Anthropogenic Chemicals: Potential and New PBTs in the Great Lakes

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Outline

- **Criteria used by the US and Canada to categorize chemicals as Persistent, Bioaccumulative and Toxic (PB&T)**
- **What are new chemicals of concern in the Great Lakes?**
- **Recent "new" chemical measurements in the Great Lakes**
- **Conclusions and recommendations**

The objective of this presentation is to introduce you to recent measurements of new PB&T chemicals in the Great Lakes.

To do this I will first define some of the criteria that are used to distinguish such chemicals from the large number in commerce. Those of you familiar with the properties of PCBs and DDT, which we now describe as legacy contaminants, will be familiar with some of these criteria.

I'll then provide a list of substances which have properties and measurements suggesting they are or could be problems, in some cases of similar scope to PCBs

Criteria for identifying PB&T chemicals

Organization	Long range transport			Persistence t½ (d)			Bioaccumulation		Toxicity
	Remote areas	VP[1] (Pa)	AO t½ (d)[2]	water	Soil	Sedi-ment	BAF/BCF[3]	Log Kow	
Canada (TSMP)	Yes			>180	>180	>360	5000	5	CEPA defined
US EPA TSCA PBTs				>180			5000		Toxicity data
US EPA TSCA release controls				>60			1000		Toxicity data
UNEP (POPs)	Yes	<1000	2	>60	>180	>180	5000	5	Risk profile

[1]Vapor pressure (Pascals)
[2]Half-life in the atmosphere due to reaction with hydroxy radicals (days)
[3] Bioaccumulation factor and bioconcentration factor. Amount in biota divided by concentration in water

While all synthetic chemicals are to some extent persistent and/or bioaccumulative, and indeed many wouldn't be effective for their various uses if they broke down too rapidly or could not enter biological cells, most of the substances that I am going to discuss today exceed various values that have been established to distinguish them from other substances. These values used in Canada, the USA and globally are listed in this slide. In particular, note the atmospheric half-life criterion of 2 days and the BCF's in the thousands because I will refer back to these criteria when I discuss each chemical.

Most currently used pesticides, most pharmaceuticals and personal care products do not exceed these criteria.

Legacy chemicals in the Great Lakes such as PCBs, toxaphene and DDT are clearly classified as PB&T chemicals with these criteria. For the approximately 30,000 chemicals in commerce there are limited data with which to assess these characteristics. This makes the discovery of new chemical contaminants very challenging. Categorization of existing chemicals by the USEPA and Environment Canada show that there are hundreds of substances meeting at least P and B criteria although they may not be currently manufactured.

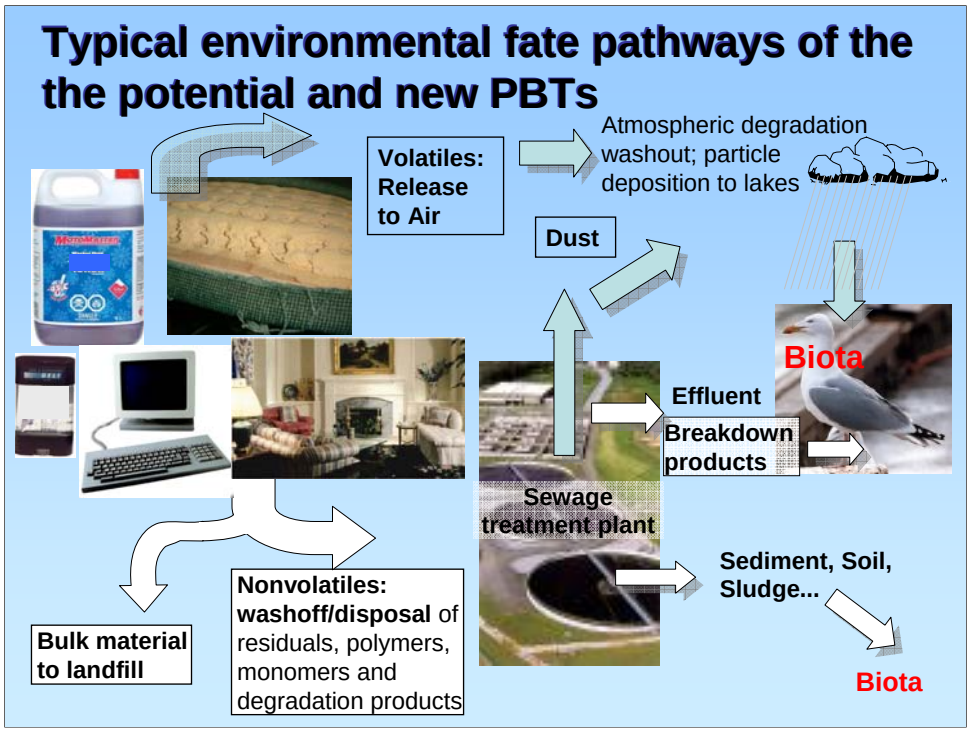
Recent measurements of new (potentially) PBT chemicals in the Great Lakes

Brominated flame retardants and related compounds	PBDEs (penta, octa, deca) Hexabromocyclododecane Brominated benzenes Brominated carbazoles Bis(tribromo-phenoxy)ethane Decabromodiphenyl ethane	Air, sediments, fish, water
Chlorinated flame retardants	Dechlorane Plus Chlorinated paraffins	Sediments, fish, water
Silicone related lubricants	Cyclic siloxanes D4, D5, D6	Air, STP effluents
Perfluorinated alkyl acids and precursors	PFOA, PFOS, fluorotelomer alcohols	Air, Precipitation, fish, sediments
Synthetic musks	HHCB (Galaxolide), AHTN (Tonalide)	Air, sediments

Much as the work on new chemicals has been conducted by looking at substances with similar chemical structure to known PB&T e.g. polybrominated diphenyl ether flame retardants have similar structure as PCBs, chlorinated flame retardants have similar chlorine content and physical properties to some PCBs.

Two groups on this list, the silicone related compounds and the fluorinated chemicals do not resemble the legacy chemicals. However environmental measurements and laboratory data show that they are relatively P and B. There are also concerns regarding their toxicity. Thus I have included them here.

The synthetic musks are substances that exceed some, but not all of the criteria listed in the previous slide.



This slide illustrates the pathways of potential and new PB&Ts. Most are used in consumer products. Most are semi-volatile and are released to the atmosphere, including indoor air. The bulk of the releases occur thru washoff (e.g. fluorinated stain repellents) or normal use (e.g. musks, siloxanes) and thru landfilling at the end of the product life cycle. In some cases e.g. fluorinated compounds, it is the transformation products that are particularly a concern. What distinguishes P and B compounds from other consumer and industrial products is that they do not degrade efficiently or at all, in STPs. Thus they may be directly released in treated effluent or via application of sewage sludges.

Brominated flame retardants (BFRs)

Polymer	BFR content (%)	Additive BFR	Reactive BFR	Production (1000 t/yr)
Polystyrene foam	0.8 – 4	HBCDD		600
High-impact polystyrene	11 – 15	Deca-BDE	Br Polystyrene	350
Polyamides	13 – 16	Deca-BDE	Br Polystyrene	200
Polyolefins	5– 8	Deca-BDE	Propylene polystyrene	200
Styrene copolymers	12 – 15	~~Octa-BDE~~	Br Polystyrene	50
Polyurethanes	10 – 18	~~penta-BDE~~	Br Polyols	150
Epoxy resin	19 – 33		TBBPA	300
Polyterephthalate	8 – 11	Br Polystyrene	TB	
Unsaturated polyesters	13 – 28		TB	
Polycarbonate	4 – 6	Br Polystyrene	TB	
Polyurethanes	?	Penta-BDE replacement		

Table from Alaee et al. Environ Intern'l 2003

PB&T ranking of PBDEs

AO $t_{1/2}$	2-19 days
BCF	6200-32000
Toxicity	PBDEs – thyroid effects

This slide describes the various substances that are all called brominated flame retardants.

2nd click to cross of penta and octa BDE

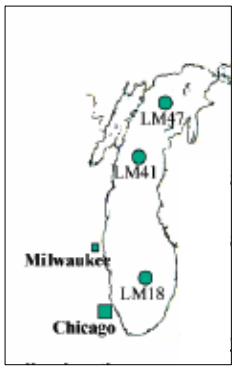
Some are now no longer produced e.g. Penta and octa BDE but continue to be used in consumer products. Some are "reactive" meaning that they are less likely to escape from the end use product and therefore of less concern.

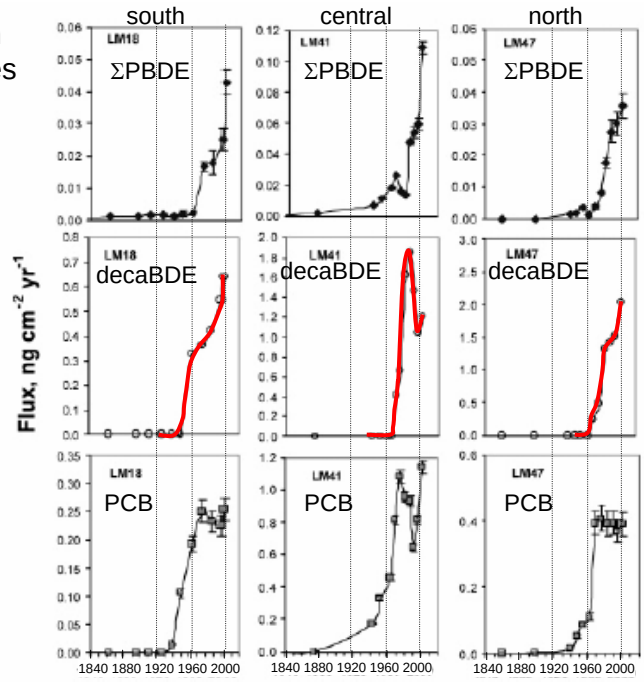
3rd click to show PB&T characteristics

The characteristics of PBDEs exceed all of the PB&T criteria that were shown on one of the previous slides. For example predicted Bioconcentration factors for fish exceed the Bioaccumulation threshold of 5000.

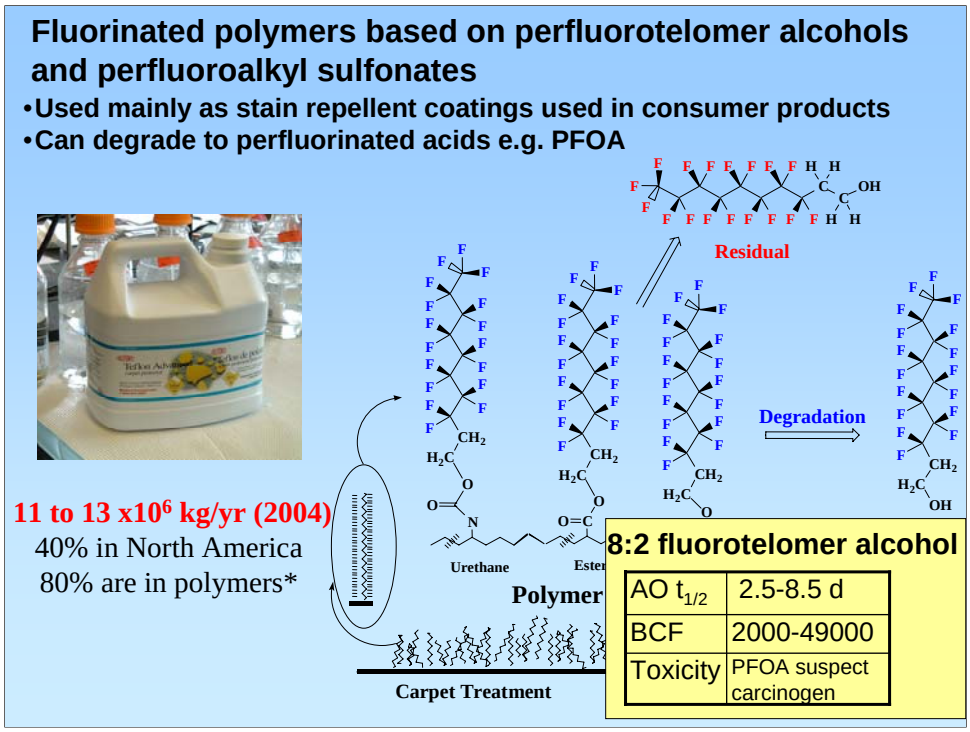
PBDEs and PCBs in dated sediment cores from Lake Michigan
(Song et al. ES&T 2005)

Current fluxes of deca BDE to the sediment are higher than the PCBs ever were





This slide illustrates recent results from Dr An Li's group at University of Illinois Chicago on PBDEs in Great Lakes sediments. I have drawn a red line to indicate the results for decabromodiphenyl ether. Note that concentrations started to go up in the 1960s and continue to increase. The inventory in sediments i.e. total amount of DecaBDE now equals or exceeds PCBs, in Lake Michigan.



The fluorinated polymers, widely used in stain repellent coatings, are thought to be one of the major sources of the next group of PB&T chemicals recently detected in the Great lakes. The structure of the polymers are shown here. These polymers have been shown to off-gas volatile components that eventually degrade in the atmosphere to acids which are persistent and bioaccumulative.

2nd click to show residual and degradation products

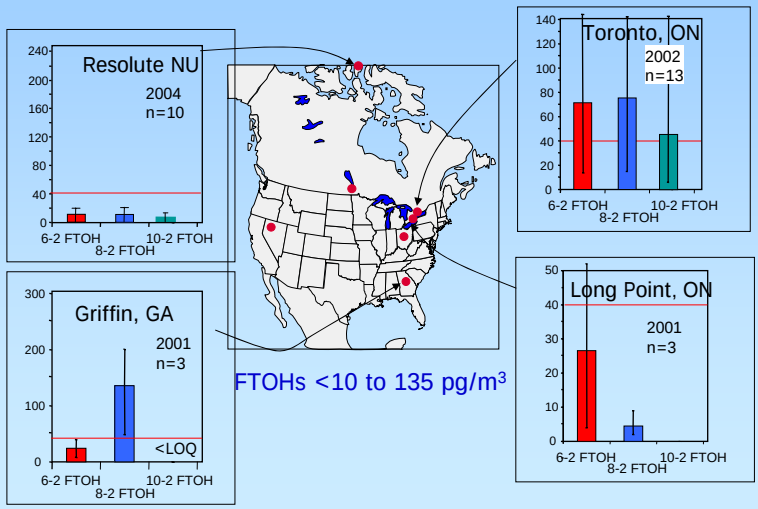
The best known degradation product is PFOA which has been identified by the EPA as a toxic substance which causes tumours in rats and immunotoxic effects in mice. However the extent to which these polymers are degraded is still unknown and is a matter of great interest given the large amounts in consumer goods, sewage sludges etc.

3rd click to show PB&T characteristics

The alcohol shown here is a potential PB&T chemical on the basis of being persistent in the atmosphere and giving rise to persistent and toxic degradation products.

Fluorotelomer alcohols (FTOHs) associated with fluoropolymer production are found in air throughout North America

The concentrations imply emissions of 100-1000 tonnes/yr of FTOHs
Urban areas are important sources



(Stock et al. ES&T 2004; Stock et al. ES&T 2007)

This slide shows the concentrations of the alcohols associated with fluoropolymer production in air including 2 locations in the Great lakes region. Vertical lines show the range of concentrations. Urban areas are likely sources as are special sites such as the region near Griffon GA where carpet manufacturing for all of North America is concentrated. These results represent a “snap shot” of concentrations in air in a one month period during 2001 in the case of Long Point and Griffin GA. There are so far no published results for continuous measurements within the Great lakes but studies are underway. Concentrations of the perfluoroalcohols in air are typically higher than most legacy PB&T chemicals such as PCBs.

References:

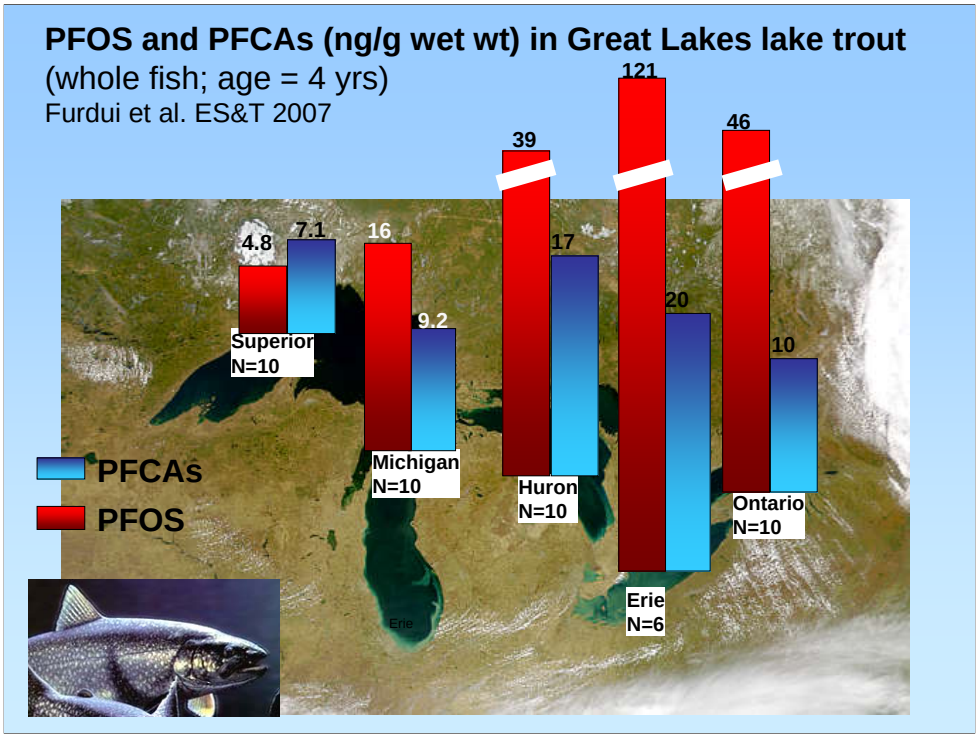
Martin, JW., D.C.G. Muir, W.C. Kwan, C.A. Moody, K.R. Solomon, and S.A. Mabury. 2002. Collection of Airborne

Fluorinated Organics and Analysis by Gas Chromatography-Chemical Ionization-Mass Spectrometry. *Anal. Chem. .* **74:**584-590**.**

Stock, NL, FK Lau, DA Ellis, JW Martin, DCG Muir, and SA Mabury. 2004. Polyfluorinated Alcohols and Amides in the

North American Troposphere. *Envion. Sci. Technol.* **38**:991-996.

Resolute: Stock et al. Mean concentrations (blank corrected) from July-Aug 2004 – N=10; 4 day sampling intervals



The perfluoro acids also are found in all aquatic organisms in the Great lakes at low part per billion concentrations. This slide shows the sum of PFOA, PFN and related perfluorocarboxylic acids (or PFCAs) in Lake trout of the same age class from all the lakes. PFOS shows the largest differences among lakes with much higher concentrations in Lake Erie and Ontario than in Lake Superior. The concentrations are shown at the top of each bar. For PFOS, concentrations in lakes Erie, Huron and Ontairo and much higher than other locations so bars are not to scale. Lake Michigan lake trout are from northern Lake Michigan and may not be representative of the entire lake. These concentrations represent bioaccumulation factors from water to fish that are comparable to those of some of the legacy pollutants. The main pathway to top predators is likely to be from food and not directly from water i.e. uptake from forage fish in the case of lake trout.

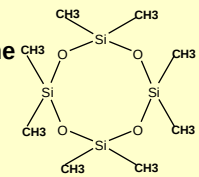
Volatile cyclic methyl siloxanes

Cyclic siloxanes (D4, D5)

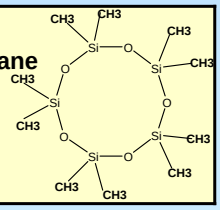
AO $t_{1/2}$	10 days
BCF	5300-12400
Toxicity	D5 – suspect carcinogen

- **Carrier in antiperspirants/deodorant**
- **Shampoo and conditioners**
- **VOC exempt cleaning solvents**
- **Estimated 1993 U.S. releases – 20 kT/yr not including industrial use for PDMS production**
- **No published global estimates**

D4 octamethyl-cyclotetrasiloxane



D5 decamethyl-cyclopentasiloxane

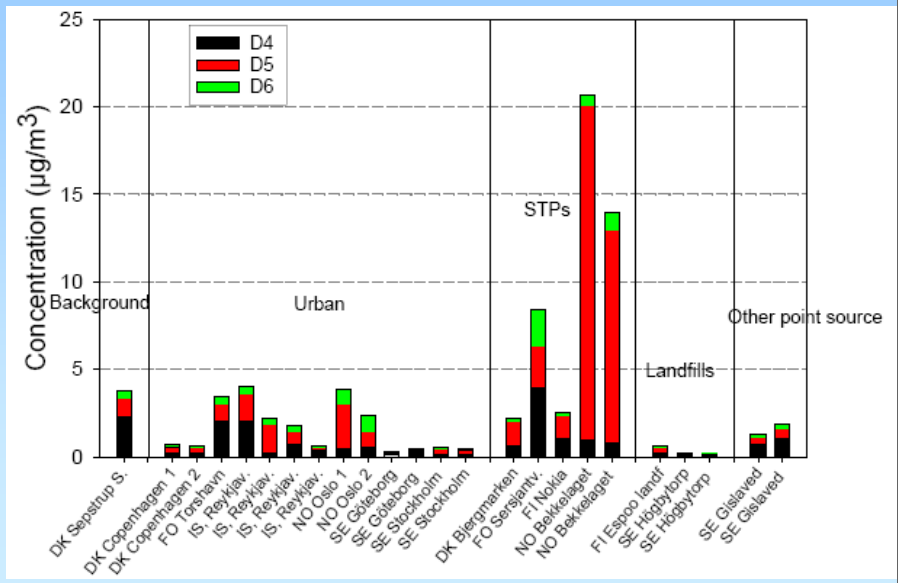


This group of chemicals are new comers in terms of contaminant measurements. The first measurements in air were recently reported at the 2006 conference of the Assoc of Great Lakes Research. They are widely used in personal care products.

2nd click to get criteria up

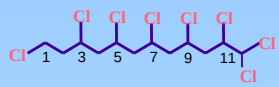
These chemicals meet several of the criteria for PB&T chemicals. For example they are predicted to have long atmospheric half-lives and can thus under go long range transport.

Concentration of cyclic siloxanes in air in urban and background sites in Scandinavian countries (Kaj et al 2005)



The air measurements in the Great Lakes region that I mentioned are preliminary and not available for presentation. However a major study in Scandinavia has shown the cyclic siloxanes are present in urban and rural areas at low microgram per cubic meter concentrations. These are relatively high concentrations in air compared to other PB&T chemicals and suggest the urgent need for further investigation. High concentrations are also seen in air (biogas) emitted from STPs. Analysis of the volatile cyclic siloxanes is very challenging due to the wide use of these compounds which results in high background concentrations from lab air and solvents.

Short and Medium Chain Chlorinated paraffins



Characteristics

- carbon chain lengths range from 10 to 17
- chlorine content from ~ 40% to 70% (by weight)
- huge number of congeners (~100,000) and homologs (~48)

Sources and regulatory status

- **Short chain** – flame retardant additives in extreme-pressure lubricating oils
  - N.A. production ~ 7 kilotonnes per year (**declining**)
- **Medium chain** – PVC plasticizer-flame retardants additives
  - N.A. production ~ 18 kilotonnes per yea
    growing)
- phase out of short chains in Germany, and
  proposed in Canada

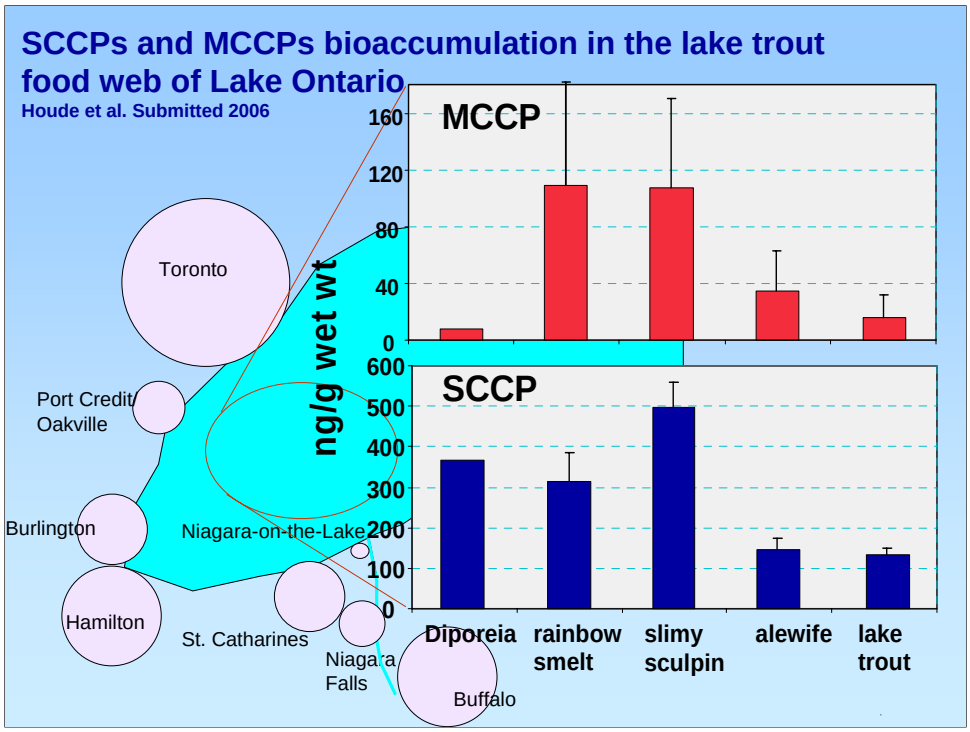
C10-C13 CPs

AO $t_{1/2}$	1-10 days
BCF	2000-78000
Toxicity	SCCP – suspect carcinogen

The chlorinated paraffins are widely used flame retardants. There have been concerns about the PB&T characteristics of CPs for many years and the EPA has listed them on the Toxics Release Inventory (TRI). Environment Canada has circulated a draft risk assessment recommending the phase out of short and medium chain CPs under the Toxic Substances Management policy but has not yet moved to ban them. The short chain CPs meet the criteria for PB&T chemicals. They have been phased out in Germany.

2nd click to show PBT criteria

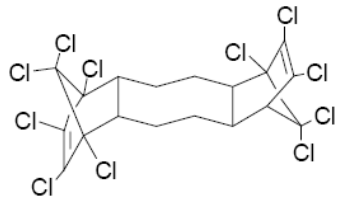
The table on the lower right lists some of their predicted and measured PB&T characteristics



The accumulation of short and medium chain CPs in the Lake Ontario food web is shown in this slide. Relatively high concentrations of both groups of CPs were detected in forage fishes such as rainbow smelt and slimy sculpin, Lower concentrations were found in lake trout. Laboratory studies with rainbow trout suggest that short and medium chain CPs can be metabolized slowly and this may explain the lower amounts in lake trout in Lake Ontario compared to their diet. Nevertheless the concentrations in lake trout represent extremely high bioaccumulation factors for short chain and medium chain CPs i.e. highly bioaccumulative compared to the perfluorinated acids discussed earlier.

Dechlorane Plus (Hoh et al ES&T 2006)

- Chlorinated flame retardant (for plastics used in cable sheathing)
- High production volume chemical (US/Canada)
- Ranked as P but not B in Canadian DSL and TSCA screening for PB&T chemicals

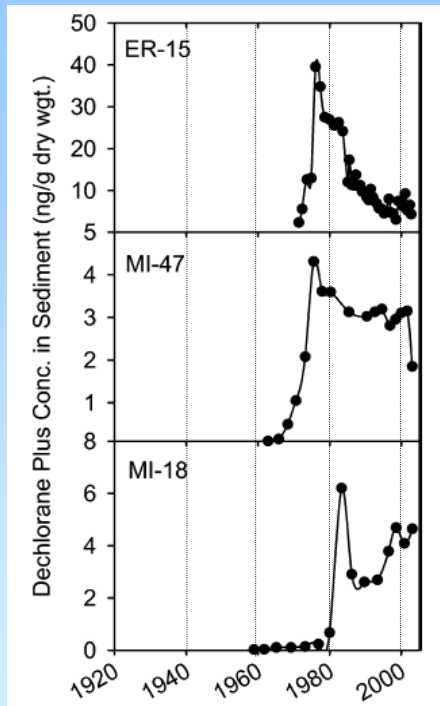


Dechlorane Plus	
AO $t_{1/2}$	0.5 days
Persistence (soils)	>182 days
BCF	30 (predicted)
BAF	6000 (food web model)
Toxicity	Uncertain (Environ Canada 2006)

Dechlorane Plus a highly chlorinated compound used as a flame retardant was discovered in 2005 by the group of Ron Hites at Indiana University. This chemical has similar uses as the medium chain chlorinated paraffins mentioned previously. Screening of chemicals in commerce by the USEPA and Environment Canada has concluded that it is not a high priority chemical because it is not expected to bioaccumulate due to its large molecular size. However it is highly persistent. No toxicity data was available and thus toxicity is assessed as “uncertain” in the recent Environment Canada assessment

Dechlorane Plus in dated sediment cores from Lake Erie (ER), northern Lake Michigan (MI-47) and southern Lake Michigan (M-18)

Hoh et al ES&T 2006



This slide shows that Dechlorane plus is present in Great lakes sediments at concentrations similar to other chlorinated flame retardants such as chlorinated paraffins, but lower than decabromodiphenyl ether or PCBs. The evidence from sediment cores suggests that larger amounts entered Lake Michigan in the late 1970's and early 1980s than at present.

These measurements combined with the predicted properties shown on the previous slide suggest that Dechlorane Plus is not a priority for future measurement. It also illustrates that using environmental measurementsto to confirm predictions is a fruitful approach to setting priorities for new PB&T chemicals in the Great Lakes

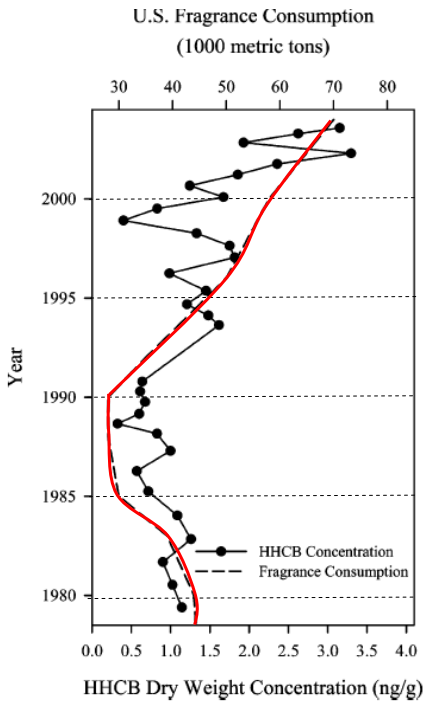
Nitro- and polycyclic musks

- Fragrance ingredients in soaps, laundry detergents and cosmetics
- Some musk compounds are regarded as persistent, bioaccumulative and toxic in Germany and Japan
- Relatively few measurements in North America and no regulatory action
- High production volume (>454 t or 1 million lbs) per year in USA

Fragrance related compounds have some characteristics which suggest they could be persistent and bioaccumulative chemicals. These are high production volume chemicals widely used in soaps, laundry detergents and cosmetics. Recently detailed measurements of synthetic musks have been made in the Great Lakes by Dr. Keri Hornbuckle and her group at University of Iowa.

Trend in deposition of synthetic musk HHCB in a sediment core from Lake Erie
(Peck et al. ES&T 2006)

- HHCB (or **galaxolide)** is a high production volume chemical with wide use in perfumes, laundry detergents, fabric softeners
- HHCB previously detected in Lake Michigan at 1.1 ng/m^3 in air and 4.7 ng/L in water.
  Peck & Hornbuckle ES&T 2004



Results for the major synthetic musk, HHCB (or galaxolide) from a sediment core taken from the deep zone in eastern Lake Erie show that inputs are increasing in line with increased fragrance consumption (red line) in the USA. This suggests that Great Lakes sediments will be a significant reservoir for these chemicals for years to come. Concentrations are, however, much lower than for some other “new” contaminants such as decabromodiphenyl ether, Dechlorane Plus and chlorinated paraffins.

Conclusions

- New PB&T substances have been measured recently in the Great Lakes. The highlights:
  - Decabromodiphenyl ether deposition rates and inventory in sediments now exceeds that of PCBs
  - Perfluorinated chemicals such as PFOS and PFCAs are prominent contaminants in water and fishes
  - Synthetic musks are prominent in lakes waters, air and sediments
  - Siloxane measurements in the Great Lakes will soon be available

Conclusions

- Measurements have generally confirmed that predicted PBTs will be found in the environment
- Based on current screening results of the TSCA inventory and the DSL there are hundreds of chemicals with similar properties that could be surveyed
- To implement future more systematic programs for new PBTs in the Great Lakes will require investment in instrumentation and people