases that capture Chlorine and Chlorinated chemicals.**

<b>Database</b>	<b>Source</b>	<b>Phone</b>	<b>Availability</b>	<b>Notes:</b>
NY - TRI	NYDEC	(518) 457-2553	Diskette. Hard copy	
Toxic Release Inventory	USEPA	(202) 260-0556	Diskette; CD-ROM, On-line, RTK-net	SARA Title III EPCRA
County Business Patterns	USDoC		CD-ROM, Hardcopy	
Gross State Product	USDoC		CD-ROM, Hardcopy	
Chemicals in Commerce Information System	USEPA	(202) 554-1404	Diskette, Hardcopy, FOIA	TSCA
Chemical Update System	USEPA	(202) 554-1404	FOIA	TSCA update rule
Contract Laboratory Program Analytical Result Database	USEPA	(703) 603-8827	see notes	generally limited to EPA staff and contractors
Safe Drinking Water Information System	USEPA	(202) 260-2804	On-line; see notes	Need to obtain a user ID and account
Storage and Retrieval of US Waterways Parametric Data-	USEPA	(800) 424-9067	See notes	State agencies may obtain access
Biennial Reporting System	RTKNet	(202) 797-7200	On-line; see notes	Free accounts available
Air Quality Subsystem of the Aerometric Information Retrieval System	US EPA	(919) 541-5454	On-line, FTP	AIRS Executive provides tabular and graphic display of data & maps.
CCRIS	National Cancer Institute		TOXNET	
RTECS	NIOSH		TOXNET	
HSDB	ATSDR		TOXNET	
IRIS	USEPA		TOXNET	
DART*	NLM		TOXNET	
ETICBACK	NLM		TOXNET	
EMICBACK	ORNL		TOXNET	

\*continuation of ETICBACK

\* Alston 1991; Inform 1995; US EPA 1994

## Appendix B

Table B1. Timeline\* of Significant Events\*\*

Science and Engineering	Year	Policy and Regulation
Chlorine discovered by Swedish chemist Carl Wilhelm Scheele	1774	
Chlorine was used commercially by the French to whiten fabrics	1790	
Vinyl chloride (VC), monomer, was discovered by Justus von Liebig	1835	
Chlorine used experimentally in US drinking water	1890	
Jersey City, NJ - one of the first large scale uses of chlorine as a disinfectant to eliminate disease-causing microorganisms	1908	
Polyvinyl chloride (PVC), polymer, was produced commercially for the first time in the US-	1928	
PCB manufacturing in US begins	1929	
PCBs cause Cable Haulers Disease - male workers chronically exposed develop acnelike skin lesions	1930	
	1949	2,4,5-T registered as a pesticide by USDA
TCDD identified as causing the occupational skin disease, chloracne	1957	
Millions of chick die of chick edema factor (culprit identified as HexaCDD, a dioxin	1958	
Rachel Carson publishes Silent Spring	1962	Herbicides first used in Vietnam
	1963	Use of Agent Orange begins in Vietnam
		Clean Air Act passed
	1967	(to 1970) Spraying of Agent Orange peaks in Vietnam
Yusho, Japan - A pregnant woman exposed to PCBs and dibenzofurans from the consumption of rice bran oil - acute toxicosis, tooth deformities); small birth sizes and low IQ		
Initial laboratory studies report 2,4,5-T as teratogen		Use of Agent Orange ends in Vietnam
Role of TCDD established		
	1970	USDA reduces domestic uses of pesticides 2,4,5-T OSHA passed
Louisville, Kentucky - A physician at B.F. Goodrich recognized a connection between the monomer vinyl chloride and cancer in humans (latency period of 26 years)	1972	Use of DDT banned in the US; Use of PCBs placed under regulatory control
		Insecticide, Fungicide and Rodenticide Act passed
Times Beach, Missouri - TCDD from a chemical waste implicated in illness in horses (and possibly children)	1974	Safe Water Drinking Act passed
Seveso, Italy - a blast at a trichlorophenol plant released 1 pound of dioxin into the atmosphere, some children developed chloracne		
Bellar et al. and Rook found chlorine reacts with organic mater in drinking water to form		

Science and Engineering	Year	Policy and Regulation
organohalides, trihalomethanes (formaldehyde and formalin), both of which are carcinogenic in minute amounts		
	1976	RCRA and TSCA passed
	1977	PCB production stopped in the US
		Clean Air Act passed
Concern about miscarriages with herbicide leads to cancellation of all uses of pesticide 2,4,5-T spraying	1978	EPA announces it was considering a revision of US-Canada Great Lakes Water Quality Agreement to address the contamination by persistent toxic substances
		Hazardous Materials Transportation Act and Great Lakes Water Quality Act passed
Love Canal	1979	EPA suspends use of 2,4,5-T
TCDD a carcinogen in laboratory studies		Vietnam Veterans start class action lawsuit
Alsea, Oregon II study - epidemiology study associates soft tissue sarcoma in humans with exposure to herbicides		
Taiwan - rice oil contaminated with PCBs, dioxins - 2,000 people exposed, mothers passed on ectodermal dysplasia, development delay, and abnormal sexual development (Rogan et al. 1988)	1979	
	1980	PCB production or import prohibited in Canada
		CERCLA passed
Seveso 5 Year Report - no ... effects	1981	
Times Beach, Missouri - ... buys all homes due to flooding, town evacuated and remains abandoned	1982	
	1984	Vietnam Veterans class action lawsuit settled for \$180 million
		EPA cancels 2,4,5-T registration
	1985	IJC identified 11 critical pollutants that are persistent, bioaccumulative, and toxic (8 are organochlorines)
Ad hoc expert committee advises the EPA that linearized model for cancer is inappropriate	1986	Emergency Planning and Community Right to Know Act and SARA passed
	1987	A declaration of intent was signed by the US and Canada to reduce the discharge of specific toxic chemicals in the Niagara River by at least 50% by 1996
EPA scientific group recommends moderating cancer risk estimate	1988	
EPA Science Advisory Board finds no new science data to support change in cancer risk model	1989	Vietnam Veterans win lawsuit - compensated for soft tissue sarcoma, porphyria, non-Hodgkin's lymphoma, and chloracne
		Inuit Circumpolar Conference called for an international agreement to control toxic contaminants
Royal Academy of Engineering Sciences reported chlorine from natural sources	1989	
	1990	Pollution Prevention Act and Great Lakes Critical Programs Act passed

Science and Engineering	Year	Policy and Regulation
Banbury Conference finds that dioxin exerts most, if not all, of its toxic effects through a mechanism that involves a protein receptor found in individual cells (framework for a new EPA model)	1992	(Sixth Biennial Report) IJC recommends Hunssetting <b>chlorine</b> and chlorine containing compounds as a class
		Paris Convention: planned the phasing out of toxic, persistent and bioaccumulative substances and prohibit organohalogens
		Greenpeace called for a ban of all organochlorine compounds
National Academy of sciences publishes report on Agent Orange	1993	American Public Health Association called for phasing out chlorine and chlorinated chemicals, as a class
Bertazzi paper on cancer linked Seveso herbicide exposure with cancer		Barcelona Convention (21 nations): agreed to <b>reduce and phase out toxic, persistent, bioaccumulative substances by 2005</b>
Wolff et al. Found decreasing breast cancer paralleled by a decline in DDT and Benzene hexachloride contamination	1993	
Sharpe et al. Suggested that environmental estrogens are responsible for declining sperm levels		
Davis et al. Believe that organochlorines cause part of the increase in breast cancer rates	1994	<b>Zero Discharge Act (HR 2898) resolution in Congress-5 year phase out of chlorine in US</b>
Kreiger et al. Study found that the levels of DDE and PCB in the serum were not elevated in breast cancer patient		EPA Risk Assessment Published weight of evidence evaluation suggest that dioxins and dioxin-like compounds (PCBs) are likely to present a cancer hazard to humans
Jacobsen et al. And Fien et al. Found severe risks for the children of mothers who consume fish that have been exposed to PCBs		Carol Browner, EPA Administrator, pushes for an Amendment to the Clean Air Act and a task force to study chlorine as a class
Regulatory Toxicology and Pharmacology need to learn more about chlorine but ban unjustified (4,000 references reviewed)		American College of Occupational and Environmental Medicine supported chemical by chemical basis look at chlorine
World Health Organization says acceptable exposure to dioxin is 10pg/kg/day		French Academy of Science found that dioxins are not a major health risk
TCDF) is 0.006 pg/kg/day		Society of Toxicology Report suggests a chemical by chemical assessment
	1995	(October) NAFTA representatives agreed to phase out or ban DDT, aldrin, dieldrin, endrin, chlordane, heptachlor, mirex, hexachlorobenzene, toxaphene, dioxins, furans and PCBs
		(November) Swedish government passes resolution to phase out the use of PVC due to health risk
	1996	(November) Federal Advisory Committee Act establishes the Endocrine Disrupters Screening and Testing Advisory Committee ( <b>EDSTAC</b> ) under EPA to advise the agency on development on a strategy to screen and test chemicals, including pesticides, for their potential to disrupt endocrine functions in humans, fish and other wildlife.
	1997	(April 7) <b>US and Canada move to eliminate toxics in Great Lakes by 2006 - no new</b>

Science and Engineering	Year	Policy and Regulation
		releases of 5 pesticides (chlordane, aldrin/dieldrin, DDT, mirex, and toxaphene), 90% reduction in PCB, 75% reduction in dioxin - based on 1991 agreement and 1985 memorandum.
		(April 22) EPA expands TRI reporting to capture 6,100 new facilities bringing grand total to 31,000 facilities.
		(April 25) EPA completed TSCA Compliance Audit Program enforcement initiative to gather reports of substantial risks from toxic chemicals. EPA discovered some industries were not reporting data so they started volunteer program with reduced fines.

\* Adapted from Physicians for Social Responsibility and Environmental Defense Fund, 1994. Other sources include EPA 1997; Holland 1995; Greenpeace 1995; IJC 1993, ATSDR 1990, 1992, 1993; Hileman 1993.

\*\* Due to the amount of chlorine related events that have transpired over the past hundred years many events are likely to be omitted.

## Appendix C

### Relevant New York Statutes covering Chlorine\*

Conservation Law	(1911 New York Laws ch.647, <b>as</b> amended)
New York conforms statute to Federal Water Pollution Control Act Amendments of 1970	(Public Law 95-500)
Environmental Conservation Law (ECL) enacted	(1970 New York Laws ch. 140, as amended)
Controls on chloroflourocarbons added to ECL	(1975 New York Laws ch.713)
State Pollution Discharge Elimination System (SPDES) added to ECL	(1973 New York Laws ch.713)
Authority to regulate release <b>of</b> hazardous substances to environment added to ECL	(1973 New York Laws ch.801)
Industrial Hazardous Waste Management added to ECL (under RCRA)	(1978 New York Laws ch.639)
Inactive Hazardous Waste Disposal Site controls added to ECL	(1979 New York Laws ch.282)
Collection, Treatment, and Disposal of Refuse and Solid Waste regulation authorization recodified and expanded ECL	(1980 New York Laws ch.552)
Pesticide Controls Recodified and expanded in ECL	(1983 New York Laws ch.612)
Hazardous Substance <b>Bulk</b> Storage Act	(1986 New York Laws ch.672)
Environmental Quality Bond Act	(1987 New York Laws ch.511&512)
Regulation of commercial lawn application of pesticides authorized	(1987 New York Laws ch.559&560)
Solid Waste Management Act established a state solid waste management policy and a solid waste management planning process	(1988 New York Laws ch.70)
State Pollution Discharge Elimination System requirements updated to maintain conformity <b>with</b> federal law	(1988 New York Laws ch.360)
Great Lakes Protection Fund established in 1990	
Sale of certain containers of CFCs banned, and recapture and recycling of CFCs vented during the repair of disposal of automobile air conditioners	(1990 New York Laws ch.294)
Hazardous Waste minimization program established and state laws conformed to federal hazardous waste regulations	(1990 New York Laws ch.831)
Clean <b>Air</b> Act Compliance Act enacted to meet stationary and mobile source air pollution control requirements of the Federal Clean Air Act	(1993 New York Laws ch.608&609)
Environmental Protection Fund	(1993 New York Laws ch.610&611)

Other:

Water Pollution is contained in ECL ch.512 Article 17.

Management of Hazardous Waste from generation to disposal is in ECL ch.512 Article 27.

\*Sources: Lasher, 1988; Robinson, 1992.

## Appendix D

The LTI Toxics model is formulated using a mass balance equation for the water column and a mass balance equation for the sediment layer. The two equations are solved simultaneously to yield the concentration of contaminant in each compartment. The mass balance for a contaminant in the water column and is shown below as Equation 1.

$$V_w \frac{dC_t}{dt} = W_c(t) - QC_t - k_d V_w C_t - v_a A_w F_a C_t - v_b A_w F_b C_t + k_{sl} A_d (F_{ds} C_s - F_d C_t) + D_{aw} \left( fa - \frac{F_d C_t}{Z_w} \right) A_w + v_r A_d F_a C_s \quad (1)$$

where:

$V_w$	= lake volume	$m^3$
$C_t$	= total water column contaminant concentration	$g/m^3$
$W_c$	= rate of contaminant loading	$g/yr$
$Q$	= lake outflow	$m^3/yr$
$k_d$	= degradation <del>rate</del> constant	$1/yr$
$v_a$	= abiotic <b>settling</b> velocity	$m/yr$
$F_a$	= fraction of contaminant on abiotic solids	$g/g$
$v_b$	= biotic <b>settling</b> velocity	$m/yr$
$F_b$	= fraction of contaminant on biotic solids	$g/g$
$k_{sl}$	= sediment water diffusion coefficient	$m^2/yr$
$F_{ds}$	= fraction of contaminant dissolved in sediment	$g/g$
$C_s$	= total concentration of contaminant in sediment	$g/m^3$
$F_d$	= fraction of contaminant dissolved in water column	$g/g$
$D_{aw}$	= atmospheric mass transport parameter	$mole/(m^2 Pa) yr$
$fa$	= fugacity of the atmosphere	$Pa$
$Z_w$	= water column contaminant fugacity capacity	$mole/(m^3 Pa)$
$v_r$	= resuspension velocity of Contaminant from sediment	$m/yr$
$A_d$	= Area of deposition for sediment layer	$m^2$

and where:

$1/D_{aw}$	= $1/D_w + 1/D_a$	$mole/(m^2 Pa yr)$
$D_w$	= $k_w Z_w$	$mole/(m^2 Pa yr)$
$D_a$	= $k_a Z_a$	$mole/(m^2 Pa yr)$
$k_w$	= water transfer coefficient	$m/yr$

$ka$	=	air transfer coefficient	m/yr
$Z_w$	=	1/H	mol/(m <sup>3</sup> Pa)
$Z_a$	=	1/(RT)	mol/(m <sup>3</sup> Pa)
$H$	=	Henry's constant for contaminant	(Pa m <sup>3</sup> /mole)
$R$	=	ideal gas constant	Pa m <sup>3</sup> /(mole °K)
$T$	=	air-water interface temperature	°K
$fa$	=	$C_a/Z_a$	Pa
$C_a$	=	atmospheric concentration of contaminant	mol/m <sup>3</sup>

The mass balance equation for a contaminant in the sediment layer is:

$$V_m \frac{dC_s}{dt} = v_a A_w F_a C_i + v_b A_w F_b C_i + k_{si} A_d (F_d C_i - F_{ds} C_s) - v_s A_d C_s F_{ps} - v_r A_d F_a C_s \quad (2)$$

where:

$V_m$	=	volume of sediment segment	m <sup>3</sup>
$F_{ds}$	=	fraction dissolved in the sediment layer	g/g
$F_{ps}$	=	fraction of contaminant attached to particulates in	g/g

The partitioning of a contaminant among solids in the water column is described by the following equations:

$$F_a = (Pa Sa)/(1 + Pa Sa + Pb Sb) \quad (3)$$

$$F_b = (Pb Sb)/(1 + Pa Sa + Pb Sb) \quad (4)$$

$$F_d = 1/(1 + Pa Sa + Pb Sb) \quad (5)$$

$$F_a + F_b + F_d = 1 \quad (6)$$

$$C_t = C_a + C_b + C_d = F_a C_t + F_b C_t + F_d C_t \quad (7)$$

where :

$Pa$	=	$f_{oca} Koc$	
$Pb$	=	$f_{ocb} Koc$	
$f_{oca}$	=	percent organic carbon for abiotic solids	
$f_{ocb}$	=	percent organic carbon for biotic solids	
$Koc$	=	organic carbon equilibrium partitioning coefficient for a contaminant	
$Sa$	=	abiotic suspended solids concentration	g/m <sup>3</sup>
$Sb$	=	biotic suspended solids concentration	g/m <sup>3</sup>

The partitioning in the sediment layer is described by the following:

$$F_{ds} = 1/(1 + P_s C_{ss}) \quad (8)$$

$$F_{ps} = P_s C_{ss}/(1 + P_s C_{ss}) \quad (9)$$

$$P_s = K_{ocs} f_{ocs} \quad (10)$$

where:

- $P_s$  =  $f_{ocs} K_{ocs}$
- $C_{ss}$  = solids concentration in the sediment  $g/m^3$
- $f_{ocs}$  = percent organic carbon in sediments
- $K_{ocs}$  = organic carbon equilibrium partitioning coefficient in sediments

Table D1. Parameters Used for Each Contaminant in LTI Model (taken from Rodgers et al 1988)

Parameter	Value	Units
$V_w$	$1.67 \times 10^{12}$	$m^3$
$Q$	$2.13 \times 10^{11}$	$m^3/yr$
$v_a$	500	$m/yr$
$v_b$	110	$m/yr$
$ksl$	0.01	$m^2/yr$
$A_w$	$1.949 \times 10^{10}$	$m^2$
$A_d$	$1.04 \times 10^{10}$	$m^2$
$R$	8.314	$Pa \ m^3/(mole \ ^\circ K)$
$T$	25	$^\circ K$
$V_m$	$5.2 \times 10^8$	$m^3$
$S_a$	0.50	$g/m^3$
$S_b$	0.15	$g/m^3$
$f_{oca}$	0.04	---
$f_{ocb}$	0.35	---
$f_{ocs}$	0.04	---
$v_r$	0.000138	$m/yr$
$v_s$	0.00125	$m/yr$
$C_{ss}$	360000	$g/m^3$

The following equations were used to calculate contaminant-specific parameters. The water transfer coefficient,  $k_w$ , was calculated as (Chapra, 1997):

$$k_w = \left( \frac{32}{MW} \right)^{1/4} K_L \quad (11)$$

where  $MW$  = the molecular weight of the contaminant and  $K_L$  = the oxygen transfer coefficient which was taken to be 1.6 m/day. The gas transfer coefficient,  $k_a$ , was calculated as (Chapra, 1997):

$$k_a = 168 \left( \frac{18}{MW} \right)^{1/4} U_w \quad (12)$$

where  $U_w$  is a representative wind speed for Lake Ontario which was assumed to be 2.3 m/s. The organic carbon partitioning coefficient was calculated using a formulation from Endicott (19\*\*\*\*);

$$\text{Log } K_{oc} = 3.54 + 0.442 (\text{Log } K_{ow}) \quad (13)$$

Where  $K_{ow}$  is the octanol-water partition coefficient for a contaminant. In agreement with Rodgers et al. (1988), the value of the organic carbon partition coefficient for the sediment layer was taken to be an order of magnitude less than that calculated from Equation (13).

Half-life values for each of the contaminants were taken from Howard (1991) and Henry's constants were taken from Mackay et al. (1992), Schwarzenbach et al. (1993), and from the U.S. Department of Agriculture Agricultural Research Service's Pesticide Property database.

## Appendix E

Table **EL. 95** Chlorinated Compounds on Pollutant Lists from the Clean Water Act, Clean Air Act, Great Lakes Initiative (GLI), and International Joint Commission (IJC).

CWA = Clean Water Act

CAA = Clean Air Act

BCC = Bioaccumulative Chemical of Concern from GLI

GLI Other = Other compounds of concern from GLI

IJC L I = Level I from IJC

IJC L II = Level II from IJC List

IJC CP = Critical Pollutants from IJC List

Chemical Name	Priority Pollutant Lists						
	CWA	CAA	BCC	GLI Other	IJC L I	IJC L II	IJC CP
1,1,2 Trichloroethane	X	X		X			
1,1,2,2 Tetrachloroethane	X	X		X			
1,2 Dichlorobenzene	X			X			
1,2 Dichloroethylene	X						
1,2 Dibromo 3 Chloropropane		X					
1,2,3,4 Tetrachlorobenzene	X		X			X	
1,2,3,5 Tetrachlorobenzene	X					X	
1,2,4 Trichlorobenzene	X	X		X			
1,2,4,5 Tetrachlorobenzene	X		X				
1,2-Trans-Dichloroethylene				X			
1,3 Dichlorobenzene	X			X			
1,3 Dichloropropene		X		X			
1,3,5 Trichlorobenzene	X						
1,4 Dichlorobenzene	X	X		X		X	
2 Chloroacetophenone		X					
2,3,7,8-TCDD	X	X	X		X		X
2,4 Dichlorophenol	X			X			
2,4,5 Trichlorophenol		X					
2,4,6 Trichlorophenol		X		X			
2,4-Dichlorophenoxyacetic Acid				X			
2-Chloroethyl Vinyl Ether	X			X			

Chemical Name	Priority Pollutant Lists						
	CWA	CAA	BCC	GLI Other	UCL I	UCL II	UCL CP
2-Chloronaphthalene				X			
2-Chlorophenol				X			
3,3 Dichlorobenzidine		X		X		X	
4 Chlorophenyl Phenyl Ether	X			X			
4,4'-DDE		X	X		X		X
4,4'-DDT	X		X		X		X
4,4' DDD			X		X		X
Aldrin	X			X	X		
Allyl Chloride		X					
Alpha-Endosulfan				X			
Aniline		X					
Benzotrichloride		X					
Benzyl Chloride		X					
Beta-Endosulfan				X			
Bis (2 Chloroethoxy) Methane	X			X			
Bis(2-Chloroisopropyl) Ether	X			X			
Bis(Chloromethyl) Ether		X					
Captan		X					
Carbon Tetrachloride	X	X		X			
Chloroacetic Acid		X					
Chloramben		X					
Chlordane	X	X	X		X		
Chlorine		X					
Chlorobenzene	X	X		X			
Chlorobezilate		X					
Chloroform	X	X		X			
Chloromethyl Methyl Ether		X					
Chloroprene		X					
Chloropyrifos				X			
Dichlorobromomethane	X			X			
Dichloroethyl Ether (Bis(2 Chloroethyl) Ether)		X					
Dichlorvos		X					
Dieldrin	X		X		X		X

Chemical Name	Priority Pollutant Lists						
	CWA	CAA	BCC	GLI/Other	HCL I	HCL II	HCP
Dimethyl Carbamoyl Chloride		X					
Endosulfan	X			X			
Endosulfan Sulfate				X			
Endrin	X			X		X	
Epichlorohydrin (1 Chloro 2,3 Epoxypropane)		X					
Ethyl Chloride (Chloroethane)	X	X		X			
Ethylene Dichloride (1,2 Dichloroethane)	X	X		X			
Ethylidene Dichloride (1,1 Dichloroethane)	X	X		X			
Heptachlor	X	X	X	X		X	
Heptachlor Epoxide				X		X	
Hexachlorobenzene	X	X	X		X		X
Hexachlorobutadiene	X	X	X			X	
Hexachlorocyclohexane-Alpha	X		X			X	
Hexachlorocyclohexane-Beta	X		X			X	
Hexachlorocyclohexane-Delta	X		X			X	
Hexachlorocyclohexane-Gamma (Lindane)	X		X			X	
Hexachlorocyclopentadiene	X	X		X			
Hexachloroethane	X	X		X			
Hydrochloric Acid		X					
Methoxychlor		X		X		X	
Methyl Chloride (Chloromethane)	X	X		X			
Methyl Chloroform (1,1,1 Trichloroethane)	X	X		X			
Methylene Chloride (Dichloromethane)	X	X		X			
Mirex			X		X		X
Octachlorostyrene			X		X		
P-Chloro-M-Cresol				X			
PCBs	X	X	X		X		X
Pentachlorobenzene	X		X			X	

Chemical Name	Priority Pollutant Lists						
	CWA	CAA	BCC	GLIOBET	HC LI	HC LI I	HC CP
Pentachloronitrobenzene		X					
Pentachlorophenol	X	X		X		X	
Phosgene		X					
Photomirex			X				
Propylene Dichloride (1,2 Dichloropropane)		X		X			
Tetrachloroethylene (Perchloroethylene)		X		X			
Titanium Tetrachloride		X					
Toxaphene	X	X			X		X
Trichloroethylene	X	X		X			
Vinyl Chloride	X	X		X			
Vinylidene Chloride (1,1 Dichloroethylene)	X	X		X			
4,4'-Methylenbis (2-Chloroaniline)						X	
2,3,7,8-TCDF							X

Table E2. Air and Water Release Data from the New York State TRI and PCS and Niagara River Loading Data Sets for 95 Chlorinated Compounds on Pollutant Lists.

TRI = New York State Toxic Release Inventory

PCS = New York State Permit Compliance System

Niagra R. = Niagara River Loading

#n/a = Chemical is not included in the data set for a given database

< detect = Measured concentrations were below the analytical detection limit

Chemical Name	CAS no.	Water Releases (kg/yr)					Air Releases	
		Lake Ontario Basin Releases			Statewide Releases		Statewide (kg/yr)	
		Niagara R.	TRI	PCS	TRI	PCS	Fugitive - TRI	Stack - TRI
1,1,2 Trichloroethane	79005	#n/a	268.81	131.16	268.81	155.31	1,085.09	2,992.80
1,1,2,2 Tetrachloroethane	79345	#n/a	0.00	0.05	0.00	218.03	0.00	0.00
1,2 Dichlorobenzene	95501	355.95	0.00	0.45	23.97	19.48	1,908.62	2,354.78
1,2 Dichloroethylene	540590	#n/a	0.00	3.69	0.00	377.39	0.00	0.00
1,2 Dibromo 3 Chloropropane	96128	#n/a	0.00	#n/a	0.00	#n/a	0.00	0.00
1,2,3,4 Tetrachlorobenzene	634661	162.37	#n/a	#n/a	#n/a	#n/a	#n/a	#n/a
1,2,3,5 Tetrachlorobenzene	634902	#n/a	#n/a	#n/a	#n/a	#n/a	#n/a	#n/a
1,2,4 Trichlorobenzene	120821	293.39	0.00	193.15	66.72	249.07	19.56	4.28
1,2,4,5 Tetrachlorobenzene	95943	#n/a	#n/a	#n/a	#n/a	#n/a	#n/a	#n/a
1,2-Trans-Dichloroethylene	156605	#n/a	#n/a	773.24	#n/a	804.40	#n/a	#n/a
1,3 Dichlorobenzene	541731	186.81	0.00	0.00	0.00	0.00	0.00	0.00
1,3 Dichloropropene	542756	#n/a	0.00	#n/a	0.00	#n/a	0.00	0.00
1,3,5 Trichlorobenzene	108703	20.26	#n/a	#n/a	#n/a	#n/a	#n/a	#n/a
1,4 Dichlorobenzene	106467	544.71	0.00	0.11	0.00	30.51	0.00	0.00
2 Chloroacetophenone	532274	#n/a	0.00	#n/a	0.00	#n/a	0.00	0.00
2,3,7,8-TCDD	1746016	< detect	#n/a	#n/a	#n/a	#n/a	#n/a	#n/a
2,4 Dichlorophenol	120832	6.47	8.23	0.00	8.23	5.53	0.91	0.00
2,4,5 Trichlorophenol	95954	4.11	0.00	0.00	0.00	0.21	0.00	0.00
2,4,6 Trichlorophenol	88062	231.99	0.00	0.00	0.00	0.10	0.00	0.00
2,4-Dichlorophenoxyacetic Acid	94757	#n/a	0.00	0.19	0.00	0.19	0.00	0.00
2-Chloroethyl Vinyl Ether	110758	#n/a	#n/a	0.00	#n/a	1.13	#n/a	#n/a
2-Chloronaphthalene	494031	#n/a	#n/a	#n/a	#n/a	#n/a	#n/a	#n/a
2-Chlorophenol	95578	#n/a	#n/a	0.00	#n/a	9.39	#n/a	#n/a
3,3 Dichlorobenzidine	91941	#n/a	0.00	0.00	0.00	2.34	0.00	0.00

Chemical Name	CAS no.	Water Releases (kg/yr)					Air Releases	
		Lake Ontario Basin Releases			Statewide Releases		Statewide (kg/yr)	
		Niagara R	TRI	PCS	TRI	PCS	Fugitive - TRI	Stack - TRI
4 Chlorophenyl Phenyl Ether	7005723	#n/a	#n/a	0.00	#n/a	0.06	#n/a	#n/a
4,4'-DDE	72559	10.19	#n/a	0.00	#n/a	0.00	#n/a	#n/a
4,4'-DDT	50293	9.03	#n/a	0.01	#n/a	0.01	#n/a	#n/a
4,4' DDD	72548	6.46	#n/a	0.01	#n/a	14.38	#n/a	#n/a
Aldrin	309002	#n/a	0.00	0.11	0.00	0.11	0.00	0.00
Allyl Chloride	107051	#n/a	0.00	#n/a	0.00	#n/a	243.81	82.07
Alpha-Endosulfan	959988	8.35	#n/a	2.52	#n/a	2.52	#n/a	#n/a
Aniline	62533	#n/a	2.53	#n/a	1,815.28	#n/a	3,996.66	11,680.94
Benzotrichloride	98077	#n/a	0.00	#n/a	0.00	#n/a	1,019.67	23.90
Benzyl Chloride	100447	#n/a	0.00	#n/a	0.00	#n/a	68.34	0.39
Beta-Endosulfan	33213659	1.32	#n/a	0.00	#n/a	0.00	#n/a	#n/a
Bis (2 Chloroethoxy) Methane	11911	#n/a	#n/a	#n/a	#n/a	#n/a	#n/a	#n/a
Bis(2-Chloroisopropyl) Ether	108601	#n/a	0.00	#n/a	0.00	#n/a	0.00	0.00
Bis(Chloromethyl )Ether	542881	#n/a	0.00	#n/a	0.00	#n/a	0.00	0.00
Captan	133062	#n/a	0.00	#n/a	0.00	#n/a	0.00	1.04
Carbon Tetrachloride	56235	< detect	0.65	0.02	0.65	54.81	2,468.46	805.46
Chloracetic Acid	79118	#n/a	0.00	#n/a	0.00	#n/a	351.98	8.74
Chloramben	133904	#n/a	0.00	#n/a	0.00	#n/a	0.00	0.00
Chlordane	57749	#n/a	0.00	#n/a	0.00	#n/a	0.00	0.00
Chlorine	7782505	#n/a	235.13	677,090.91	7,051.90	4,233,789.19	7,353.29	63,319.86
Chlorobenzene	108907	#n/a	0.45	3.74	39.64	194.86	502.97	2,145.04
Chlorobezilate	510156	#n/a	0.00	#n/a	0.00	#n/a	0.00	0.00
Chloroform	67663	2,645.89	129.55	1,709.79	842.32	3,596.68	16,806.86	9,744.60
Chloromethyl Methyl Ether	107302	#n/a	0.00	#n/a	0.00	#n/a	0.00	0.00
Chloroprene	126998	#n/a	0.00	#n/a	0.00	#n/a	0.00	0.00
Chloropyrifos	2921882	#n/a	#n/a	#n/a	#n/a	#n/a	#n/a	#n/a
Dichlorobromomethane	75274	#n/a	0.00	157.25	0.00	859.90	0.00	0.00
Dichloroethyl Ether (Bis(2 Chloroethyl) Ether)	111444	#n/a	0.00	27.20	0.00	27.27	0.00	0.00
Dichlorvos	62737	#n/a	0.00	#n/a	0.00	#n/a	0.00	0.00
Dieldrin	60571	60.44	#n/a	0.01	#n/a	0.01	#n/a	#n/a
Dimethyl Carbamoyl Chloride	79447	#n/a	0.00	#n/a	0.00	#n/a	0.00	0.00
Endosulfan	115297	#n/a	0.00	0.01	0.00	28.74	0.00	0.00

Chemical Name	CAS no.	Water Releases (kg/yr)					Air Releases	
		Lake Ontario Basin Releases			Statewide Releases		Statewide (kg/yr)	
		Niagara R.	TRI	PCS	TRI	PCS	Fugitive - TRI	Stack - TRI
Endosulfan Sulfate	1031078	#n/a	#n/a	#n/a	#n/a	#n/a	#n/a	#n/a
Endrin	72208	0.53	0.00	#n/a	0.00	#n/a	0.00	0.00
Epichlorohydrin (1 Chloro 2,3 Epoxypropane)	106898	#n/a	14.38	#n/a	14.38	#n/a	171.00	29.54
Ethyl Chloride (Chloroethane)	75003	#n/a	0.00	17.58	0.00	17.58	0.00	0.00
Ethylene Dichloride (1,2 Dichloroethane)	107062	#n/a	697.61	2,350.50	698.65	2,350.52	1,920.80	3,684.00
Ethylidene Dichloride (1,1 Dichloroethane)	75343	#n/a	0.00	568.27	0.00	570.40	0.00	0.00
Heptachlor	76448	#n/a	0.00	0.00	0.00	0.01	0.00	0.00
Heptachlor Epoxide	1024573	24.58	#n/a	0.00	#n/a	0.00	#n/a	#n/a
Hexachlorobenzene	118741	48.58	0.00	0.00	0.00	1.45	0.00	0.00
Hexachlorobutadiene	87683	32.47	0.00	0.00	0.00	0.33	11.01	0.45
Hexachlorocyclohexane-Alpha	319846	389.13	#n/a	0.00	#n/a	0.00	#n/a	#n/a
Hexachlorocyclohexane-Beta	319857	#n/a	#n/a	#n/a	#n/a	#n/a	#n/a	#n/a
Hexachlorocyclohexane-Delta		#n/a	#n/a	#n/a	#n/a	#n/a	#n/a	#n/a
Hexachlorocyclohexane-Gamma (Lindane)	58899	120.57	0.00	0.00	0.00	0.00	0.00	0.00
Hexachlorocyclopentadiene	77474	#n/a	0.00	0.00	2.59	0.43	365.97	30.38
Hexachloroethane	67721	#n/a	0.00	0.00	0.00	0.01	0.00	0.00
Hydrochloric Acid	7647010	#n/a	327.82	#n/a	916.16	#n/a	46,692.16	2,016,508.35
Methoxychlor	72435	< detect	0.00	#n/a	0.00	#n/a	0.00	0.00
Methyl Chloride (Chloromethane)	74873	#n/a	0.00	0.03	380.22	0.03	8,161.47	6,198.83
Methyl Chloroform (1,1,1 Trichloroethane)	71556	#n/a	235.78	596.87	291.09	625.77	819,279.84	1,375,329.86
Methylene Chloride (Dichloromethane)	75092	10,800,173.83	3,829.87	6,404.15	3,868.08	6,404.15	1,168,674.51	2,679,739.91
Mirex	2385855	4.26	#n/a	0.00	#n/a	0.19	#n/a	#n/a
Octachlorostyrene		#n/a	#n/a	#n/a	#n/a	#n/a	#n/a	#n/a
P-Chloro-M-Cresol	59507	#n/a	#n/a	0.00	#n/a	0.00	#n/a	#n/a
PCBs	1336363	404.51	0.00	2.74	0.00	10.94	0.00	0.00
Pentachlorobenzene	608935	55.99	#n/a	0.00	#n/a	0.00	#n/a	#n/a
Pentachloronitrobenzene	82688	#n/a	0.00	#n/a	0.00	#n/a	0.00	0.00

Chemical Name	CAS no.	Water Releases (kg/yr)					Air Releases	
		Lake Ontario Basin Releases			Statewide Releases		Statewide (kg/yr)	
		Niagara R.	TRI	PCS	TRI	PCS	Fugitive - TRI	Stack - TRI
Pentachlorophenol	87865	351.13	0.00	0.09	0.00	0.67	0.00	0.00
Phosgene	75445	#n/a	0.00	#n/a	0.00	#n/a	96.12	218.42
Photomirex		#n/a	#n/a	#n/a	#n/a	#n/a	#n/a	#n/a
Propylene Dichloride (1,2 Dichloropropane)	78875	#n/a	1,891.39	2,142.27	1,891.39	2,142.27	35,042.50	121,774.31
Tetrachloroethylene (Perchloroethylene)	127184	31,964.06	66.85	881.13	281.57	1,529.83	292,766.76	360,473.67
Titanium Tetrachloride	7550450	#n/a	0.00	#n/a	0.00	#n/a	7.64	1.55
Toxaphene	8001352	#n/a	0.00	#n/a	0.00	#n/a	0.00	0.00
Trichloroethylene	79016	#n/a	203.26	443.02	278.53	1,112.42	472,485.83	607,260.07
Vinyl Chloride	75014	#n/a	0.00	17.95	1.04	30.68	9,147.52	23,882.27
Vinylidene Chloride (1,1 Dichloroethylene)	75354	#n/a	15.74	7,585.24	15.74	7,644.82	161.03	58.10
4,4'-Methylenibis (2-Chloroaniline)	101144	#n/a	0.00	#n/a	0.00	#n/a	0.00	0.71
2,3,7,8-TCDF	51207309	#n/a	#n/a	#n/a	#n/a	M a	#n/a	#n/a