Contaminants of Emerging Concern in the Great Lakes Activities Overview

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GLBTS Substances Meeting

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Outline

- IJC Literature Review Findings
- TSCA and DSL Screening Studies
- Great Lakes Monitoring and Surveillance Programs

Analysis of Chemicals of Emerging Concern in the Great Lakes Basin and Watershed (IJC CEC Near Shore Initiative)

Goals of the Study

- To assess the current status of chemicals of emerging concern in the basin with a focus on water quality
  - Literature search
  - Database of reported concentrations
  - Statistical analysis to define current environmental exposures
- To develop a preliminary assessment of their potential ecological significance, the concentrations were compared with currently available regulatory standards, guidelines, or criteria

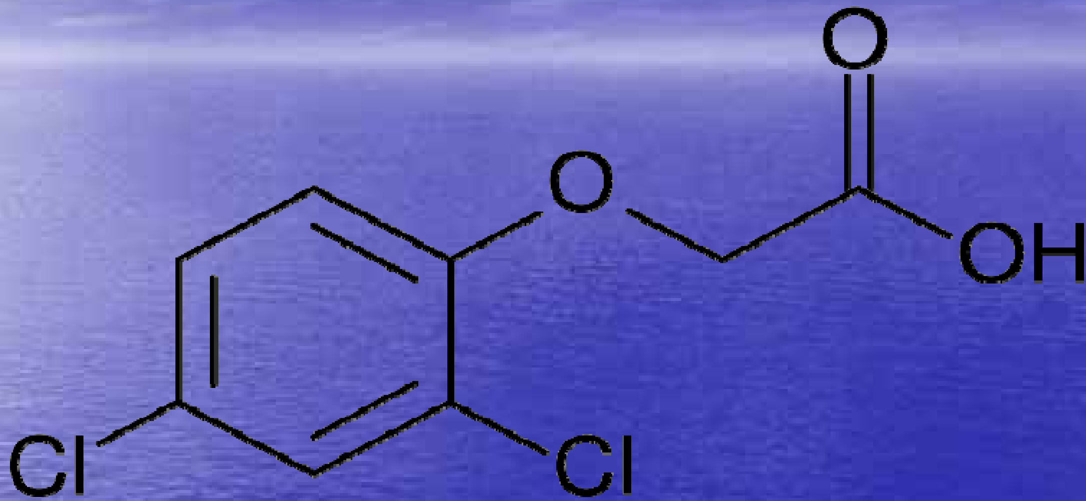
Chemical Classes

- Current Use Pesticides
- Synthetic Musks
- Fluorinated Surfactants
- Brominated Diphenyl Ethers
- Other Flame Retardants
- Alkylphenol Ethoxylates
- Chlorinated Paraffins
- Pharmaceuticals, Veterinary Drugs and Personal Care Products

Available US, Canadian and International Criteria

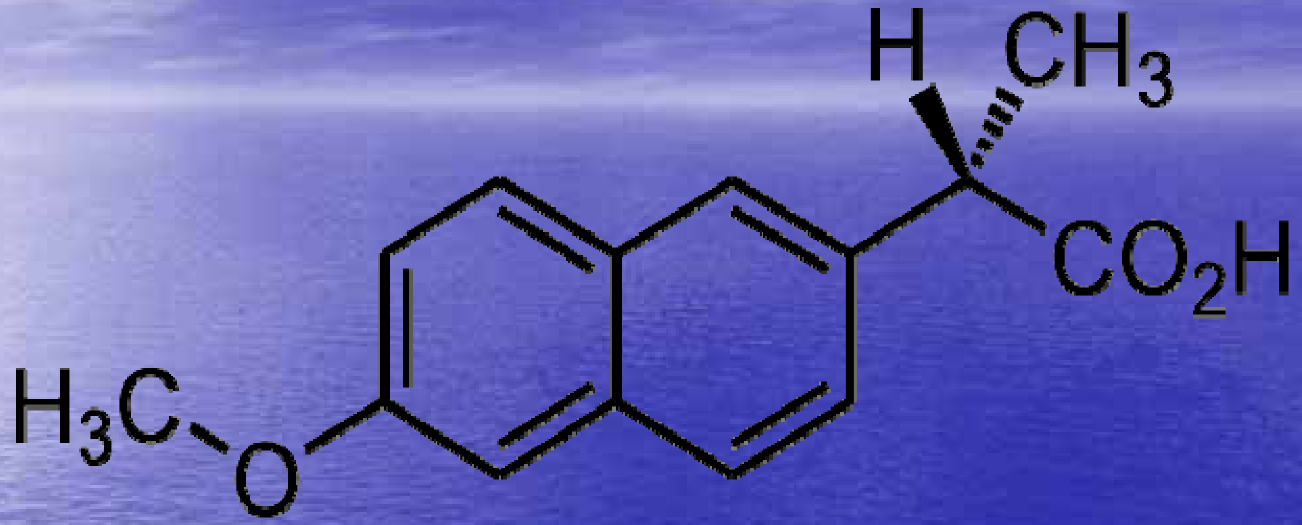
Various Regulatory Standards, Guidelines and Criteria.doc

Current Use Pesticides (88)



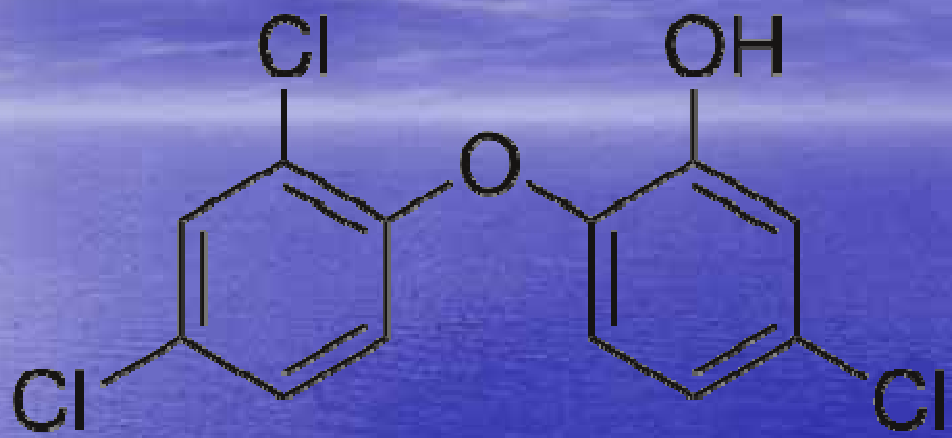
- 2,4-D, metolachlor, and metribuzin (maximums) atrazine, azinophos-methyl, chlorpyrifos, diazinon, and parathion exceeded the regulatory standards in 10 to 20% of the samples

Pharmaceuticals (60)



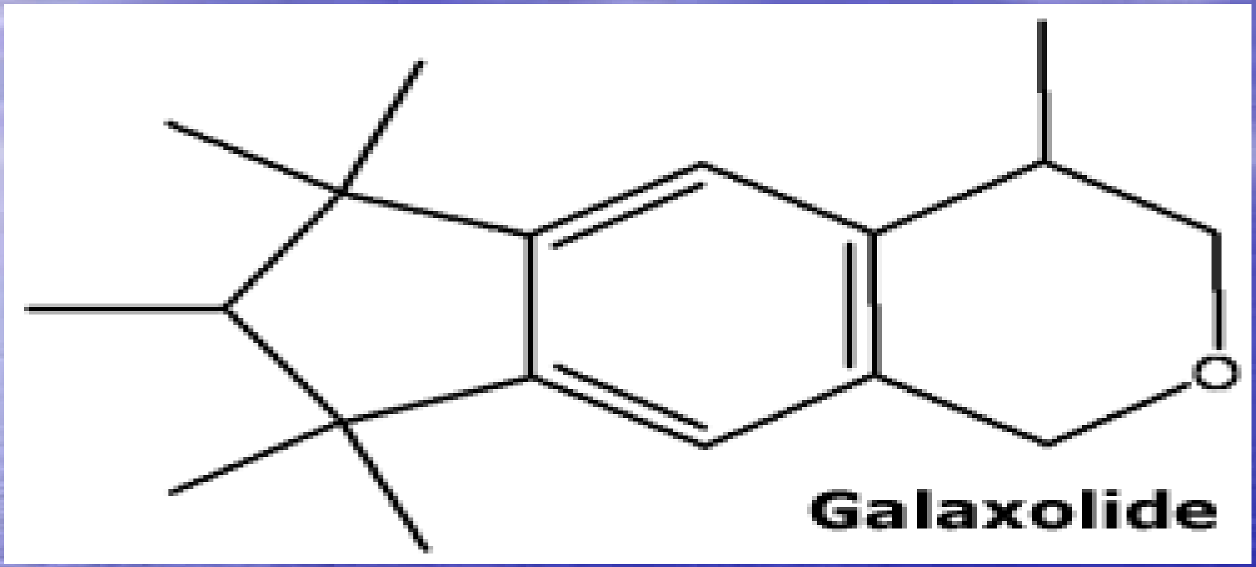
At present, there are no standards, guidelines or criteria with which to compare the concentrations.

Organic Wastewater Contaminants, Personal Care Products, Steroids and Hormones (66)



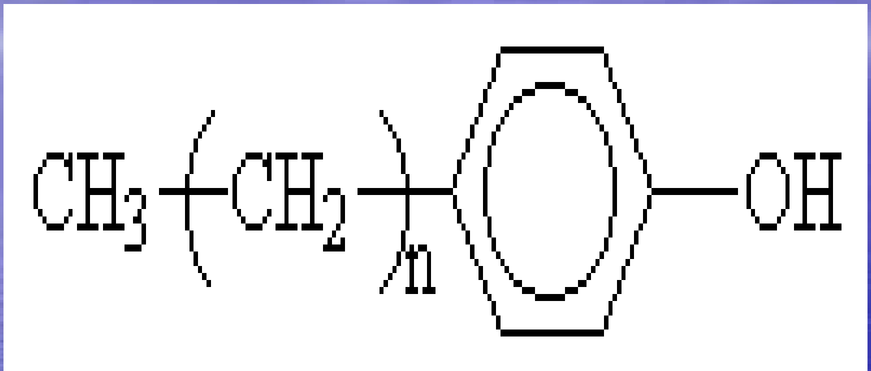
- Bis(2-ethylhexyl) phthalate (DEHP)values exceeds the US EPA MCL for drinking water the EC Interim Water Quality Guideline and the EU predicted no effect value.
- Bisphenol-a the maximum concentration exceeds the Canadian PNEC for water, but is below the PNEC for sediment organisms.

Synthetic Musks (9)



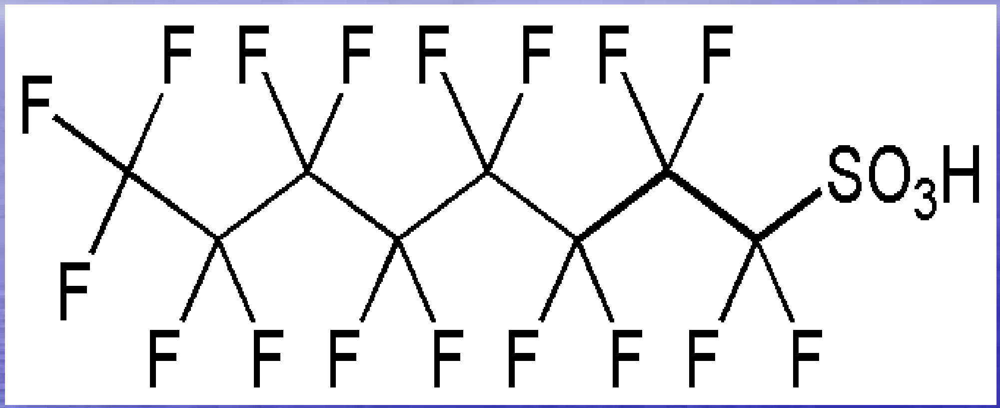
Maximum concentrations of for musk xylene, musk ketone, in environmental media from the Great Lakes indicates that are values are below the PNEC.

AlkylphenolEthoxylates(24)



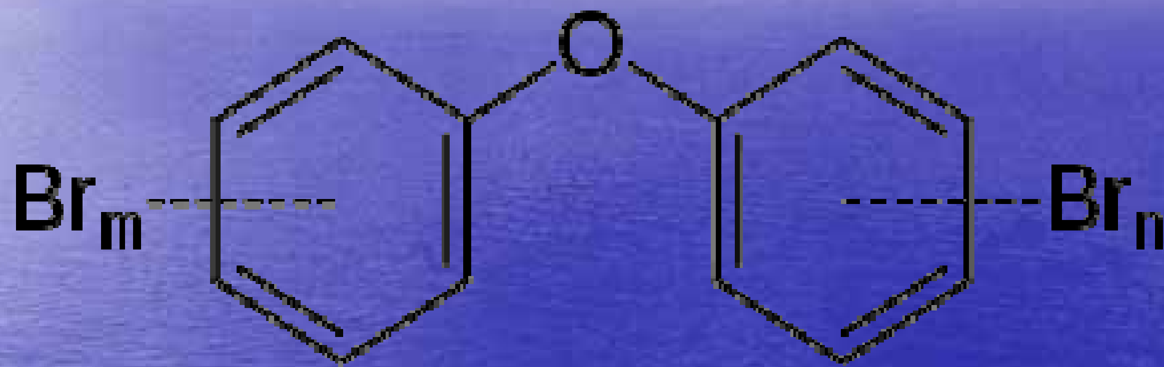
- None of the samples exceed the US EPA Water Quality Criterion for NP
- 22% of the samples exceed the NP equivalent Canadian Water Quality Guideline.
- Sediment concentrations exceeded the NP equivalent Canadian Sediment Guideline in 31% of the samples

Perfluorinated Surfactants(31)



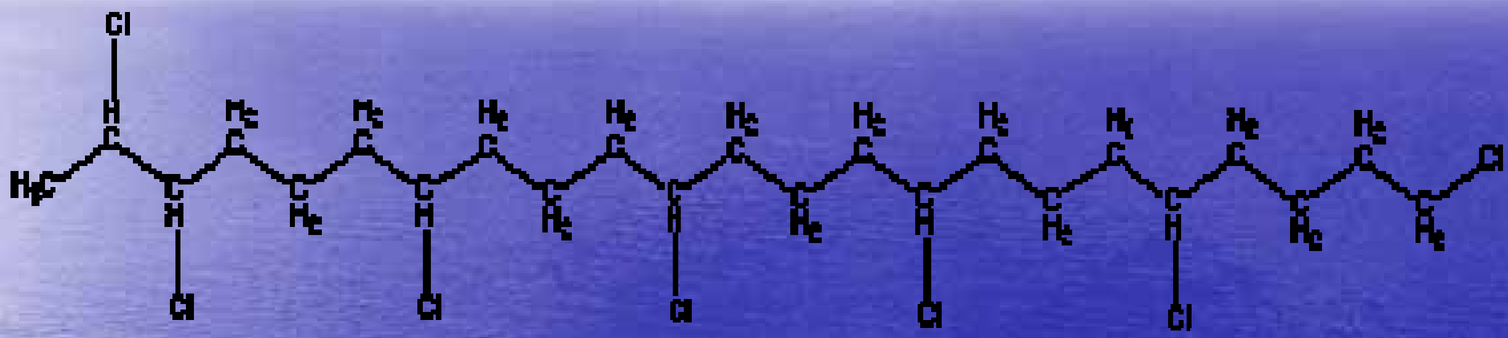
- Risks for secondary poisoning from the ingestion of food are indicated for PFOS and total PFS concentrations

PolybrominatedDiphenylEthers (28)



- Tetra and pentra-brominated congeners concentrations are above the Canadian ENEV criteria value for secondary consumers (0.0084 mg/kg food)

Chlorinated Parrafin (10)



- All exposures are below the no effect values (ENEV/PNEC)

Findings

- There has been an increasing shift in focus from industrial point sources to dispersed, non-point releases of chemicals and substances, such as those in consumer products and pharmaceuticals that may require new analyses and approaches, including risk management approaches.
  - Substances contained in imported consumer products pose special challenges.

Summary - CECs

- Wide variety of chemicals have been detected in various media within the Great Lakes basin
- Our ability to detect chemicals in the environment exceeds our ability to understand the significance of the findings
- Availability of data varies considerably:
  - Some have relatively extensive datasets covering broad regions of the basin
  - Others studies focused on more localized areas, regions
  - Small amount of data available for many

Summary – CECs (cont'd)

- For many, concentrations are < 1 ug/L;
  - Highest levels in the vicinity of sources (e.g., WWTP),
  - Decline with increasing distance from sources
  - Low to ND in open waters
- Results of comparison of environmental exposures versus regulatory criteria yields mixed results:
  - For some - levels are below ENEVs, PNECs, WQS
  - With others current exposures may indicate a potential risk
  - Criteria have not been established for many
- Regulatory and/or voluntary actions to reduce or eliminate emissions are underway for a number of substances included in our analysis

Screening Chemicals in Commerce to Identify Possible Persistent and Bioaccumulative Chemicals of Concern in the Great Lakes

Outline

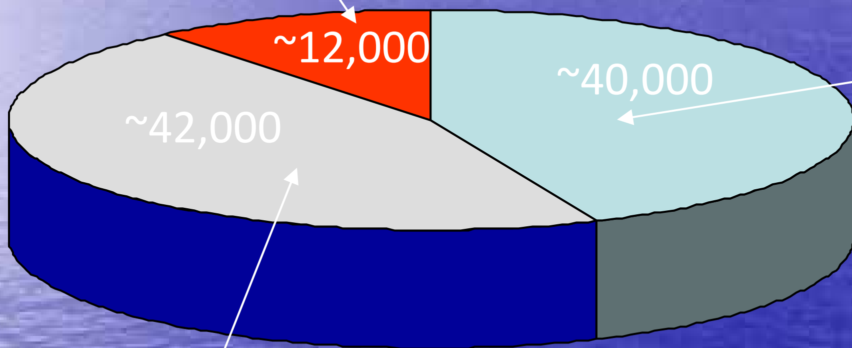
- Study Goals
- Description of the database of 22,263 substances
- Identification of meeting various persistent and bioaccumulative (P&B) criteria
- Comparison with other screening studies
- Success stories
- Examples of priority chemicals
- Limitations of the screening approach
  - Pharmas, organometallics
- State of knowledge of environmentally relevant properties for hazard and risk assessment
- Availability of database

Goals of the Study

- Develop a North American rather than Canadian or US list of potentially P&B chemicals
  - Greater relevance to the Great Lakes (GL) and trans-boundary long range transport than CMP or CHAMP priorities
- Using Quantitative Structure-Property Relationships (QSPRs), and scientific judgment, identify organic chemicals in commerce that may be P&B and have not been previously measured in environmental media
- Assess whether selected chemicals can be analyzed by existing methods in use for POPs and new P&B chemicals in the Great Lakes and the Arctic
- Analyze use and potential environmental release of new emerging contaminants
- Chemicals become concerns because of widespread detection, biomagnification, increasing trends, and high persistence and not because much is known about toxicity

Overview of the Major Chemicals Registered for Commercial Use in North America Starting in the 1980s (>100 kg per yr in Canada; >4540 kg/yr US)

Pharmaceuticals & Cosmetics (Food, Drug & Cosmetic Act); **Pesticides** (FIFRA)



Polymers
- High molecular weight >1000 Daltons
- Residuals and byproducts often not well characterized

Industrial Chemicals (TSCA/CEPA)
- Individual organic chemicals, organometallics, UVCBs under TSCA and CEPA
- ~21,000 substances since 1976 or 700 new substances per year under TSCA
- Molecular weight generally <1000 and >50 Daltons (99% of organics)

Not included:
- Minor use products (<4.5 t/yr)
- Degradation products
- Byproducts/impurities
- Isomers/congeners

Development of a Combined Canadian and US Database of Chemicals in Commerce (Howard and Meylan 2007; 2008)

Source	No. substances	Reporting threshold	Reporting date
US EPA High Production Volume (HPV) program and EHPV program*	4049	1,000,000 lbs/yr (454 t/yr)	Post-1990
US EPA TSCA Inventory Update Rule (IUR) web site**	13,958 organics	>10,000 lbs/yr (4540 kg/yr)	IUR reporting years; 1986 to 2002
Canadian DSL categorization***	11,317 organics	>100 kg	Mid-1980s
UVCBs**** (1400 on the DSL)	3059 organics	>100 kg	Mid-1980s
TSCA IUR update 2006	220	>25,000 lbs/yr	Reporting year 2006
Total (after duplicates removed)	**22,263**		

*Available from: US EPA - http://www.epa.gov/HPV/hpvchmlt.htm
** Available from: US EPA - http://www.epa.gov/oppt/iur
*** Available from: Environment Canada - http://www.ec.gc.ca/substances/
**** UVCB = Unknown, of Variable Composition, or of Biological Origin – organic chemicals

Persistence and Bioaccumulation Characteristics of the 22,263 Chemicals Estimated Using EPISuite™ Version 3.12

Characteristics*	No.	Percent	Notes
log K_{ow} >5	4239	19%	Indicates tendency to adsorb to sediments and to bioaccumulate
BCF >2000 BCF >5000 BCF >50,000	924 566 19	4.6% 2.8% 0.1%	Bioaccumulation from water exposure – does not include biomagnification
AO* half-life >2 days AO half-life >10 days	1973 840	10% 4%	AO half-life indicates stability to atmospheric oxidation and potential long range transport
log K_{aw} >-5 and log K_{aw} <-1	6515	32%	K_{aw} describes air-water partitioning. Compounds with log K_{aw} >-5 & <-1 are "hoppers"
log K_{ow} ~2-5 and high log K_{oa} ~6-12	2000	10%	Biomagnification in air-breathing organisms (Kelly et al. 2007)

*K_{ow} = octanol water partition coefficient
BCF = bioconcentration factor predicted with EPISuite™ software
AO = atmospheric oxidation half-life
K_{aw} = air-water partition coefficient

Comparison with Brown and Wania (*ES&T* 42:5202-5209, 2008)

- Used the 105,584 individual chemical database of the EPISuite™software
- Screened a list of HPV chemicals (TSCA, EINECS, OECD) and Current Use Pesticides (USA, WHO) for structural similarity to Arctic accumulating chemicals
- Identified 120 HPV chemicals as potential Arctic contaminants based on persistence, long range transport, and bioaccumulation potential

Overall good agreement

- 110 of these are in our 22,263 chemical DSL/IUR database while 10 are Current Use Pesticides which we did not survey
- Of their 110 industrial chemicals, 86 chemicals are in our 610 chemical list
- Most of the 24 in their list that are not in ours are not good potential P&B chemicals due to high reactivity (e.g., *alpha*-aminonitriles, isocyanates, diesters).

Further Prioritization Based on Lessons Learned from POPs in the Great Lakes and in the Arctic

1. High bioaccumulation/biomagnification potential – high K_{ow} can biomagnify
2. Persistence – sequestered in bottom sediments in the open lakes implying a low rate of biodegradation
3. Long range transport potential (i.e., found in mid-lake, in Lake Superior, and remote lakes such as Siskiwit Lake)
4. Quantity in use and potential for emissions (i.e., open use or as an additive vs. as a chemical intermediate)

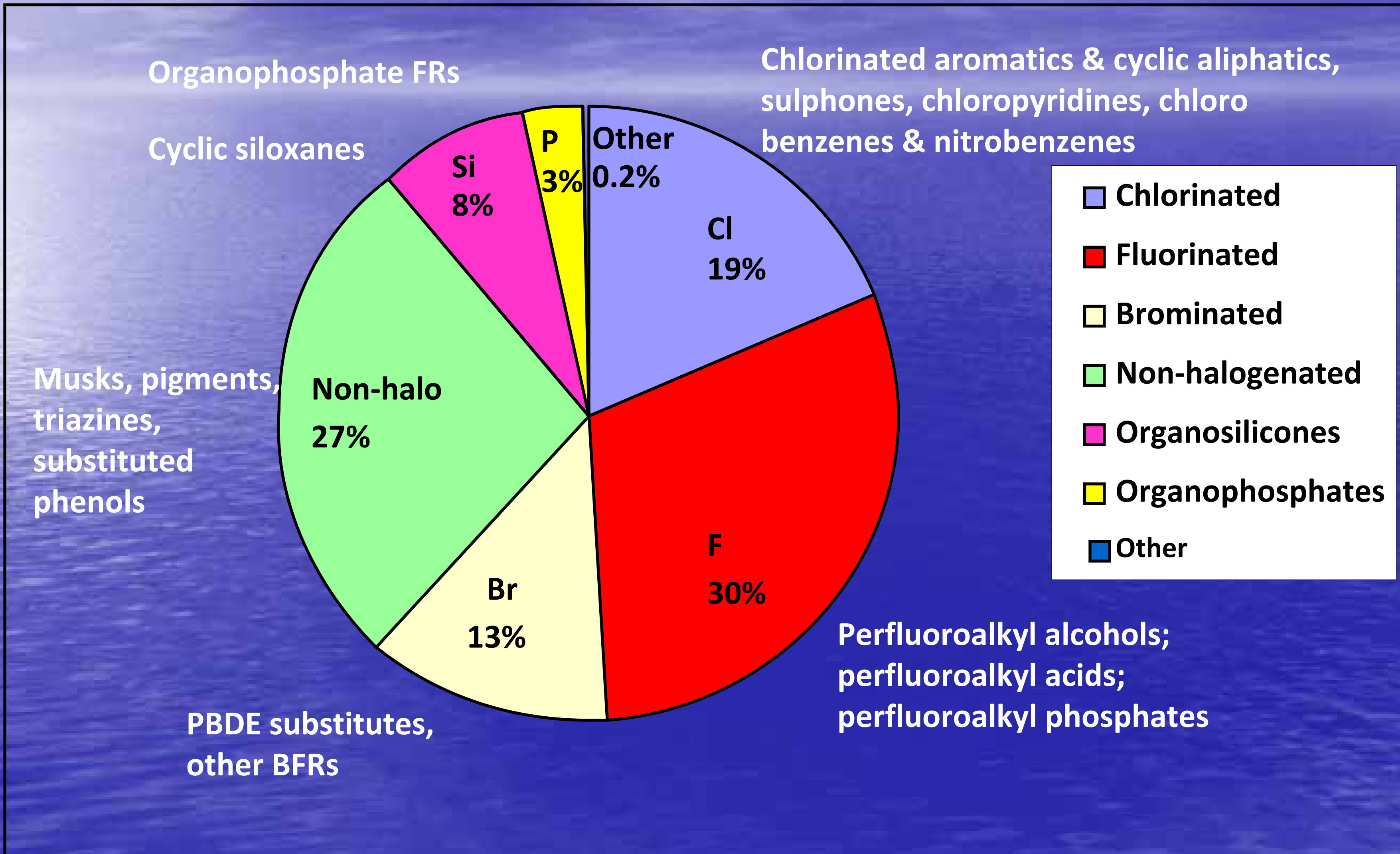
Selection Characteristics	No.	Notes
Predicted BCF: >1000 **Atmospheric Oxidation: >1 day, and** **Log K_{aw} >-5 and <-1**	105	Using EPISuite™. Mainly chemicals with LRT potential
By chemical class (Br, Cl, F, I, Si, cyclic HCs) and considering biodegradability	505	By expert judgment – includes chemicals and their degradation products with low LRT but potential for persisting in sediments and in the water column
Total	610	62% halogenated; 8% siloxanes
Neutral organics	473	Existing QSPRs are more accurate for these substances

Information on Measurement and Analyzability of the 610 Substances

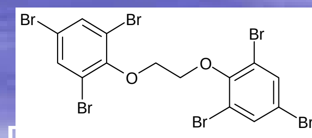
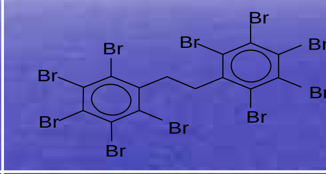
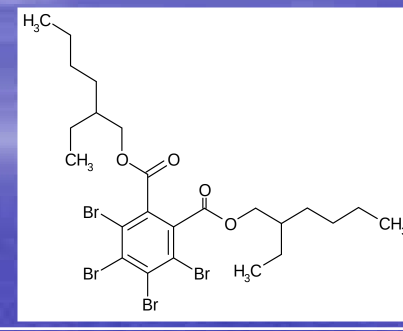
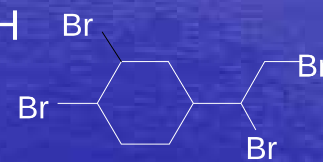
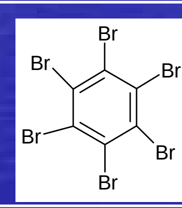
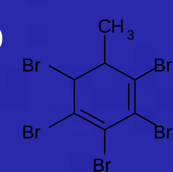
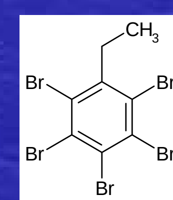
Analyzable	Well monitored in the GL region and Arctic (i.e., IADN, NCP)	Chemicals that may have been analyzed in any GL & Arctic studies	Analyzable using existing methods for neutral POPs or other neutrals such as pesticides	Analyzable by LC-MS/MS ESI mode (anionic) or positive CI mode	Analyzable degradation product
Yes	47	101	404	43	193
% Yes	7.7	16.5	66.2	7.0	31.6
No	563	509	167		
Maybe			39	24	4

Conclusion: Most could be analyzed with existing methods if standards were available

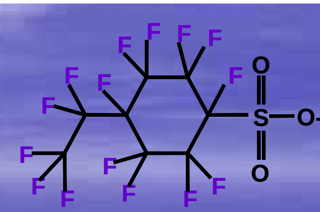
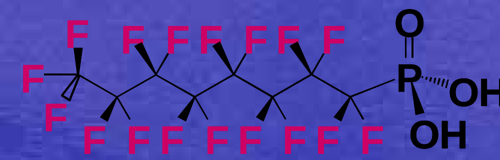
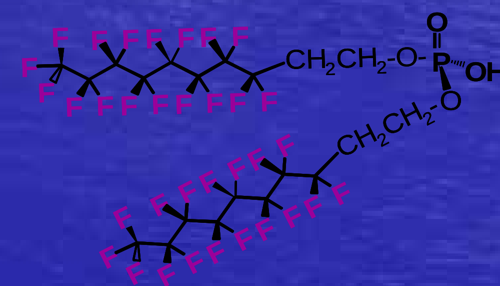
Classes of the 610 Priority Chemicals



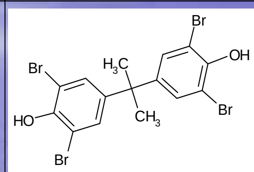
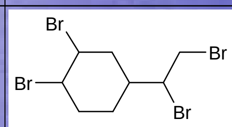
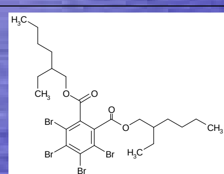
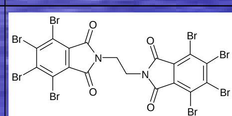
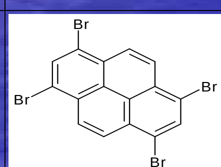
Successes

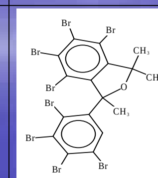
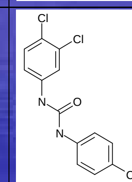
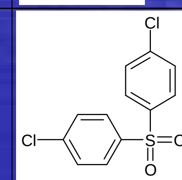
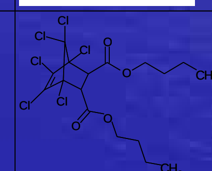
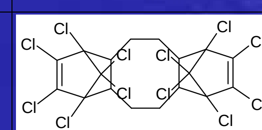
Stapleton et al. *ES&T* 2008 Quantified several PBDE replacements in house dust: BTBPE, DBDPE, 2-ethylhexyl 2,3,4,5-tetrabromobenzoate (TBB) and bis(2-ethylhexyl)-tetrabromophthalate (TBPH)	BTBPE  DBDPE  
Tomy et al. *ES&T* 2008 TBECH (1,2-dibromo-4-(1,2-dibromoethyl) Cyclohexane) in arctic beluga whales	TBECH 
Gauthier et al. *ES&T* 2009 BTBPE, DBDPE, TBECH, HBB, and others tentatively confirmed	HBB 
Gouteux et al. *ES&T* 2008 Pentabromotoluene (PBTo), pentabromo-ethyl benzene (PBEB), HBB in GL air	PBTo  PBEB 
Venier and Hites *ES&T* 2008 BTBPE and DBDPE in GL air (all US IADN sites)	

Successes

De Silva et al. *IAGLR* 2009 Perfluorocyclohexane sulfonate PF(R)CHS R = Me (CF_3) or E (CF_2CF_3)	**PFECHS** 
D'eon et al. 2009 Phosphonic acid surfactants Cx PFPA $F(CF_2)xP(O)(OH)_2$	**C8 PFPA** 
D'eon et al. 2007 Phosphoric acid surfactants x:2 diPAP $(F(CF_2)xCH_2CH_2O)_2P(O)OH$	**8:2 diPAP** 

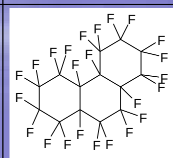
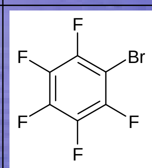
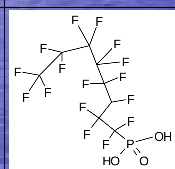
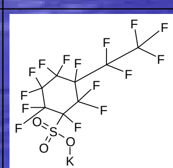
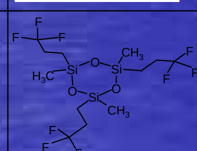
Examples of High Priority Chemicals with P&B Potential

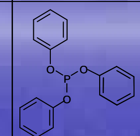
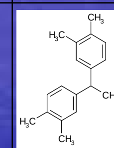
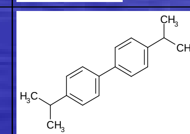
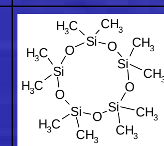
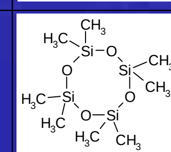
Common Name	**Class**	**Molstructure**	**BCF**	**Production Range (M lbs) (reporting year)**
Tetrabromo-bisphenol A	Br		4.13	500 (1998) 500 (2002) 500 (2006)
1,2-Dibromo-4-(1,2-di-bromoethyl) cyclohexane	Br		2153	0.5 (1998) 0.5 (2002) No data (2006)
Tetrabromo-phthalic acid di-2-ethylhexyl ester	Br		3	10 (1998) 10 (2002) 10 (2006)
Ethylene bis(tetra-bromophthal-imide)	Br		10	50 (1998) 10 (2002) 10 (2006)
Tetrabromo-pyrene	Br		2424	No data (1998) 1 (2002) 0.5 (2006)

Common Name	**Class**	**Molstructure**	**BCF**	**Production Range (M lbs) (reporting year)**
Octabromo-1,1,3-tri-methyl-3-pheny-lindane	Br		1	10 (1998) 0.5 (2002) No data (2006)
Triclocarban	Cl		1187	1 (1998) 10 (2002) 0.5 (2006)
Bis (4-chloro-phenyl) sulfone	Cl		199.5	50 (1998) 50 (2002) 50 (2006)
Dibutyl chlorendate	Cl		29340	0.5 (1998) 0.5 (2002) No data (2006)
Declorane Plus®	Cl		1	10 (1998) 10 (2002) 10 (2006)

Production range values refer to range of pounds: (0.5 = 10–500 K; 1 = 500 K–1 M; 10 = 1–10 M; 50 = 10–50 M; 100 = 50–100 M; 500 = 100–500 M; 1000 = 500–1000 M lbs for the reporting year)

Examples of High Priority Chemicals with P&B Potential *(continued)*

Common Name	Class	Molstructure	BCF	Production Range (M lbs) (reporting year)
Perfluoroper-hydrophenanthrene	F		19	0.5 (1998) No data (2002) No data (2006)
Bromopentafluoro-benzene	F		196	0.5 (1998) No data (2002) No data (2006)
Phosphonic acid, perfluoro-C_6-C_{12}-alkyl derivatives	F		19510	0.5 (1998) 0.5 (2002) No data (2006)
Decafluoro(penta-fluoroethyl)-cyclo-hexanesulfonate	F		3	No data (1998) 0.5 (2002) No data (2006)
Tris-trifluoropropyl-trimethyl-cyclotriloxane	F		343	10 (1998) 10 (2002) 0.5 (2006)

Common Name	Class	Molstructure	BCF	Production Range (M lbs) (reporting year)
Triphenyl phosphite	Other		25170	50 (1998) 50 (2002) 50 (2006)
1,1-Bis[3,4-di-methylphenyl] ethane	Other		15170	10 (1998) 10 (2002) No data (2006)
Diisopropylbiphenyl	Other		27240	10 (1998) 10 (2002) 10 (2006)
Decamethylcyclo-pentasiloxane	Si		2014	100 (1998) 500 (2002) 100 (2006)
Octamethylcyclo-tetrasiloxane	Si		1687	500 (1998) 500 (2002) 500 (2006)

Production range values refer to range of pounds: (0.5 = 10–500 K; 1= 500 K–1 M; 10 = 1–10 M; 50 = 10–50 M; 100 = 50–100 M; 500 = 100–500 M; 1000 = 500–1000 M lbs for the reporting year)

Limitations of Our Screening Approach

- Degradation and byproducts not fully assessed
  - Some chemicals were selected because they probably had stable degradation products – with F, Br, Cl groups
  - Impurities may be missed (e.g., PCB11 in dichlorobenzidine precursors to printing inks?)
- TSCA IUR chemicals with CBI not included
- Chemicals *within* imported products (e.g., DBDPE not captured)
- QSPR/QSAR model "domains" were often exceeded (e.g., BCFWIN)
- For many chemicals information on uses and releases is unknown or very limited
  - Critical to proper assessment and prioritization

More Limitations

The emphasis on P&B screening with QSPRs may
not be appropriate with other important groups of chemicals in commerce

- Pharmaceuticals (human and veterinary)
- Current use pesticides
- Food additives
- Organometallic substances
- Polymers – some containing perfluorinated or brominated moieties are in the 22,263

Difference screening approaches are required since many of the above are ionic (e.g., many pharmas, CUPs, and organometallics)

State of Knowledge of Environmentally Relevant Properties for Hazard and Risk Assessment of Chemicals in Commerce

Measured Parameters	"Industrial" chemicals (TSCA)	Human & veterinary pharmas	Current use pesticides
Molecular structure (SMILES)	Not all (due to UVCBs and CBI)	Most	All
Environmentally relevant physical and chemical properties	<5% (mostly HPVs)	Most	All
Bioaccumulation (lab or field)	<1%	Limited	All (BCF)
Metabolites/biotransformation products identified?	<1%	Mainly mammalian	Mainly mammalian
Chronic ecotoxicity data (fish, invertebrates, birds)	<1%	~1%	All
Chronic mammalian toxicity (reproductive, genetic)	<10% (mostly HPVs)	Most	Most
Quantity in use; use profile; use area	Limited to TSCA IUR; usually unknown	Generally known	Well known

Howard and Muir, Submitted 2009 Identifying New Persistent and Bioaccumulative Organics Among Chemicals in Commerce

When accepted the following will be available

- Full list of 610 chemicals
- SMILES and chemical structures
- Estimated physical/fate properties
- Estimated toxicity (ECOSAR, Oncologic, AIM)
- Available use and release information
- Analyzability
- Production volume