Identifying New Persistent Chemicals in the Great Lakes Basin

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Background

- there are at least 100,000 chemical substances in commerce and the Great Lakes region is a major use area
  - 5200 high production volume chemicals (HPVCs) on OECD list – production >1000 tonnes/yr
- USEPA TSCA Inventory created in 1976 (~70,000)
- Canada's Domestic Substances List (DSL) created in 1986 (~23,000)
- The chemicals on the 1970-80's lists were "grandfathered" in and generally no data exists on their phys-chem properties relevant to environmental fate modelling or measurement
- Are there other PB&T chemicals not currently measured?
- How to identify them?
- How to priorize them?

Historically POPs and "new" candidate POPs have been identified mainly by

Analogues: e.g. PCBs, dioxins ▪▪► PBDEs, PCNs, PBBs

Analytical advances: ▪▪► PFOS by LC-MS/MS

Isolation and full scan MS identification (e.g. MeO-PBDEs)

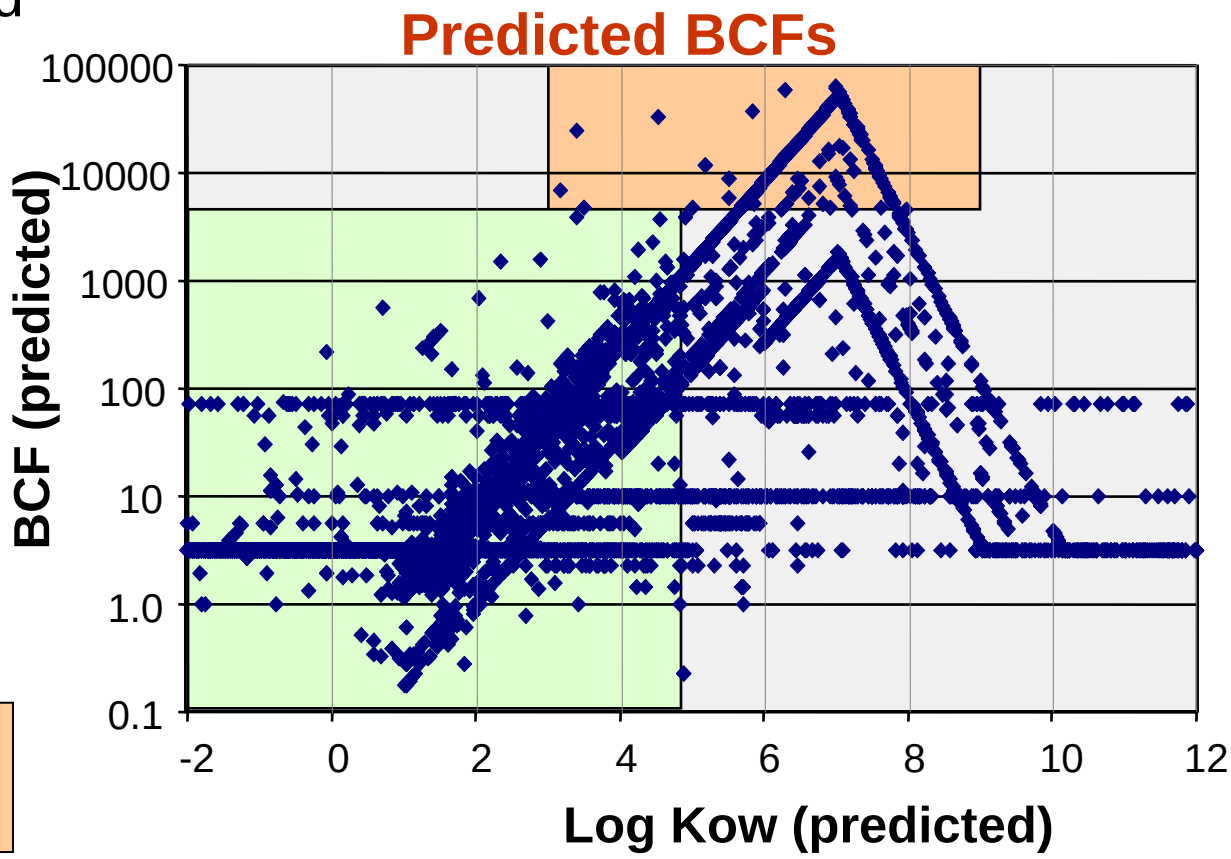
New advances in analytical instrumentation can help e.g. GCxGC-ID-TOFMS, LC-QTOF etc but generally analytical standards are required to confirm

Screening of *existing chemical* lists is widening the data available for identifying potential contaminants

- OECD member countries, ICCA – development of SIDS for high production volume chemicals (HPVCs)
- TSCA Inventory screening (US EPA)
  - EPA Screening of 8511 chemicals with production >4.5 t/yr for P & B using the EPIWIN suite of QSARs (Walker and Carlsen 2002)
  - Screening for LRT potential (Pennington 2001;Rodan et al 1999)
- Environment Canada's Domestic Substances List categorization
  - screening of 11,300 chemical substances with predicted log Kow
  - biodegradation, toxicity (production/use >100 kg/yr)
- European "REACH" (Registration, Evaluation & Authorization) program may generate a lot of phys/chem data - will require:
  - evaluation of ~5000 substances with production > 100 t/yr
  - registration of ~30,000 substances produced at >1 t/yr

Environment Canada has conducted one of the most detailed screening of "existing chemicals" to date

- 23,000 substances which were imported or manufactured in Canada at > 100 kg/yr in the period 1984-86
- Log Kow, BCF, atmospheric, soil and sediment half-lives, aquatic toxicity have been predicted for 11,300 discrete organic chemicals
- Using QSARs for P and B (TOPKAT, EPIWIN suite, Gobas BAF model)



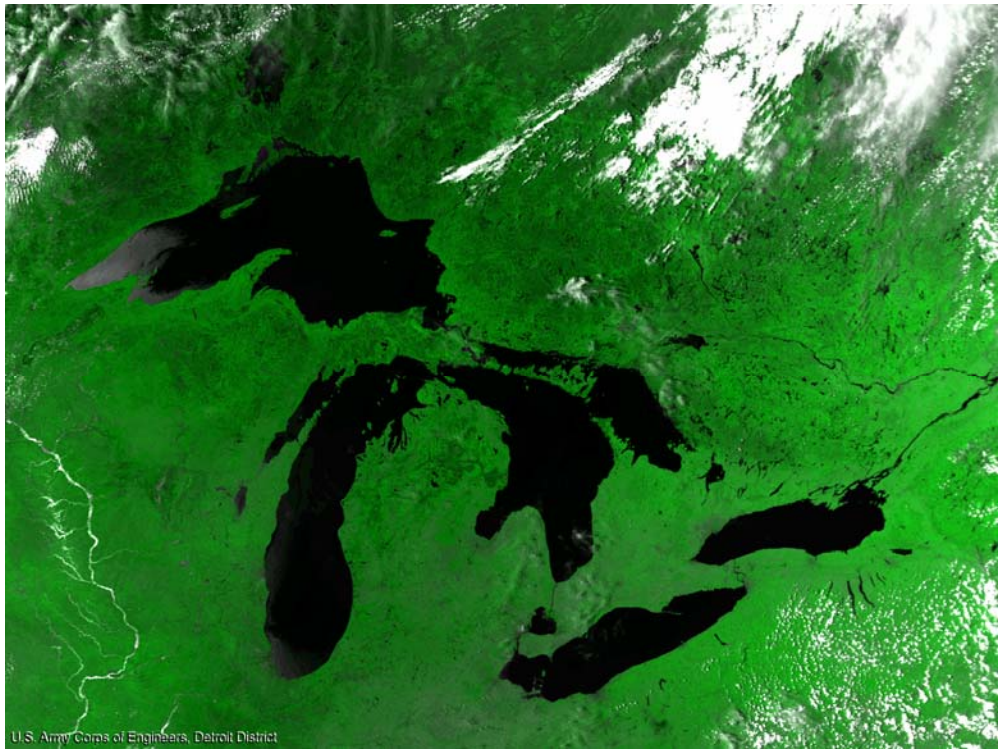
21% have predicted log Kow > 5

3.2% with BCF >5,000;
7.5% with BCF >1000

Ranking the DSL list for chemicals with potential to contaminate open waters of the Great Lakes and food webs

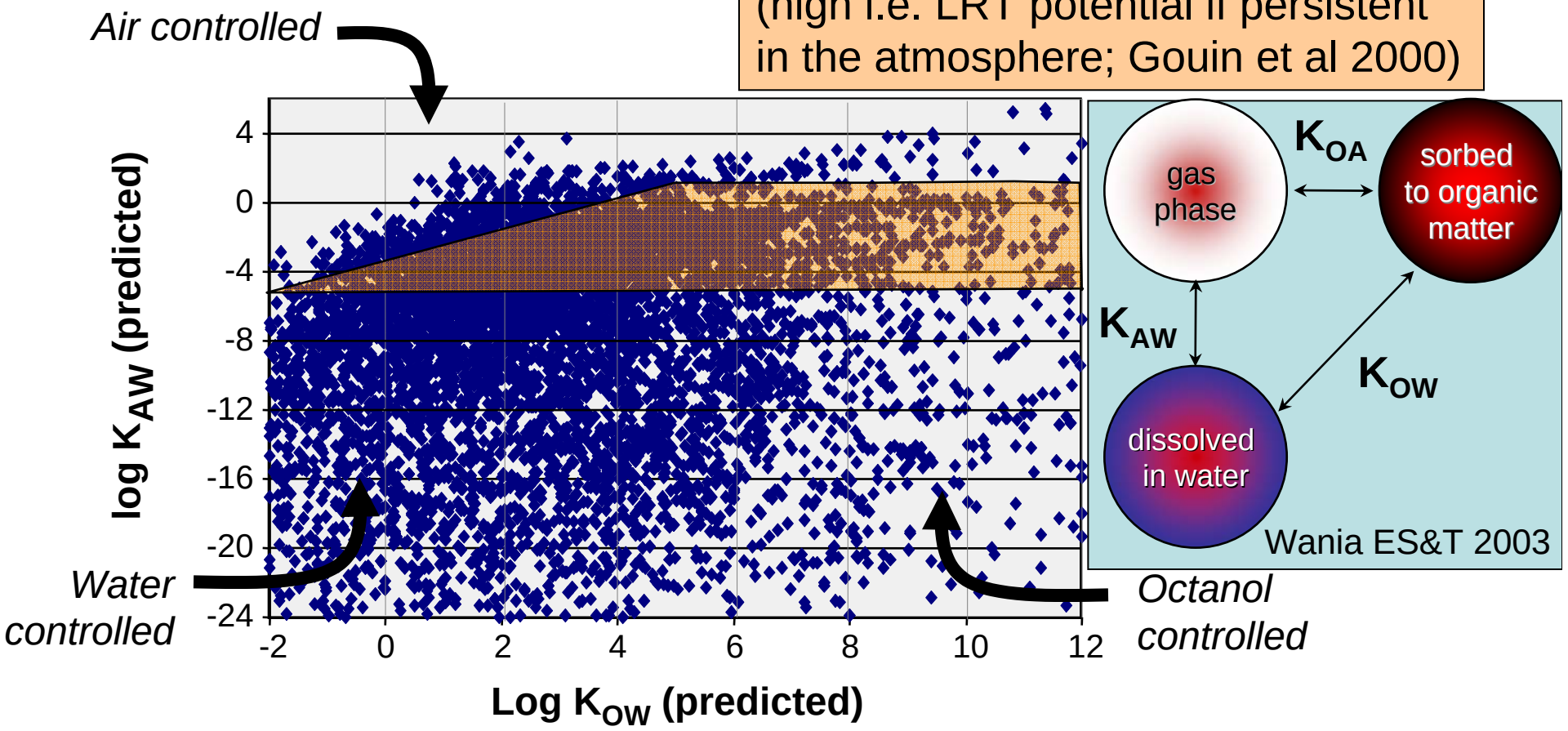
Based on lessons learned from POPs in the Great Lakes:

1. High bioaccumulation/biomagnification potential (BCF >1000)
2. Persistence – low rate of biodegradation and atmospheric oxidation potential
3. Long range transport potential (air-water partitioning, log Kaw > -6)
4. Quantity in use

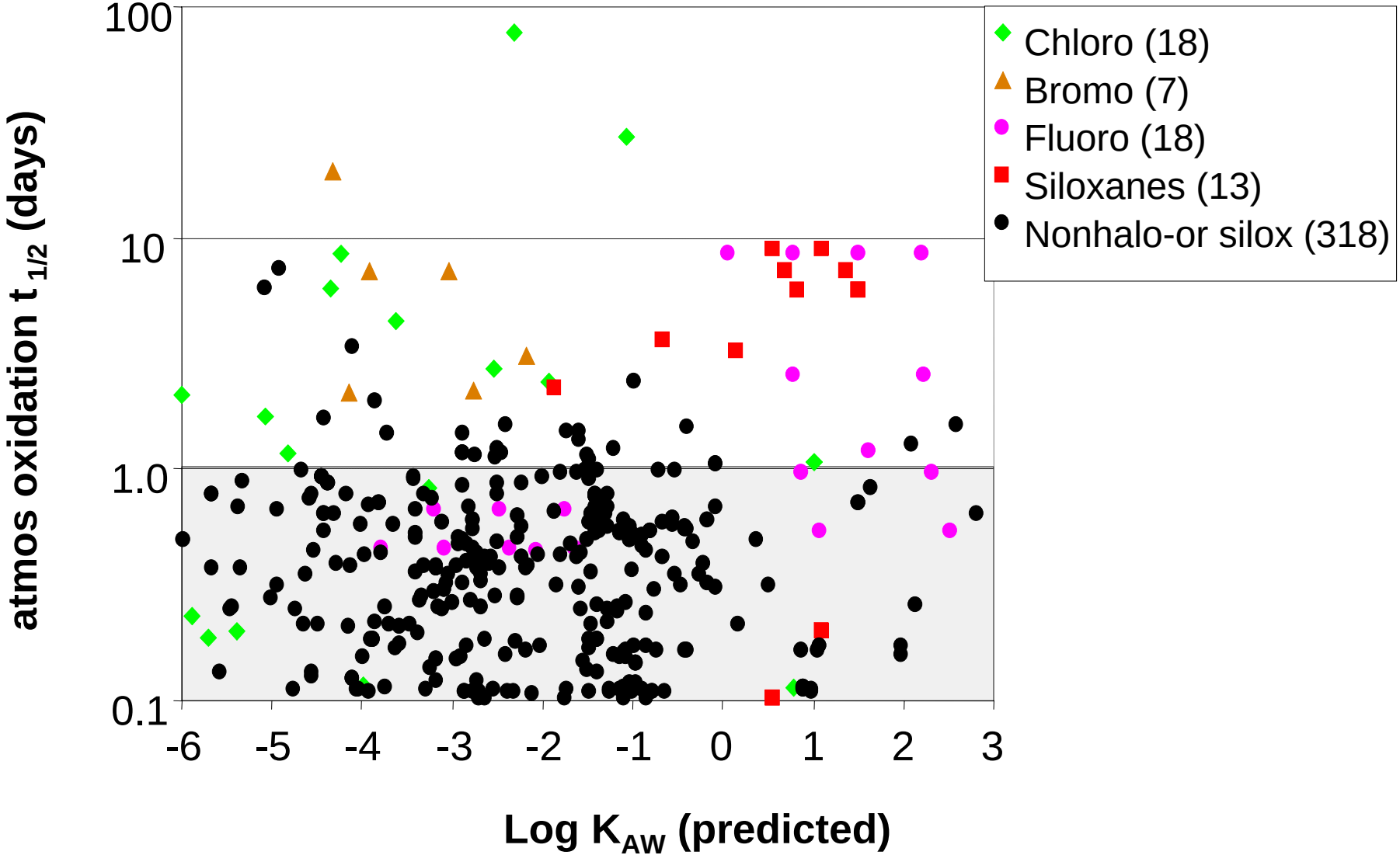


The Environment Canada list can be assessed for LRT Potential using Air-water and octanol-water partitioning and atmospheric oxidation half-life

37% with predicted K_{AW} >-5 and <-1 (high i.e. LRT potential if persistent in the atmosphere; Gouin et al 2000)

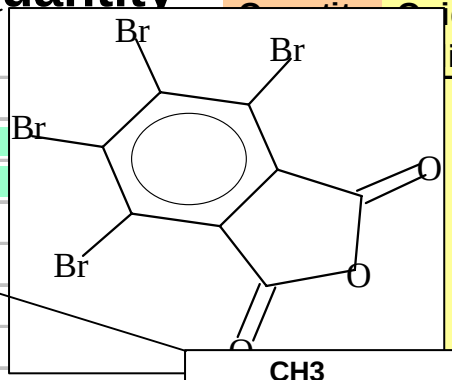


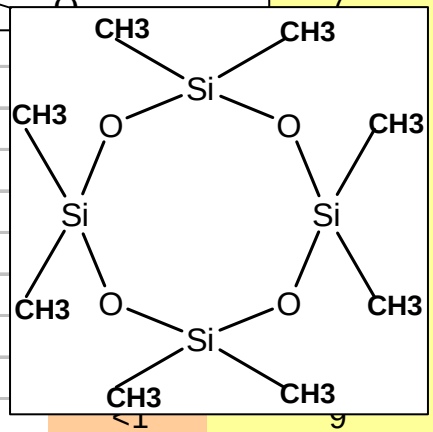
Priority “open lake” contaminant chemicals on the Environ Canada list sorted by class and BCF>1000, Log Kaw>-6, atmospheric oxidation t ½ >0.1 day

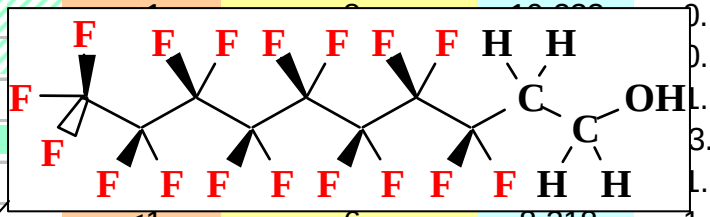


Top 30 DSL chemicals ranked by BCF>1000 and Log Kaw >-6, atmospheric oxidation half-life, and quantity

Rank	Chemical Name		Atmospheric Oxidation half-life (days)	BCF	Log Kaw
1	1,3-Isobenzofurandione, 4,5,6,7-tetrabromo-		439	4,305	-5.18
2	1,3-Cyclopentadiene, 1,2,3,4,5,5-hexachloro-		27	1,517	-1.06
3	Benzene, 1,1 -oxybis-, pentabromo deriv.		19	8,054	-4.32
4	Cyclotetrasiloxane, octamethyl-		9	1,687	0.55
5	Sulfonium, triphenyl-, chloride		9	28,314	-4.24
6	Benzene, 1-(1,1-dimethylethyl)-3,4,5-trimethyl-2,6-dinitro-		7	1,941	-4.92
7	Benzene, 1,3,5-tribromo-2-methoxy-4-methyl-		7	2,366	-3.04
8	Cyclopentasiloxane, decamethyl-			2,014	0.69
9	1H-Indene, 2,3-dihydro-1,1,3,3,5-pentamethyl-4,6-dinitro-			2,825	-5.08
10	Peroxide, bis(2,4-dichlorobenzoyl)			8,472	-4.36
11	Cyclohexasiloxane, dodecamethyl-			14,894	0.83
12	Cyclotetrasiloxane, heptamethylphenyl-			14,256	-0.66
13	Trisiloxane, 1,1,1,5,5,5-hexamethyl-3-phenyl-3-[(trimethylsilyl)oxy]-			40,272	0.16
14	Silane, dichlorodiphenyl-			1,563	-2.54
15	Peroxide, (1,1,4,4-tetramethyl-1,4-butanediyl)bis[(1,1-dimethylethyl)			22,233	-0.98
16	Benzenethiol, pentachloro-			7,063	-2.32
17	Tetrasiloxane, 1,1,3,3,5,5,7,7-octamethyl-		<1	1,062	1.09
18	1-Octanesulfonamide, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-N-me		<1	2,355	2.22
19	1-Heptanesulfonamide, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,7-pentadecafluoro-N-methy		<1	49,545	1.50
20	1-Hexanesulfonamide, 1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-N-methyl-				0.78
21	1-Pentanesulfonamide, 1,1,2,2,3,3,4,4,5,5,5-undecafluoro-N-methyl-				0.06
22	Tetrasiloxane, decamethyl-				1.37
23	Benzene, 1,1 -oxybis-, tetrabromo deriv.				3.92
24	Trisiloxane, 1,1,1,5,5,5-hexamethyl-3,3-bis[(trimethylsilyl)oxy]-				1.51
25	Pentasiloxane, dodecamethyl-		<1	8,318	1.51
26	Benzene, 1,2,3,4-tetrachloro-5,6-dimethoxy-		<1	1,102	-3.63
27	Butanoic acid, 3,3-bis[(1,1-dimethylethyl)dioxy]-, ethyl ester		<1	1,285	-4.09
28	1-Decanol, 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoro-		<1	12,190	2.23
29	1-Octanol, 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-		<1	4,064	0.79
30	Naphthalene, dichloro-		<1	2,254	-1.93

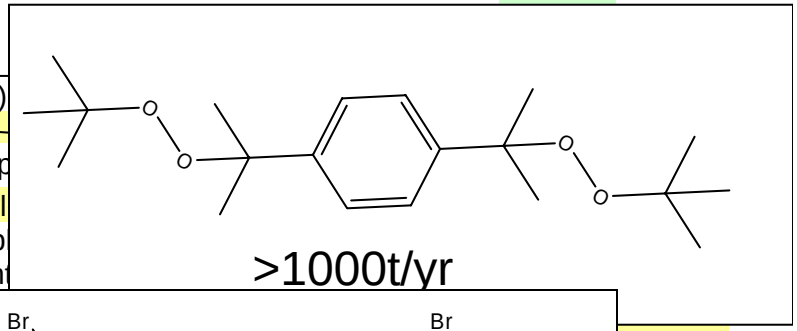


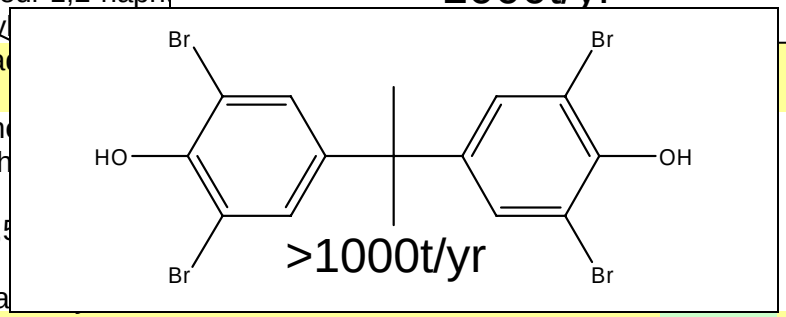


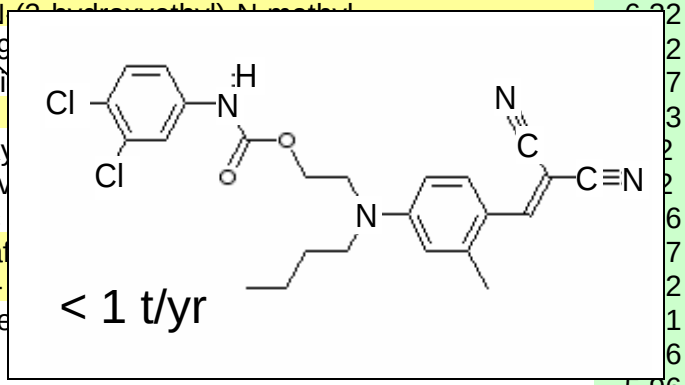


Top 30 chemicals from DSL categorization sorted by BCF, persistence and quantity used (highlighted chemicals are currently analysed – 9 of 30)

	Chemical Name		
1	Peroxide, [1,3(or 1,4)-phenylenebis(1-methylethylidene)]bis[(1,1-dimethylethyl)		
2	Phenol, 4,4 -(1-methylethylidene)bis[2,6-dibromo-		
3	Carbamic acid, (3,4-dichlorophenyl)-, 2-[butyl[4-(2,2-dicyanoethenyl)-3-methylp		
4	1-Heptanesulfonamide, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,7 -pentadecafluoro-N-methyl		
5	Methanesulfonamide, 1-chloro-N-[2,3,4,5-tetrachloro-6-(2,4-dichlorophenoxy)p		
6	1-Naphthalenesulfonic acid, 6-diazo-5,6-dihydro-5-oxo-, methylenedi-1,2-napht		
7	Butanamide, 2-[2,4-bis(1,1-dimethylpropyl)phenoxy]-N-[4-(2-formy		
8	1-Heptanesulfonamide, N-ethyl-1,1,2,2,3,3,4,4,5,5,6,6,7,7,7-penta		35075
9	Benzene, 1,1 -oxybis-, tetrabromo deriv.		32584
10	Anthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-1,3,8,10(2H,9H)-tetron		31842
11	1H-Imidazole-1-ethanol,a-(2,4-dichlorophenyl)-a-[2-(2,4-dichloroph		30269
12	21H,23H-Porphine, 5,10,15,20-tetra-4-pyridinyl-		29242
13	2H-Tetrazolium, 3,3 -(3,3 -dimethoxy[1,1 -biphenyl]-4,4 -diyl)bis[2,5		21184
14	Benz[j]aceanthrylene, 1,2-dihydro-3-methyl-		17498
15	7-Oxa-3,20-diazadispiro[5.1.11.2]heneicosan-21-one, 2,2,4,4-tetra		16672
16	1-Heptanesulfonamide, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,7 -pentadecafluoro-N-	6.22	14689
17	Anthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-1,3,8,10(2H,9H)-tetrone, 2,9	2	14655
18	Phenol, 4,4 -(3H-2,1-benzoxathiol-3-ylidene)bis[2,6-dibromo-, S,S-dioxi	7	12882
19	1-Decanol, 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10 -heptadecafluoro-	3	12190
20	Methanesulfonamide, 1-chloro-N-[2,3,4-trichloro-6-(2,4-dichlorophenoxy	2	11885
21	Methanesulfonamide, 1-chloro-N-(2-phenoxyphenyl)-, pentachloro deriv	2	11885
22	Benzenediazonium, 2-methoxy-4-nitro-, salt with naphthalenedisulfonic	6	11015
23	1-Heptanesulfonamide, N-ethyl-1,1,2,2,3,3,4,4,5,5,6,6,7,7,7 -pentadecaf	7	10544
24	1-Hexanesulfonamide, 1,1,2,2,3,3,4,4,5,5,6,6,6 -tridecafluoro-N-methyl-	2	10233
25	Benzo[b]thiophen-3(2H)-one, 5-chloro-2-(5-chloro-4,7-dimethyl-3-oxobe	1	9036
26	1,3,5-Triazine, 2,4-dimethoxy-6-(1-pyrenyl)-	6	8933
27	Phosphine oxide, (butylphenyl)bis(2,6-dichlorobenzoyl)-	5.96	7780
28	Benzenethiol, pentachloro-	5.91	7063
29	Benzoic acid, 2-[(3,5-dibromo-4-hydroxyphenyl)(3,5-dibromo-4-oxo-2,5-cyclohexadien-1-ylidene)methyl]-,ethyl ester	6.4	6714
30	5-Isobenzofurancarboxylic acid, 3-[4-(diethylamino)-2-ethoxyphenyl]-3-(1-ethyl-2-methyl-1H-indol-3-yl)-1,3-dihydro-1-oxo-, ethyl ester	7.72	6577







Limitations of the PB&T categorization process for identifying priority chemicals

- almost all QSARs have training sets of <1000 substances e.g. biodegradation, aquatic toxicity, & receptor binding
- Example: BCFWIN used 694 chemicals of which 610 were non-ionic
- possibility of **false negatives** is a concern for regulators
- **false positives** are a concern from an industry perspective
- lack of structural information for some substances that are mixtures of variable or unknown composition

The Prioritization & Analytical challenges

- A concensus on screening approaches would be useful for regulators, chemical manufacturers/users, & analytical chemists
  - OECD Multimedia Expert Group developing generic multimedia model
- Lack of concensus on next priority “POP” may be holding back environmental analytical chemists
  - i.e. not sure if analytical resources should be committed

The **good news:**

- Most of these candidate chemicals are all hydrophobic and many are halogenated
- They may be amenable to existing extraction, isolation and quantification methodology

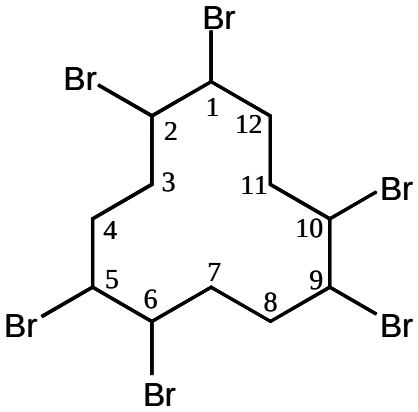
The **bad news**:

- Of the 600 chemicals with BCF >1000 and Log Kaw >-6 in the Environ Canada categorization only ~3% are currently analysed
- Currently acceptable standards of QA for POPs, pesticides, pharmaceuticals, food additives may be difficult to meet

Case studies on chemicals highly ranked chemicals

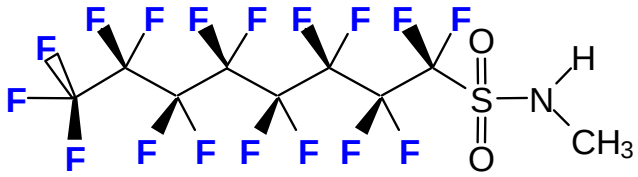
- **Brominated flame retardants e.g. PBDEs and hexabromocyclododecane**

Rank	#3,23,34
AO $t_{1/2}$	2-19 days
BCF	6200-32000



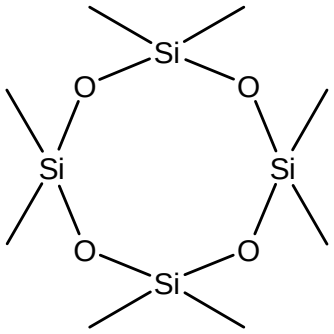
- **Polyfluoro sulfonamides, alcohols and perfluoro alkyl acids**

Rank	5 in top 30
AO $t_{1/2}$	2.5-8.5 days
BCF	2000-49000



- **methyl siloxanes and cyclic siloxanes**

Rank	10 in top 30
AO $t_{1/2}$	2-9 days
BCF	1100-40000



Using information on the presence of contaminants to infer Great Lakes contamination potential

- With detection limits for many halogenated organics in the pico- to femtogram range (10^{-15}-10^{-18} g) mere detection is not useful
- **Biomonitoring** useful for demonstrating entry into food webs especially in open lake or isolated locations
- **Air monitoring** e.g. with arrays of passive air samplers may be more appropriate for validating LRT predictions

- Samples, sampling strategy, and sampling areas must provide information on:
  - Transport routes/source regions
  - Biomagnification potential
  - Temporal trends
  - Spatial trends
- Feed into basin wide LRT and deposition modelling e.g. MacLeod et al. ETC 2002 ; Cohen et al. ES&T 2002