Appendix C:

The Lake Superior Zero Discharge Demonstration Program and Relationship to Chemical Contaminants in Lake Superior

Silver Islet. Photo Credit: John Marsden, Environment Canada.

Lake Superior Lakewide Management Plan
2006

INTRODUCTION

As noted in Chapter 4, Section 4.1, entitled Pollutant Concentrations in the Environment, enforcement of environmental regulations, changes in industrial development patterns, implementation of pollution prevention, and the efforts of individual citizens have significantly reduced releases to Lake Superior. The Zero Discharge Demonstration Program (ZDDP), and other programs, reduce toxic chemicals at their sources, resulting in their eventual reduction in the ecosystem. The assessment of monitoring data on concentrations of a suite of toxic organic contaminants in various media is within the purview of the LaMP. To that end, the Chemical Committee of the Lake Superior LaMP Work Group prepared a presentation on both the current status and trends of Lake Superior contaminants and the relationship to the ZDDP. This presentation is provided in this Appendix.

The following conclusions about Lake Superior contaminant levels and trends were drawn:

- In general, concentrations of many legacy PBT contaminants have declined over time (i.e., government intervention has been effective).
- In most cases, concentrations in various media are decreasing at much slower rates or have leveled off over time.
- Lake Superior's physical, thermal, and biological properties make it unique and particularly sensitive to retaining PBT chemicals.
- Atmospheric deposition is the main source of PBTs to the lake – some source regions have been identified.
- New chemicals of concern such as PBDEs are increasing in fish and sediments in Lake Superior.
- Fish consumption advice is continually changing due to new monitoring data and new information on toxicological interactions of individual contaminants and contaminant mixtures.

Implications for management include the following:

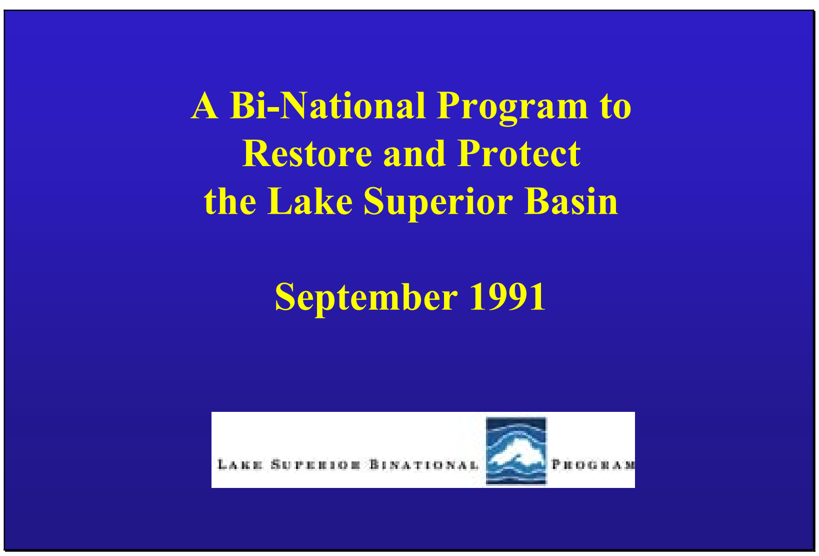
- Lake Superior is sensitive! Prevention and preservation critical (toxaphene example).
- Stop introduction of invasives - it affects contaminant transport as well as the biology of the Lakes.
- 2005-2006 coordinated monitoring effort is a great start!
- Coordinated monitoring needs to continue as agreed to by the rotational schedule - next Lake Superior monitoring year will be 2011.
- Statistical design of monitoring programs may need to change to reflect lower environmental concentrations – i.e., have greater power to detect changes in concentrations.
- Tie contaminant reduction outreach efforts to issues identified in the Community Awareness Review and Development (CARD) study.
- Action needed beyond the basin! ZDDP is critical for the basin but will have limited impact on PBTs in the Lake Superior environment in the face of regional and global sources.
- There are many positive recommendations identified in the work of the Great Lakes Regional Collaboration on the U.S. side. These need to be implemented.

- How can we learn from our past mistakes? Advocating for pollution prevention, conservation, recycling, local and renewable energy sources, and reduced dependence on synthetic chemical substances are ways to ensure a sustainable society and a healthy Lake Superior.

Slide 1

The main focus of our presentation today is chemical contaminants in Lake Superior. Before we start, we want to give a brief review of the zero discharge demonstration program for Lake Superior, which has been the main focus of the chemical committee. We will briefly discuss its relationship to chemical contaminants in the Lake. Matt Hudson will give the presentation on status and trends of contaminants in the Lake.

Slide 2



The Binational Program Agreement was signed by the governments at the IJC meeting in September 1991, in response to the challenge issued by the IJC for a zero discharge demonstration for Lake Superior.

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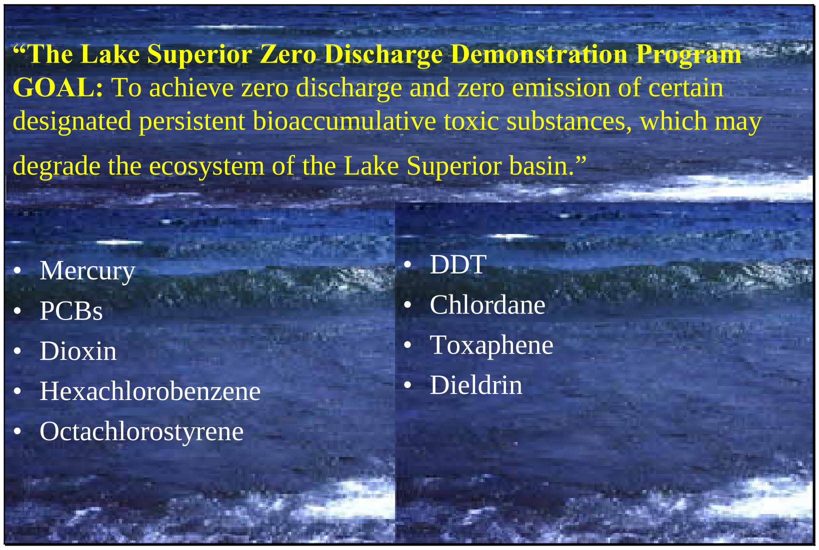
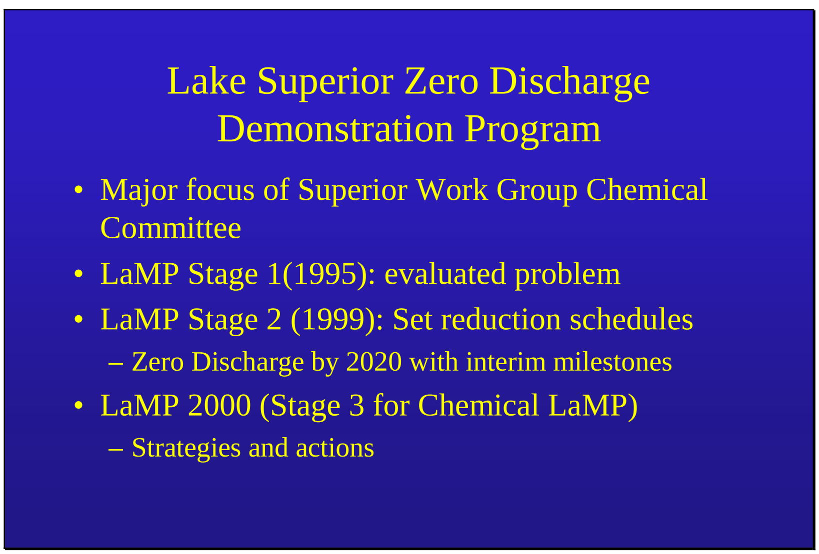


The goal statement is taken from the 1991 agreement. It is a very pro-active goal. Nine chemicals were targeted.

Zero Discharge is considered a strategy toward the virtual elimination goal for the environment.

Slide 4



Work on the LaMP began in 1992: Stage 1 was finalized in 1995. The Stage 2 has the reduction schedules, developed jointly with the forum and with significant public input. LaMP 2000 and the update we are working on include estimates for sources within the basin. We use these estimates to judge progress toward the reduction goals of the Stage 2 LaMP.

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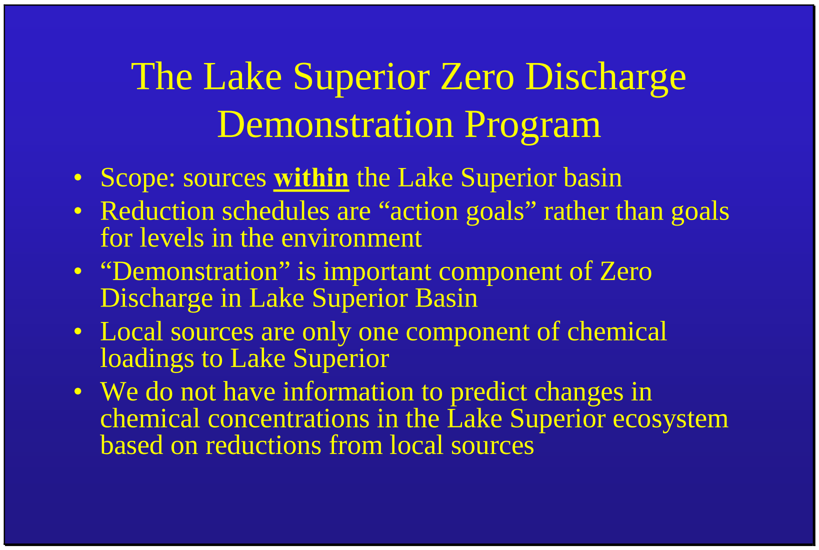

From the beginning, it was understood that the ZDDP was not going to "fix" Lake Superior since "out of basin" sources are also important. The "demonstration" aspect was a very important part of the ZDDP concept. We do not have the environmental data or predictive models to predict the effect that local source reduction will have on chemical concentrations in the Lake Superior environment.

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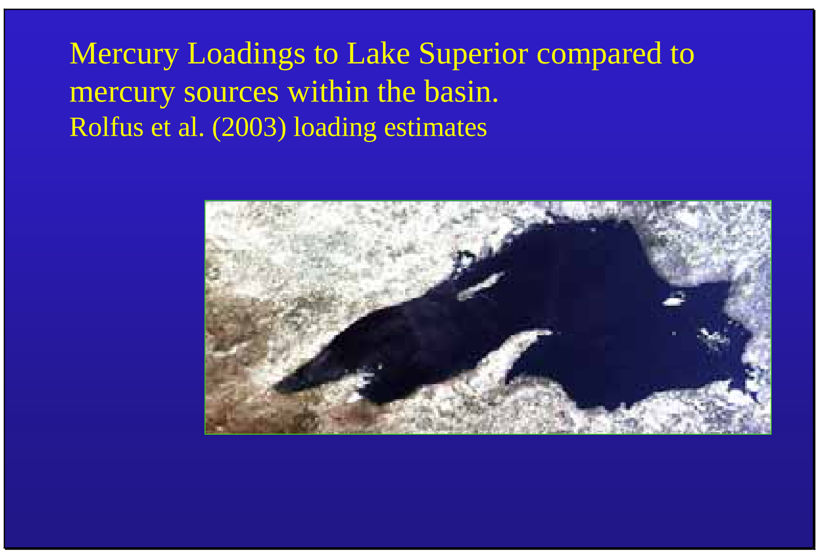

Taking mercury as an example, we can look at the work of Rolfus and colleagues in developing a mercury mass balance for L. Superior.
This summarizes where mercury enters the Lake, but does not distinguish local vs. distant sources.

Slide 7

Although most of the mercury entering Lake Superior is deposited directly from the atmosphere to the surface of the Lake, that mercury comes from distant as well as local sources.

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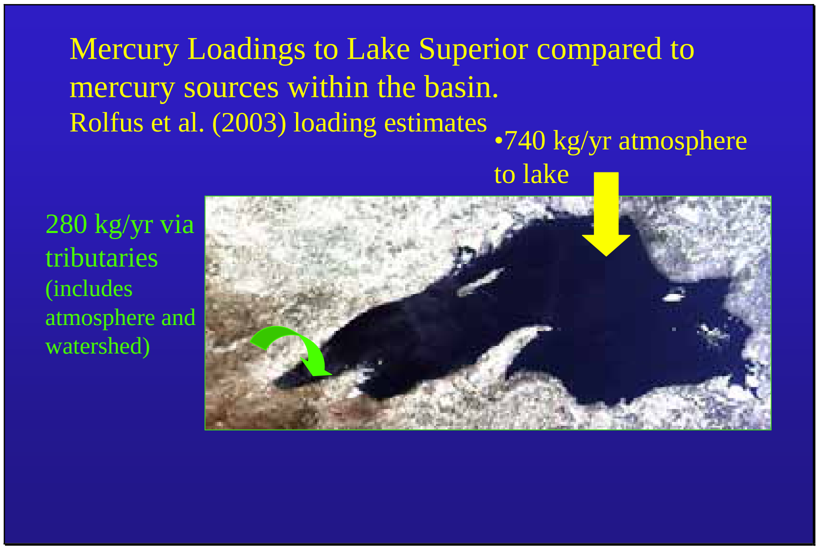

Mercury also enters via tributaries. This number includes atmospheric deposition to the watershed as well as potential sources within the watershed.

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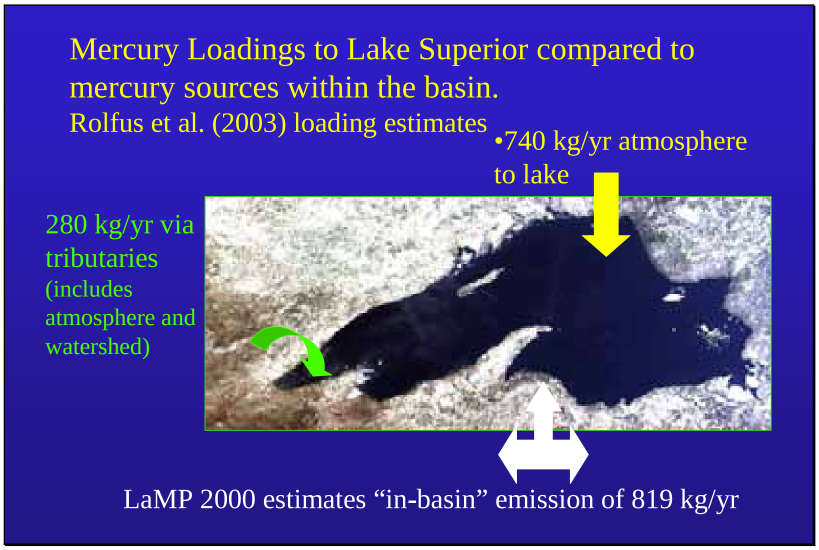

The ZDDP focuses on "in-basin" sources. Local sources also contribute to the regional and global pool of mercury. We emit roughly 80% of what we receive. Even though the actual impact of the ZDDP on chemical levels in L. Superior may be small, the philosophy of the ZDDP is to put our own house in order, as one of the steps to protect Lake Superior.

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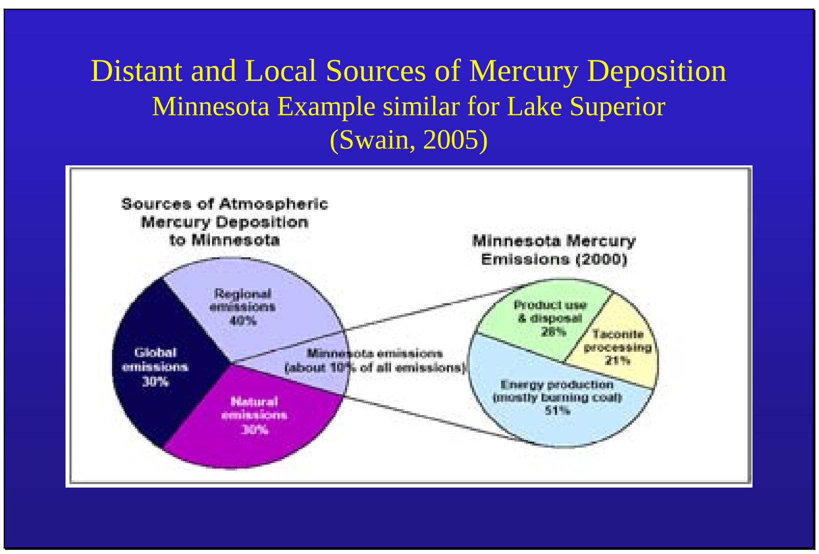

What are the sources of the atmospheric deposition to the Lake Superior basin? This Minnesota example is a reasonable stand-in for the Lake Superior basin. Only 10% of the mercury deposition in Minnesota comes from emission sources within the state. Global emissions account for 30% of the mercury deposited on the state; regional emissions account for 40%.

We don't have the info to make a similar chart for the Lake Superior basin, but this Minnesota information gives us a reasonable idea that local and regional emissions may account for about half of the mercury deposited in the basin.

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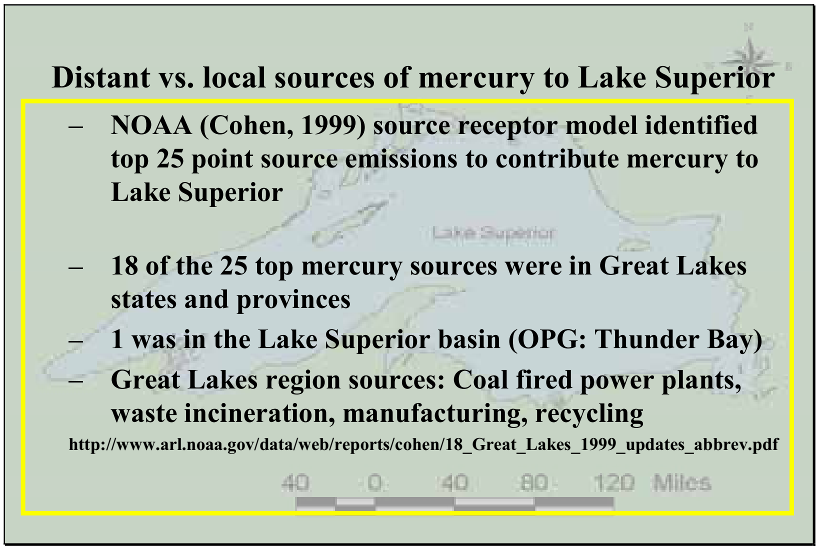

Cohen's 1999 source receptor model identified top atmospheric point sources contributing mercury to Lake Superior. This work shows the importance of sources in the Great Lakes region as a whole.

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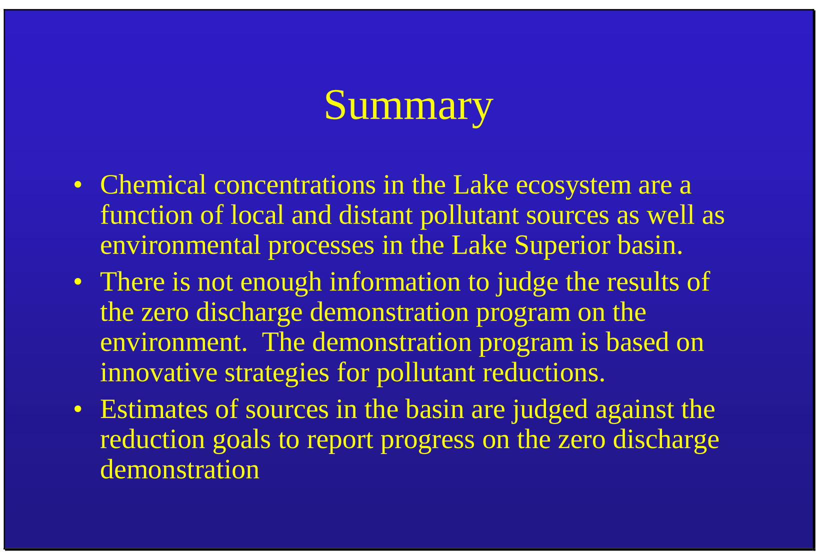

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Slide 14

Acknowledgements

- Lake Superior Workgroup, esp. Chemical Committee members!
- M. Whittle, Dept. of Fisheries and Oceans
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- T. Havelka, Canadian Wildlife Service (Environment Canada)
- V. Richardson, Environment Canada
- A. Dove, Environment Canada
- S. Backus, Environment Canada
- S. Venkatesh, Meteorological Service of Canada
- P. McCann, MN Dept. of Health
- K. Groetsch, MI Dept. of Community Health

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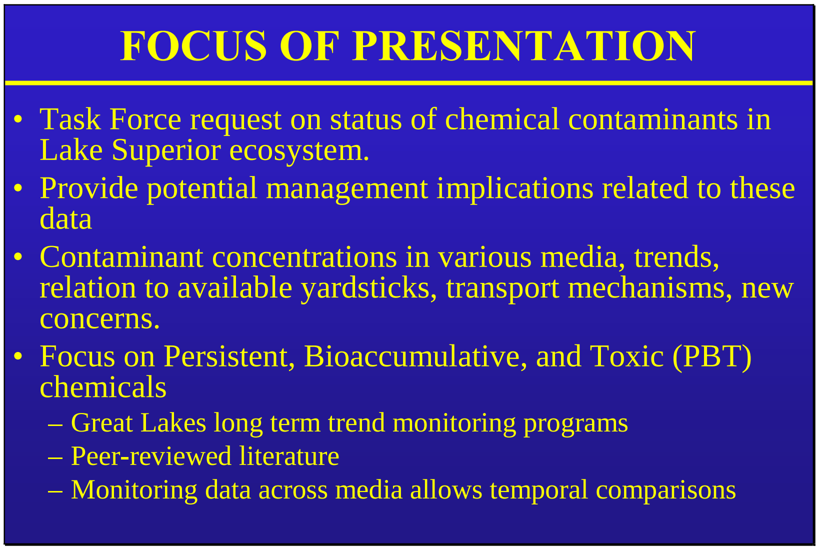

New Concerns refers to "emerging contaminants" and issues surrounding them.

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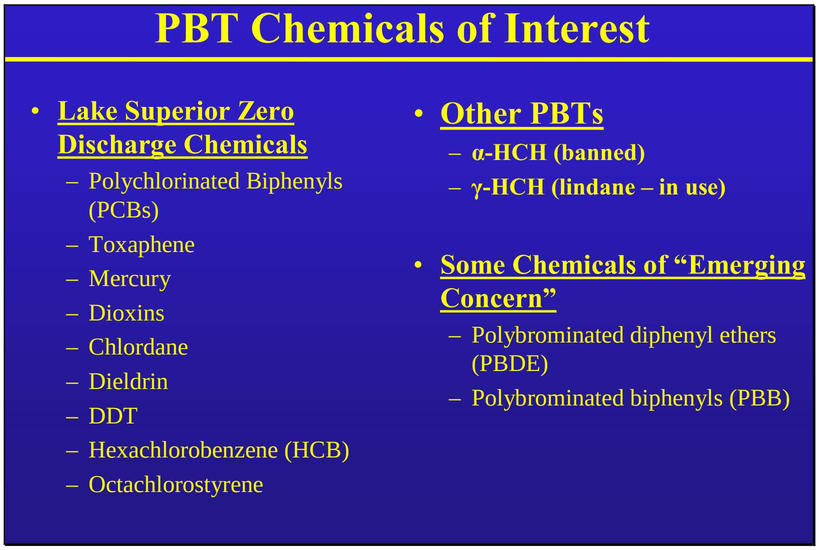
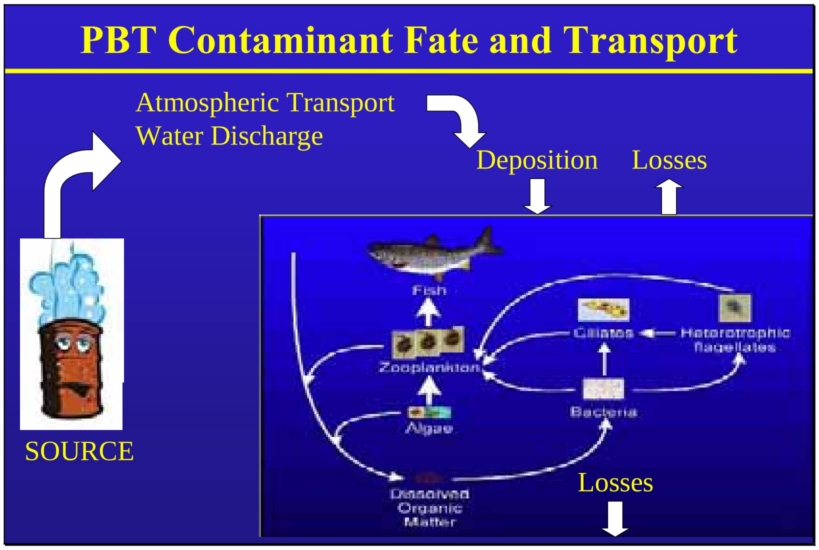


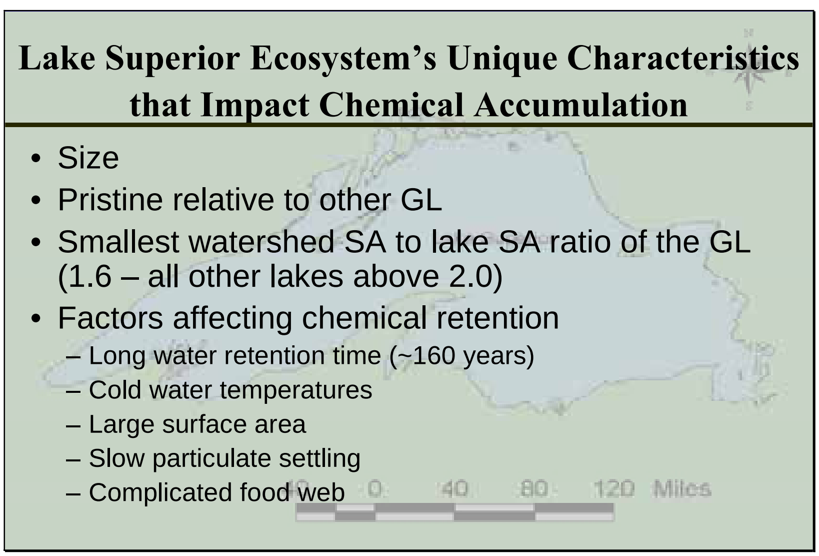
Describe chemicals:

Slide 17



Overall source transport pathways are much more complicated. This is a simplification. "Source" is an example meant to represent all sources, point and non-point. Deposition could be through precipitation, dry deposition, gas/air exchange, surface runoff. Losses include volatilization, sedimentation, and outflow. Food web is complicated and different between water bodies.

Slide 18



Largest freshwater body by surface area and 3rd largest by volume
List of characteristics that make Lake Superior susceptible to retaining chemicals for very long time, as well as the fact that the food web structure can impact concentrations in biota.

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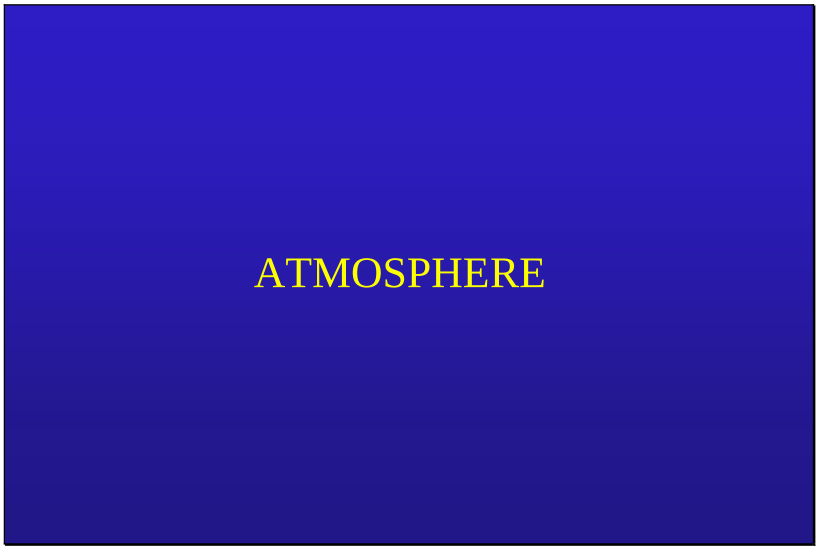

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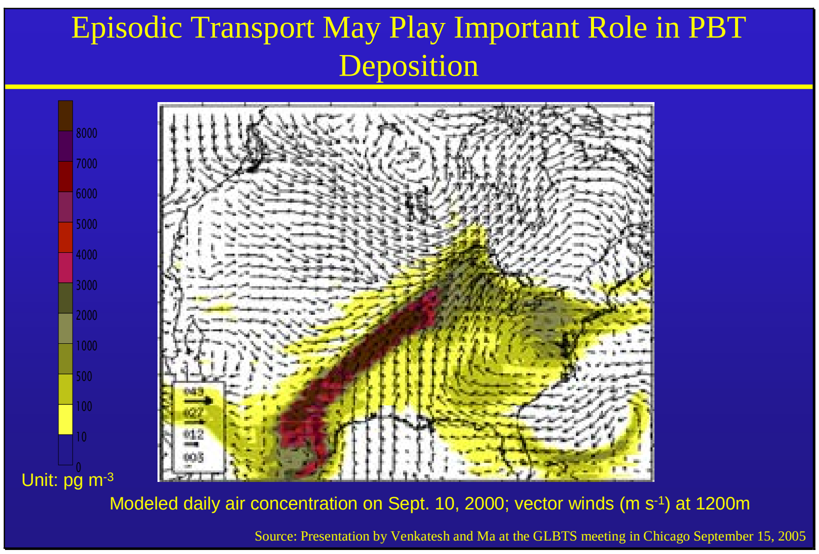
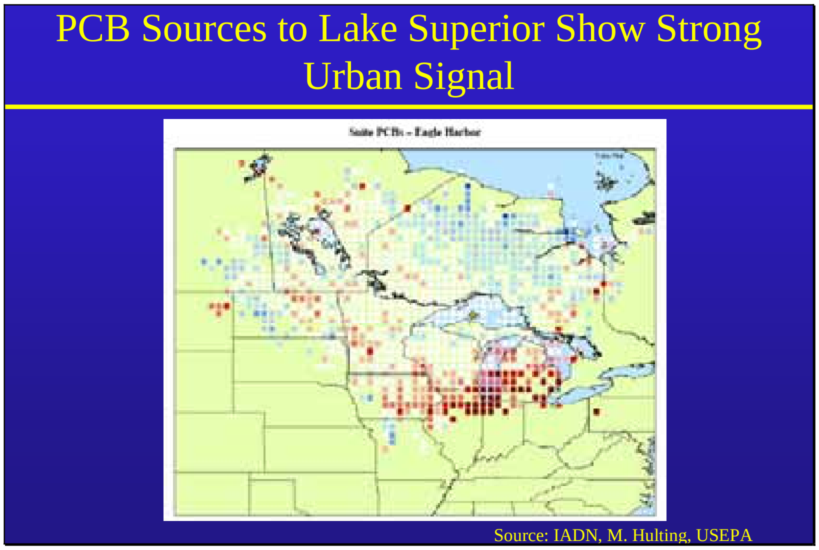


This modeling exercise was done for toxaphene. Note how reservoir sources in the soil of southeast states (where toxaphene was used on cotton crops) can be transported to the Great Lakes and other areas through these episodic atmospheric events.

Slide 21



This figure models the source regions for a suite of PCBs to the Eagle Harbor IADN station. The data show a strong urban signal from the southern Lake Michigan area.

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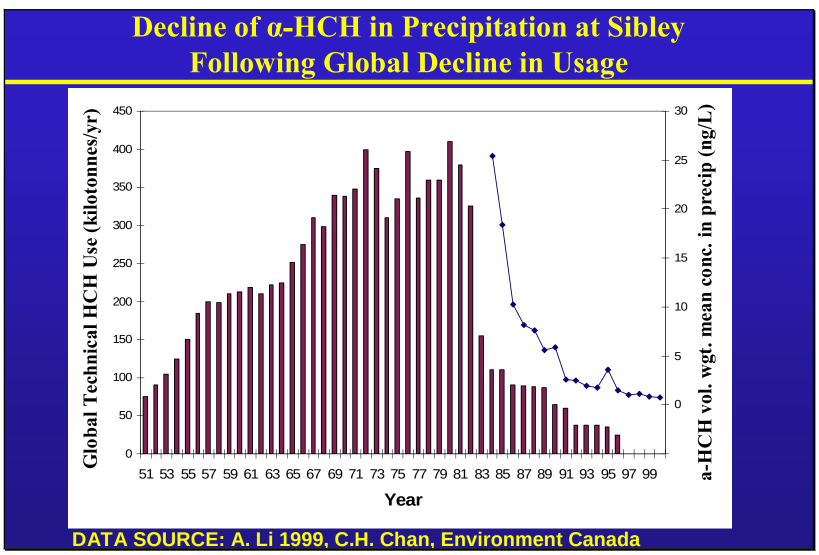

Long-term trends (1950-1996) in the global use of technical hexachlorocyclohexane (HCH) (from Li 1999) and the volume weighted mean concentration of a-HCH in precipitation (in ng/L) at Sibley, Ontario, Canada (from EHC, C.H. Chan). China dip in 1983 and India/Soviet Union dip in 1990. a-HCH is 60-70% of technical HCH.

Sibley is on the northern reach of Squaw Bay, about 90 km (56 miles) east of Thunder Bay and 300 km (186 miles) northeast of Duluth.

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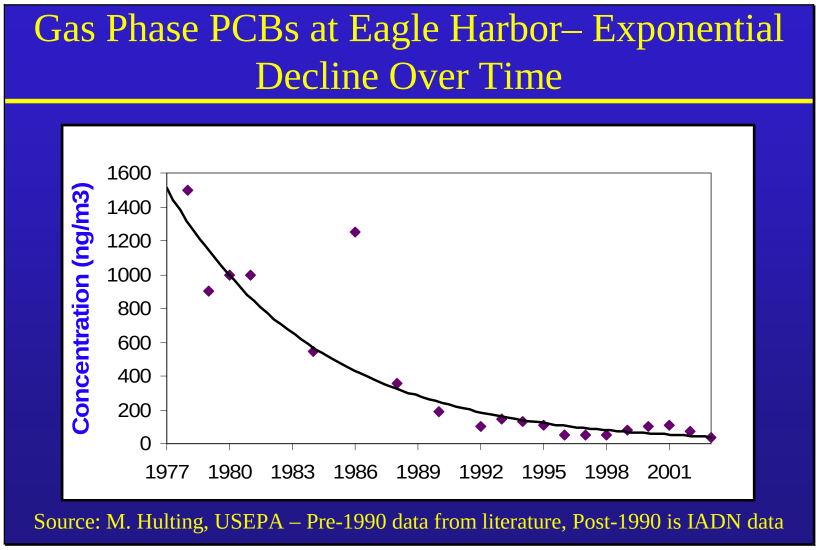

Pre-1990 data is non-IADN and is from the literature. Data through 1996 showed a general decline, followed by a slight increase for some Lakes during the late 90s. Preliminary 2000 data show another decline. Environment Canada is also seeing similar increases in PCB concentrations at Alert since 1998 which may further implicate the importance of global emissions.
EC researchers have found link between El Nino activity and increased PCB concentrations (perhaps increased transport from Asia). May also explain the increases during the same time period for HCB.

Sources for historical PCB data: Achman et al. 1993; Baker and Eisenreich 1990; Cotham and Bidleman 1995; Doskey and Andren 1981; Eisenreich et al. 1981; Eisenreich 1987; Hornbuckle et al. 1993; Hornbuckle et al. 1994; Manchester-Neesvig and Andren 1989; Monosmith and Hermanson 1996.

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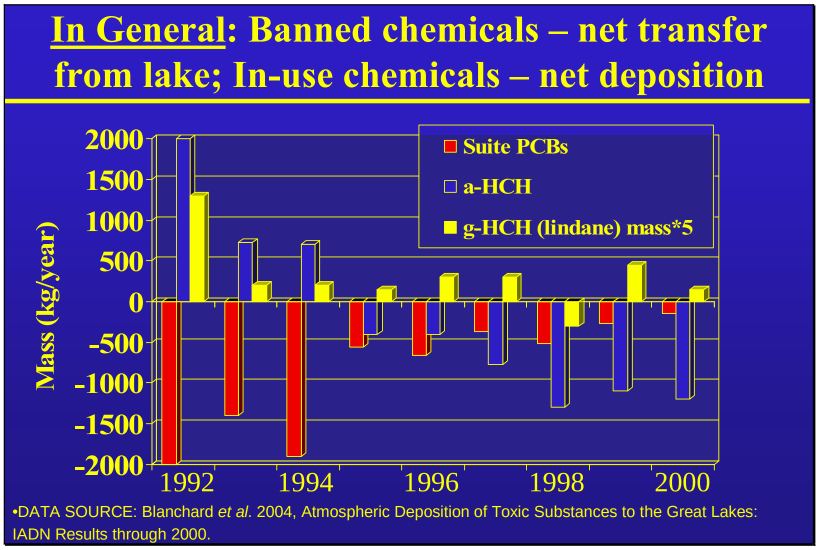
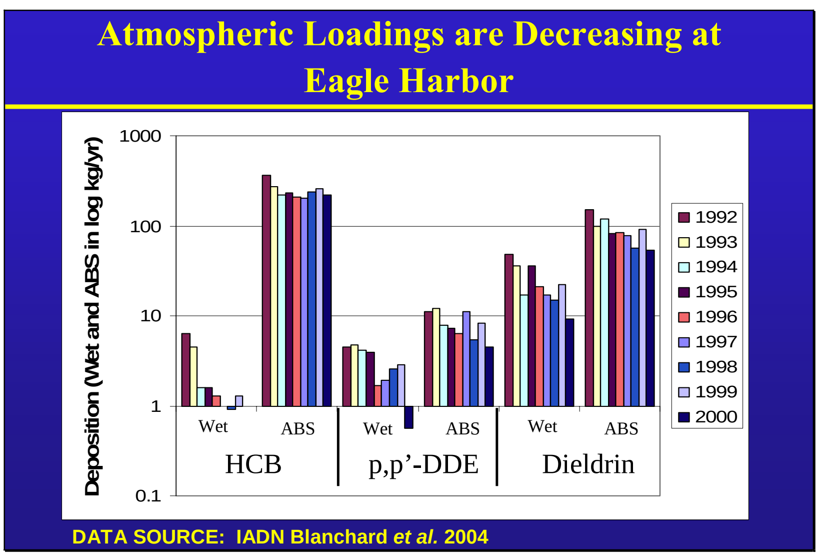


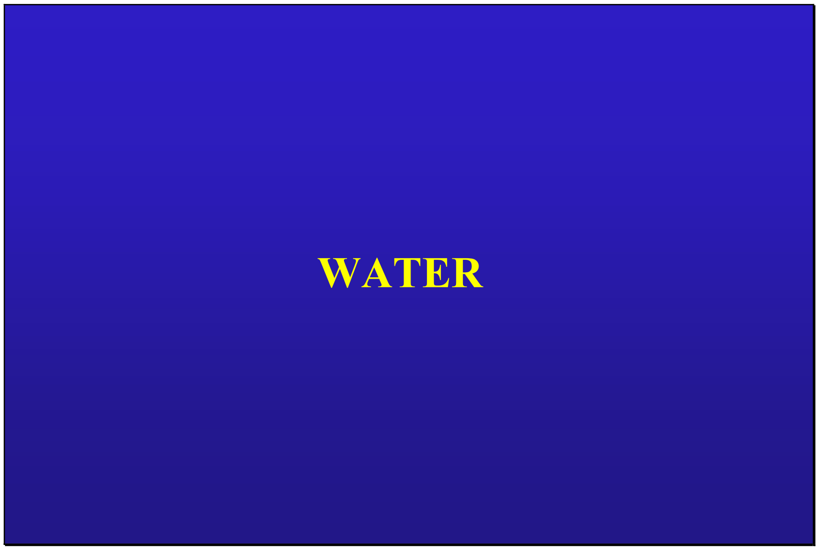
Note that lindane flows are multiplied by 5 to compensate for the scale of the graph. These data show how a lake responds slower than the atmosphere to reductions in use of a chemical. The lake is a "source" for chemicals such as PCBs and a-HCH, but over time the system moves toward steady state (shut off the spigot and the air responds quicker than the lake – aHCH from previous slide is a great example). Contrast this with lindane, which is still in use and the atmosphere is still largely a source to Lake Superior (spigot has not been shut off).

Slide 25



Describe Graph. Most PBT chemicals enter the lake via atmospheric deposition. Note the log scale - Gas phase absorption generally accounts for a much greater proportion of the overall loading than wet deposition for PCBs and pesticides, whereas wet and dry deposition account for the majority of PAH loading. Dieldrin, HCB, and p,p'-DDE demonstrate the typical trend for most regulated chlorinated PBT chemicals with declining concentrations. PCB loadings have shown less of a decline (Chicago source region??)

Slide 26



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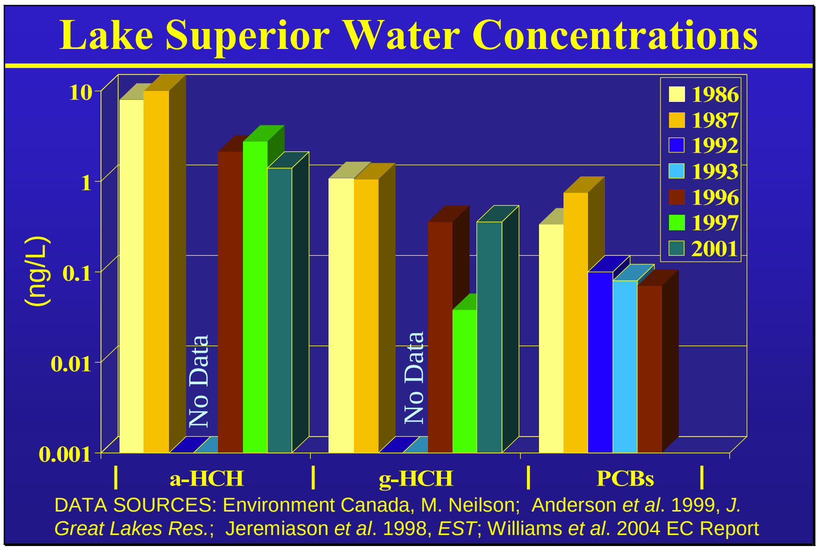


Describe Graph. Again, we have a similar set of PBT chemicals. a-HCH and PCBs have declined but g-HCH may not be (2001 data point) because it's still in-use.

Slide 28

Some Recent Open-water Contaminant Data Exceeds Most Protective Yardsticks (all data in ng/L)

	MN	MI	WI	ON	Open Lake Conc.
PCBs	0.0045	0.026	0.003	1.0	0.0705[1]
HCB	0.074	0.45	0.22	6.5	0.014[2]
Dieldrin	0.0012	0.0065	0.0027	1.0 (+Aldrin)	0.126[2]
Chlordane	0.04	0.25	0.12	60	<0.03[3], 0.0099[4]
DDT	0.011	0.011	0.011	3.0	0.005[2] (p,p'DDE)
Mercury	1.3	1.3	1.3	200	0.71[5]
Toxaphene	0.011	0.068	0.034	8.0	0.7[6], 0.6[7]
g-BHC (lindane)	80	25	18	10	0.357

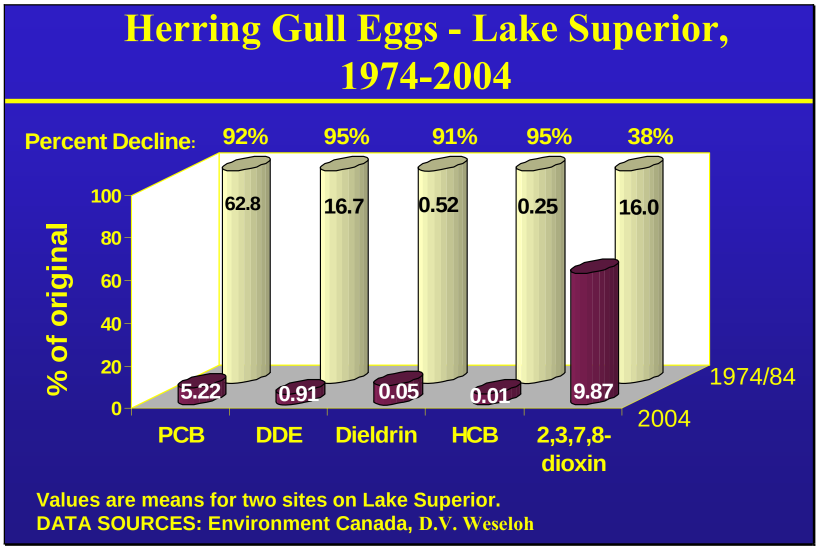
[1]Warren, US EPA, 1996 data [2]Williams *et al*., EC, 2001 data [3]Williams *et al*., EC, 1997 data [4]Jantunen, EC, 1996-1998 data [5]Dove, EC, 2003 data [6]Muir *et al*. 2004, 1998 data [7]Swackhamer, UofMN, 1998 data

All data are given in ng/L or PPB. Most protective yardsticks available for each jurisdiction are used. Red values are those that exceed one or more yardstick guidelines. The 95% confidence level of available concentrations that exceeded those yardsticks was criteria used for Stage II LaMP. We're looking at individual measurements or means rather than 95% limit. What does this say about contamination of the lake?

Slide 29

CONCENTRATIONS
IN
HERRING GULL EGGS
AND
WHOLE LAKE TROUT

Slide 30



Again, to give similar set of chlorinated PBT chemicals, all have shown between **38 and 95**% declines over the last **20 to 30 years**. Make mention Dioxin (pg/g) , other chemicals (ug/g)

(text in bold was updated by Tania Havelka)

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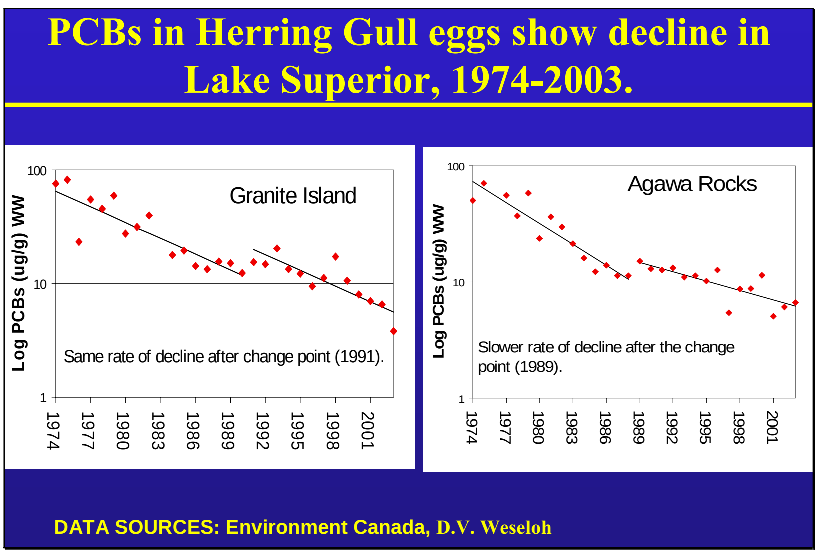
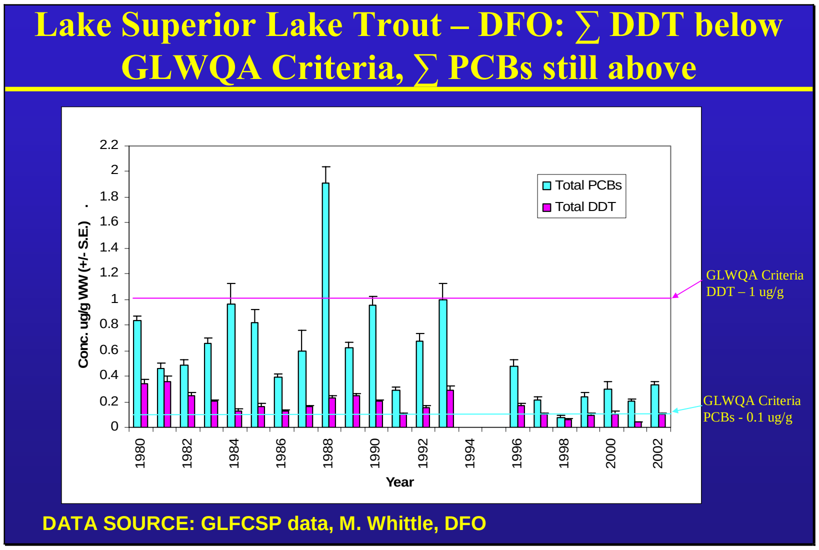


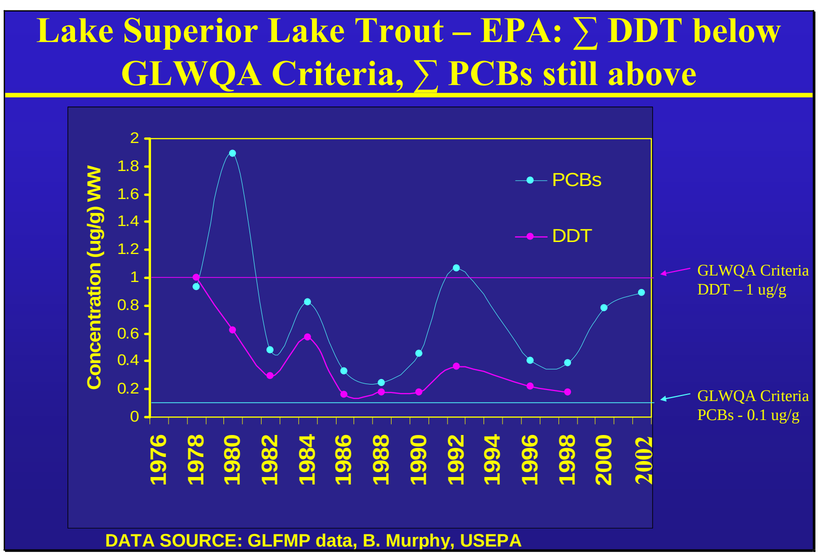
Sum PCBs in herring gull eggs show decline over past 30 years at L.S. sites. Note rate of decline remained the same at Granite Island after change point around 1991 while rate of decline slowed at Agawa Rocks after change point around 1989.

Slide 32



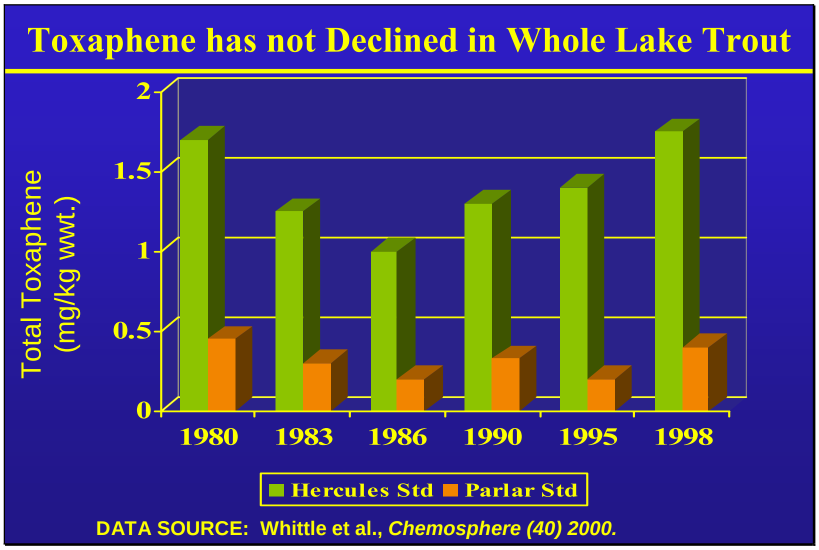
Here again, in whole lake trout we find declines in PBT concentrations between 1980 and 2000. PCBs still exceed GLWQA criteria but not DDT.
Oscillations in between years likely due to many reasons including food web changes, variability within the fish that are sampled and within the analytical method, etc.

Slide 33



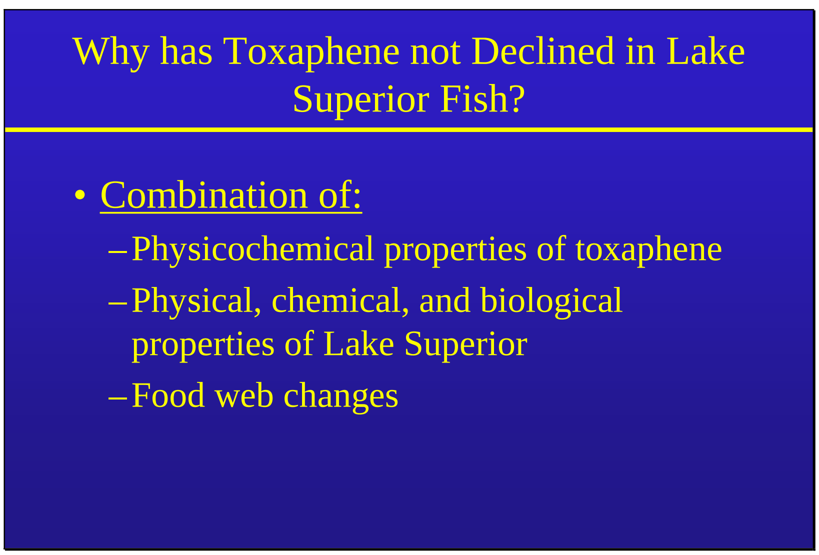
Point out that we are seeing the same types of trends in both the EPA and DFO lake trout monitoring data. Recent PCB increase likely due to change in sample location and thus now sampling a different population of lake trout. Unlikely that the increase is actually a real increase in the environment. Again PCBs above GLWQA criteria but not DDT.

Slide 34



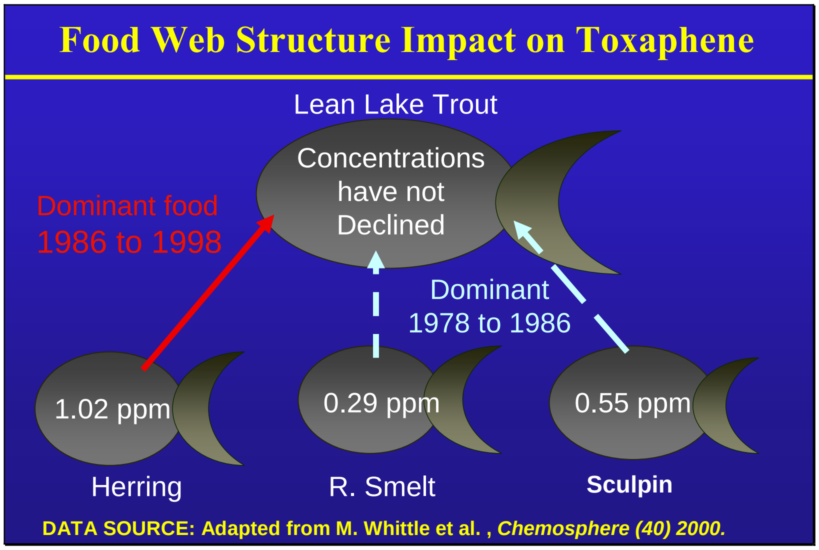
Toxaphene does not seem to be declining as the other PBT chemicals. No clear decline present.
Hercules std. was from the original manufacturer of toxaphene
Parlar std. was an original standard developed by a German researcher

Slide 35



The behavior of toxaphene based on its chemical properties leads it to persist more in an environment such as Lake Superior (relatively high vapor pressure, high solubility)
The lake is large, cold, and has a long water retention time compared to the other GLs, meaning rates of transformation of the chemical will be slower.
Biological community (food web) changes over time

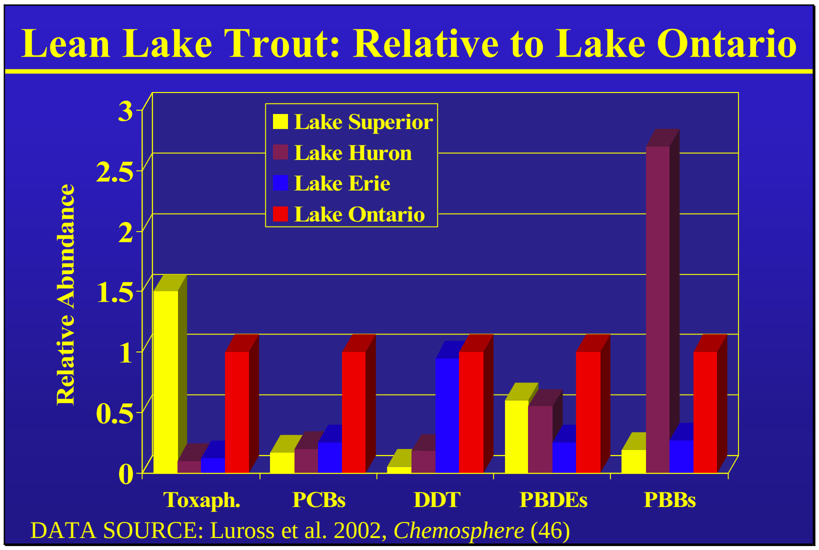
Slide 36



Describe Graph. One potential explanation is that Lake trout populations have experienced a change in their forage base shifting from feeding on mainly a smelt and sculpin dominated diet to one dominated by herring. As you can see by these numbers in herring are much higher in toxaphene than either sculpins or smelt. Thus the lake trout population, since about 1986, may have been experiencing a greater exposure to toxaphene due to their consumption of herring.

Slide 37

Slide 38



This slide shows a relative comparison among four of the Great Lakes using Ontario as the comparative standard. Therefore, Ontario, in tan, has a value of 1. If a lake, such as Superior, has a higher concentration of a chemical in whole lake trout (such as toxaphene), it will have a value greater than 1. So of these four lakes, Superior has the highest concentration of toxaphene. As we can see, Superior is lowest in PCBs and DDT relative to the other 3 lakes (These are Canadian data, so no Lake Michigan). And then, the last two are rather new or emergent chemicals of concern, PBDEs and PBB (classes of flame retardants). Notice Superior is only second to Lake Ontario, so it may be a chemical that needs to be carefully monitored over the next decade to determine its sources and if it is decreasing or increasing. We see the same general pattern with data from EPA's GLFMP program, where aside from toxaphene and alpha-HCH, Lake Superior generally has the lowest concentrations, consistent with the level of industrialization in the basin over time.

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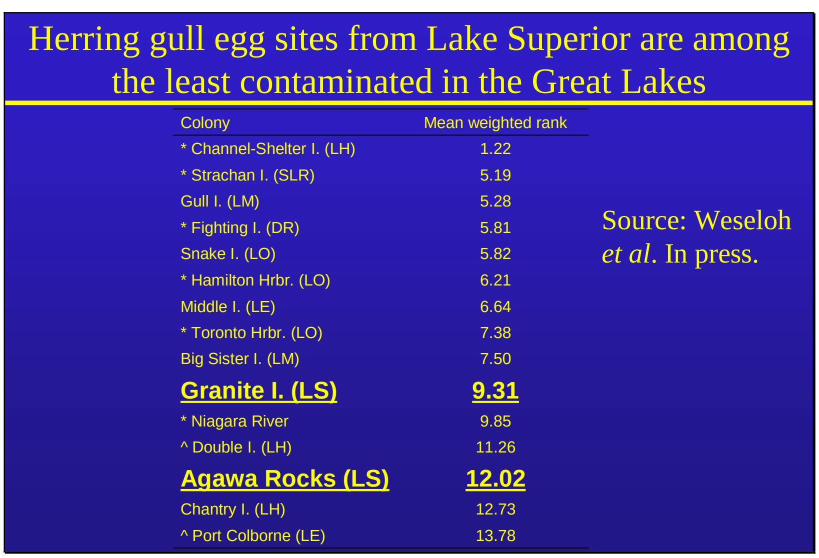

Colony	Mean weighted rank
* Channel-Shelter I. (LH)	1.22
* Strachan I. (SLR)	5.19
Gull I. (LM)	5.28
* Fighting I. (DR)	5.81
Snake I. (LO)	5.82
* Hamilton Hrbr. (LO)	6.21
Middle I. (LE)	6.64
* Toronto Hrbr. (LO)	7.38
Big Sister I. (LM)	7.50
Granite I. (LS)	**9.31**
* Niagara River	9.85
^ Double I. (LH)	11.26
Agawa Rocks (LS)	**12.02**
Chantry I. (LH)	12.73
^ Port Colborne (LE)	13.78

The mean weighted rank of each site, 1998-2002, (arranged from most to least contaminated) and range in rank (1 = most, 15 = the least contaminated site). The ranks were weighted with a measure of contaminant toxicity using the ratio between mean egg concentrations of each compound and the corresponding fish flesh criteria for the protection of piscivorous wildlife (Newell et al. 1987). The ranking is based on: p,p'DDE, dieldrin, HCB, Heptachlor Epoxide, mirex, sum PCB, and 2378-TCDD. Dieldrin and Heptachlor Epoxide concentrations were among the highest from Lake Superior sites, all other contaminants were among the lowest.

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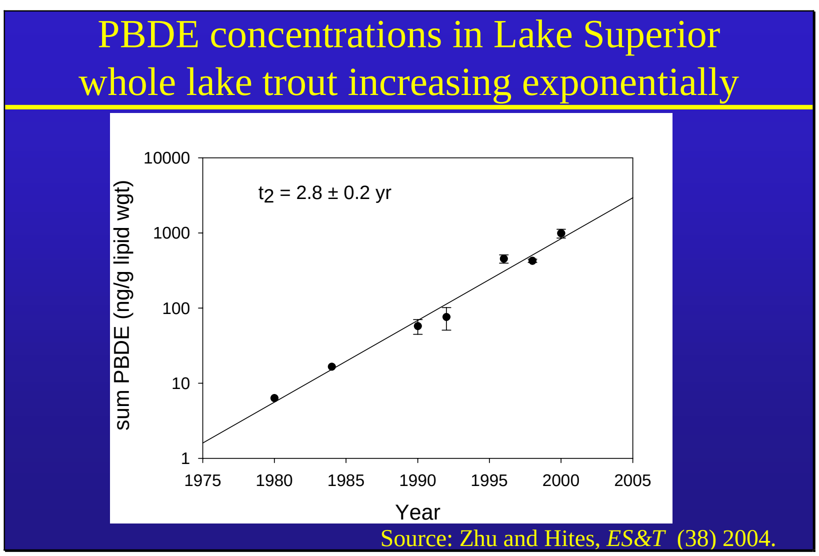
Slide 41



GLFMP archived fish were analyzed for PBDEs and PBB-153 (flame retardants). Exponential increase over time with doubling every 2.5-3 years! Most recent concentrations are about 5 times greater than those measured in fish from Europe. People in North America have about 20 times the level of PBDEs in their blood than Europeans (cite Zhu and Hites). Another study (Song et al.) shows PBDEs increasing in sediments over time while PCBs generally showing a decrease.

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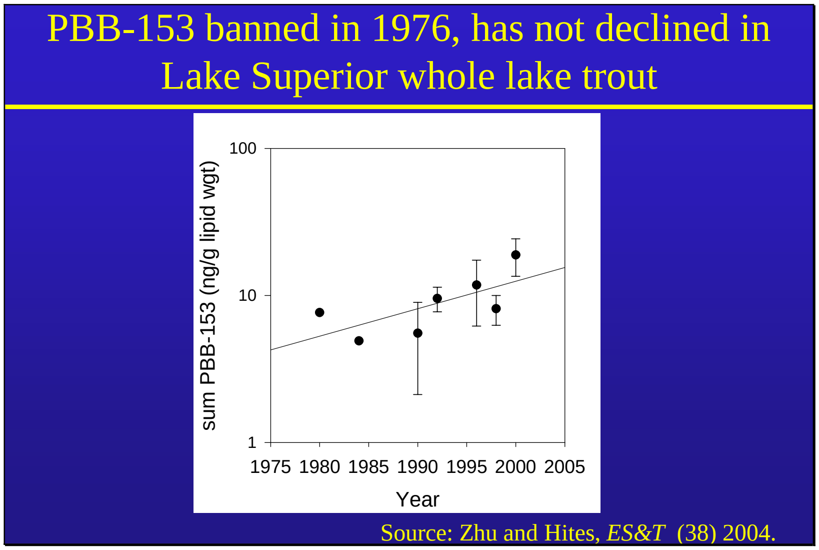

Looks like an increase, but it's not significant. Are there new sources of PBBs or do they behave similar to toxaphene in Lake Superior?

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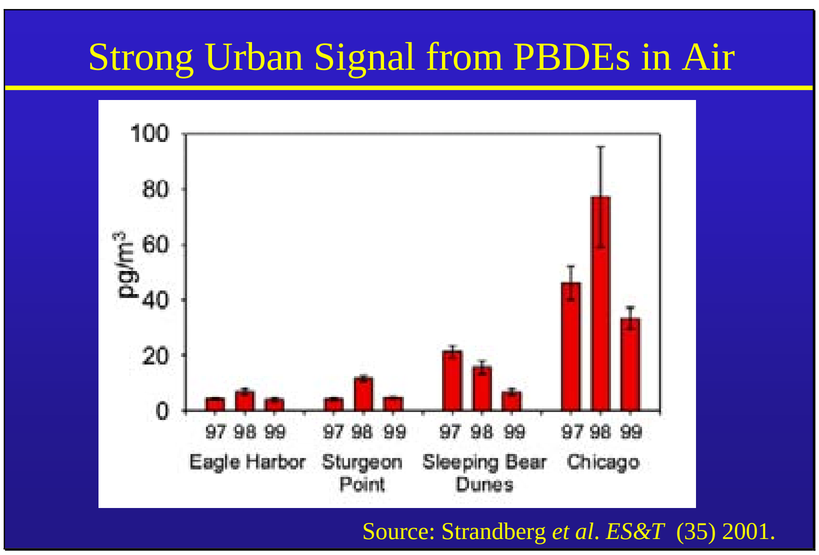

Note urban sources greater than rural

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HUMAN HEALTH

Slide 45

Sport Fish Consumption Trigger Concentrations (ppb)– Sensitive Population

Jurisdiction	Total PCBs		Mercury		Toxaphene		Dioxin-like chemicals	
	Trigger	DNE	Trigger	DNE	Trigger	DNE	Trigger	DNE
Wisconsin	50	>1900	50	>1000	-	-	10	BPJ
Minnesota	50	>1900	50	>1000	-	-	-	-
Michigan	50	>1900	500	>1500	5000	-	10	BPJ
Ontario	153	>305	260	>520	235	>469	1.62	>3.24

Sources: P. McCann, MN Dept. Health; C. Schrank, WI BFMHP; J. Bohr, MI DEQ; A. Hayton ON MOE

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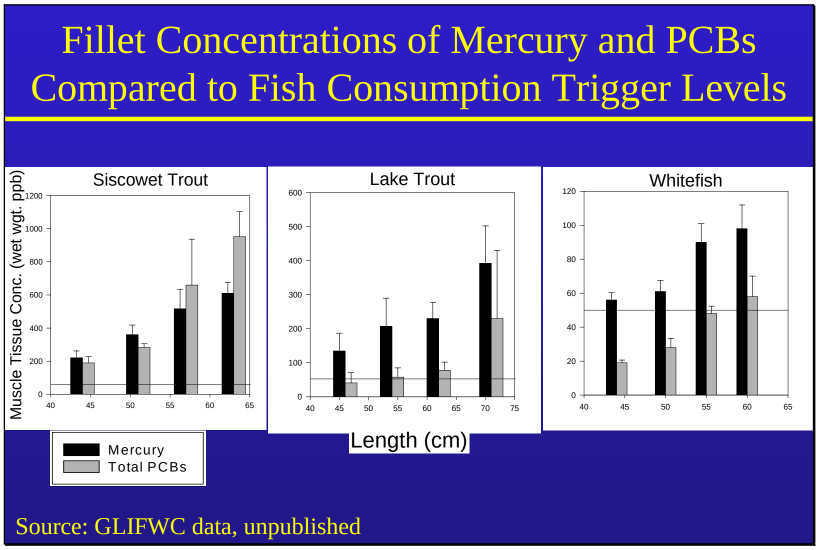

Note these are fillet concentrations and not whole fish like in previous slides. These figures show fish advisory trigger level concentrations used by one or more jurisdictions in the L.S. Basin for mercury and total PCBs, which drive most consumption advice on U.S. side of L.S. GLWQA goal is to be able to consume fish in unlimited quantities. All of these sizes and species of L.S. fish would still require some sort of consumption advice based on current trigger levels, meaning the GLWQA goal has not been met.

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Human Health

- **Presence of chemicals does NOT = negative health effects**
  - Significant exposure is required
  - Human exposure data are very limited.
- **Exposure Pathways.**
  - Air & Water: NOT a direct concern for PBTs
  - Food: Major exposure pathway, particularly fish consumption.

Exposure to PBTs is primarily from food, of which fish is typically the greatest source. In general and on average, exposure is similar over the US. Exceptions are for occupational exposures, those with a greater rate of consumption or for consumption of local foods which could either increase or decrease exposure based on contaminant concentrations in those foods.

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Human Health

- **Fish advisories will likely not decline in the foreseeable future.**
  - Small declines in fish concentrations will not = significant changes in fish consumption advice.
  - New information on toxicity could result in more advisories.
  - Emerging contaminants may become part of advisories.
  - Exposure reduction – Clear, consistent advice

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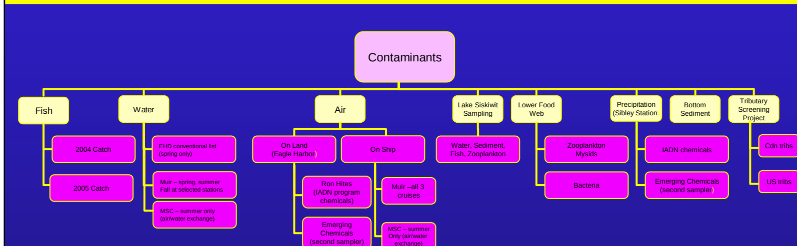
Lake Superior Coordinated Monitoring Chemical Sampling Efforts - 2005



Source: M. Neilson, V. Richardson, Environment Canada

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Summary

- In general, concentrations of many legacy PBT contaminants have declined over time – government intervention has been very effective.
- In most cases, concentrations in various media are decreasing at much slower rates or have leveled off over time
- Lake Superior's physical, thermal, and biological properties make it unique and particularly sensitive to retaining PBT chemicals.

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Summary

- Atmosphere is main source of PBTs to the lake – some source regions have been identified.
- New chemicals of concern such as PBDEs are increasing in fish and sediments in Lake Superior.
- Fish consumption advice is continually changing due to new monitoring data and new information on toxicological interactions of individual contaminants and contaminant mixtures.

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Future Management Actions

- Lake Superior is sensitive! Prevention and preservation critical (toxaphene example).
- Stop introduction of invasives - it affects contaminant transport as well as biology of the Lakes.
- 2005-2006 Coordinated monitoring effort is a great start! Needs to continue as per agreed to rotational schedule - next LS monitoring year will be 2011.
- Statistical design of monitoring programs may need to change to reflect lower environmental concentrations – i.e. have greater power to detect changes in conc.

We've learned that LS is more sensitive to contaminant inputs than other GL and will take longer to recover from degradation. We can't take the viewpoint that LS is in good shape and not devote resources to protecting it.
2. Food web effects on contaminant transport are very important to observed concentrations. We have many studies that point to how food web changes impact contaminant concentrations in top predators (cite Whittle et al. study showing change in lake trout food from smelt and sculpin to herring). Invasives can add additional trophic levels to the food web and "mask" reduction of contaminants. There is a lag time for top predators to reflect food web changes via contaminant concentrations.
3. Will provide needed and valuable data to resource managers. These efforts need to continue into the future so groups are working together to provide comparable data across space and time as well as consistent management approaches aimed at protecting the lake.

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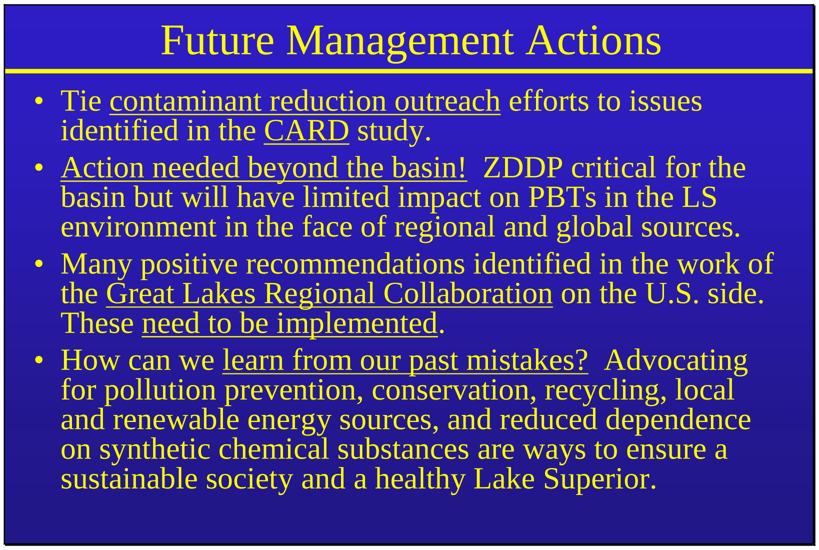

1. Personal responsibility at a grassroots level is critical to changes on a greater scale.
3. GLRC ideas: a. Adequate resources for rural trash and recycling, b. consistent and clear message on risks and benefits of fish consumption, c. adequate chemical screening and reduction in use of synthetic chemicals, d. Toxicity studies to evaluate exposure to emerging chemicals and chemical mixtures.

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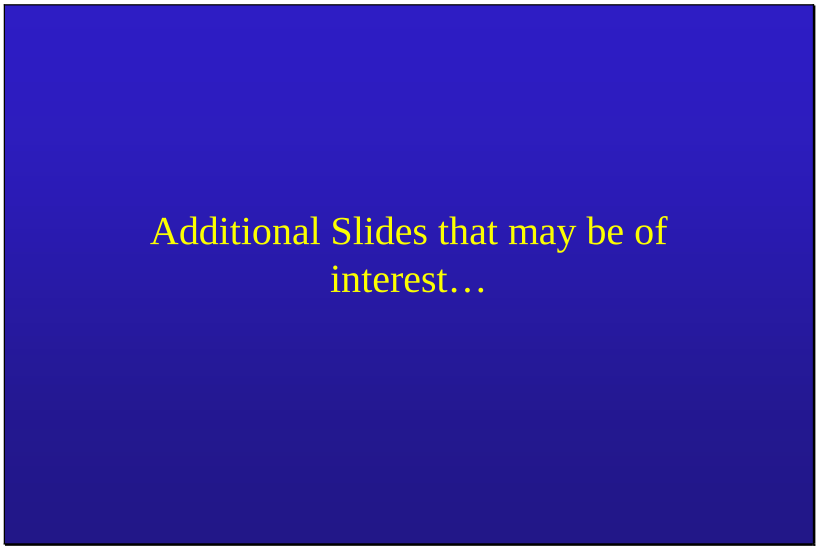
Slide 55



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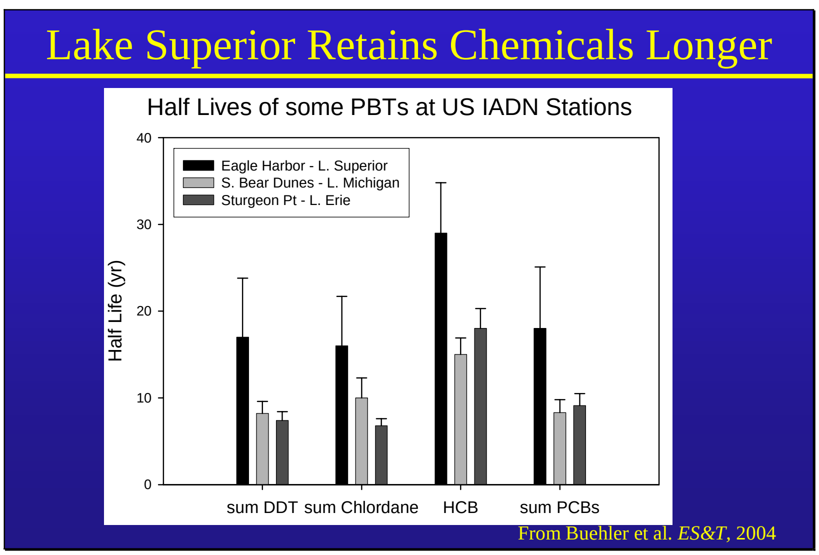

Shows the buffering capacity of each lake to retaining chemicals. Lake Superior has longest retention time for these chemicals. These data agree with others (cold temps, deep, long water retention time, little sedimentation, food web) and point out the greater susceptibility of L. Superior to contaminant inputs and subsequent “self cleansing”. While Superior may have had the lowest historical concentrations and still does of many contaminants, many are still above advisory levels and may take longer to drop below those levels than in other lakes.

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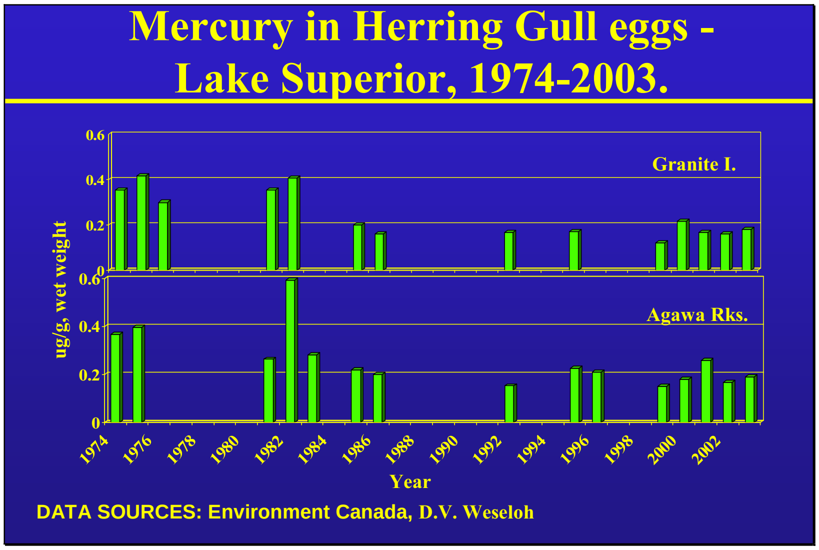

Mercury concentrations in herring gull eggs, show a potentially lower concentrations relative to the 1970s and early 80s however, very little change may have occurred in the past 17 years **(from 1992-2003 – no SIGNIFICANT declining (or increasing) trend in mercury concentrations)**.
Mercury as a slimicide, and chloralkylplants may account for early decline,

(text in bold was inserted by Tania Havelka)

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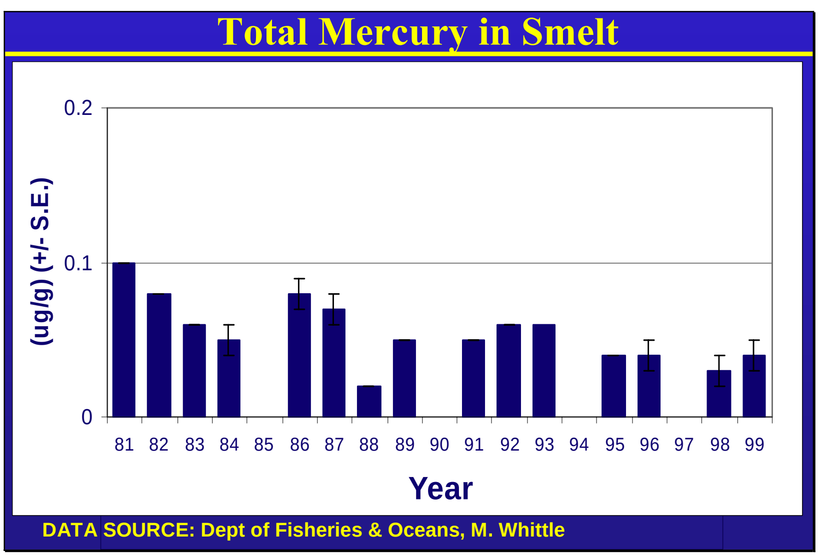

For Mercury in smelt we also seem to observe some amount of decrease in concentrations between 1981 and 1999, however, over the past decade or so the concentrations seem to be relatively stable.

Basic concentrations declined, restrictions placed on open systems, slimicides (p and P industry) and chloralkied plants to produce cl for bleaching.

Increase in importance atmospheric deposition sources (mike) similar over last 10 to 15 years, and oscillations in food web structure of Lake Superior.

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