Great Lakes Chemicals Screening Project Preliminary Results

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Goal

- Using Quantitative Structure-Property relationships, and scientific judgment, identify new chemicals not previously measured in the Great Lakes

- Assess whether selected chemicals can be analysed by existing methods in use for POPs and new PB&T chemicals in the Great Lakes

Measurements of "new" (potential) PB&Ts Great Lakes environmental media. All are in commerce except for Penta/Octa BDEs and PFOS

Class	Individual chemicals/groups	Media	Method
Brominated flame retardants and related compounds	PBDEs (penta, octa, deca) Brominated benzenes Brominated carbazoles Bis(tribromo-phenoxy)ethane Decabromodiphenyl ethane	Air, sediments, fish, water	GC-MS usually with ECNI-MS
	Hexabromocyclododecane	Sediments, fish	LC-MS/MS
Chlorinated flame retardants	Dechlorane Plus Chlorinated paraffins	Sediments, fish, water	GC-ECNI-MS
Silicone related lubricants	Cyclic siloxanes D4, D5, D6	Air, STP effluents	GC-EI-MS
Perfluorinated alkyl acids	PFOA and other PFCAs, PFOS, and other PFSAs	Air, Precipitation, fish, sediments	LC-MS/MS
Polyfluoroalcohols	Fluorotelomers, fluoroalkyl-sulfonamido alcohols	Air	GC-EI-MS
Synthetic musks	HHCB (Galaxolide),	Air, sediments	GC-EI-MS

This represents about 50 individual chemicals out of about 30,000 in commercial use

Development of a combined the Canadian and US database of chemicals in commerce (Howard and Meylan 2007)

Source	# substances	Reporting threshold	Reporting date
US EPA High production volume (HPV) program*	3549	1,000,000 lbs/yr (454 t/yr)	Post-1990
US EPA TSCA Inventory update rule (IUR) web site**	14,458 organics (combined HPV and EHPVs)	>10000 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
Total (after duplicates removed)	**22,043**		

*available from http://www.epa.gov/HPV/hpvchmlt.htm

** available from 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

TABLE 1. Screening Criteria for Identifying Chemicals that are PB&T and Potential POPs

	long-range transport			persistence $t^{1}/_{2}$ (d)			bioaccumulation		
organization	remote measurement	VP[a] (Pa)	AO[b] $t^{1}/_{2}$ (d)	water	soil	sediment	BAF/ BCF	Log K_{ow}	toxicity
UNEP (*2*)	yes	or <1000	2	>60	>180	>180	5000	5	risk profile
UNECE (*25*)	yes	or <1000	2	>60	>180	>180	5000	5	risk profile
Canada (*26*)	yes			>180	>180	>360	5000	5	CEPA defined
US EPA TSCA PBT ban (*27*)				>180			5000		toxicity data
US EPA TSCA release controls (*27*)				>60			1000		toxicity data
OSPAR (*28*)				NIB[c]			500	4	NOEC <0.1 mg/L
REACH Annex XII and EU Technical Guidance Document (*29*) - PBTs				>40 (fresh) >60 (marine)		120 (fresh) 180 (marine)	2000		chronic NOEC <0.01 mg/L or CMR[d] or EDC
REACH Annex XII and EU Technical Guidance Document (*29*) - vPvBs				>60		>180	5000		not applicable

[a] Vapor pressure (Pa). [b] Atmospheric oxidation half-life (days). [c] Not inherently biodegradable. [d] CMR = carcinogenic, mutagenic, or toxic for reproduction category; EDC = endocrine disrupting.

Persistence and Bioaccumulation Characteristics of the 20,043 Chemicals

Characteristics*	#	%	Notes
log Kow > 5	4239	19%	Indicates tendency to adsorb to sediments and to bioaccumulate
BCF > 2000 BCF > 5000 BCF > 50000	924 566 19	4.6% 2.8% 0.1%	Bioaccumulation from water exposure – does not include biomagnification
AO* half-life > 2 day AO half-life > 10 day	1973 840	10% 4%	AO half-life indicates stability to atmospheric oxidation
log Kaw > -5 and log Kaw < -1	6515	32%	Kaw describes air-water partitioning. Compounds with log Kaw >-5 & <-1 are "hoppers"

***Kow = octanol water partition coefficient**
BCF = bioconcentration factor predicted with EPIWIN software
AO= atmospheric oxidation half-life
Kaw = air-water partition coefficient

Based on lessons learned from POPs in the Great Lakes:

1. High bioaccumulation/biomagnification potential i.e. found in top predators
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	#	Notes
Predicted BCF >2000, Atmospheric Oxidation >1 day, and Log Kaw >-5 and <-1	105	Using EPIWIN software. Mainly chemicals with LRT potential
By chemical class (Br, Cl, F, I, Si, cyclic HCs) and considering biodegradability	324	By expert judgment – includes chemicals and their degradation products with low LRT but potential for persisting in sediments and in the water column
Total	429	**69% halogenated; 12% siloxanes**

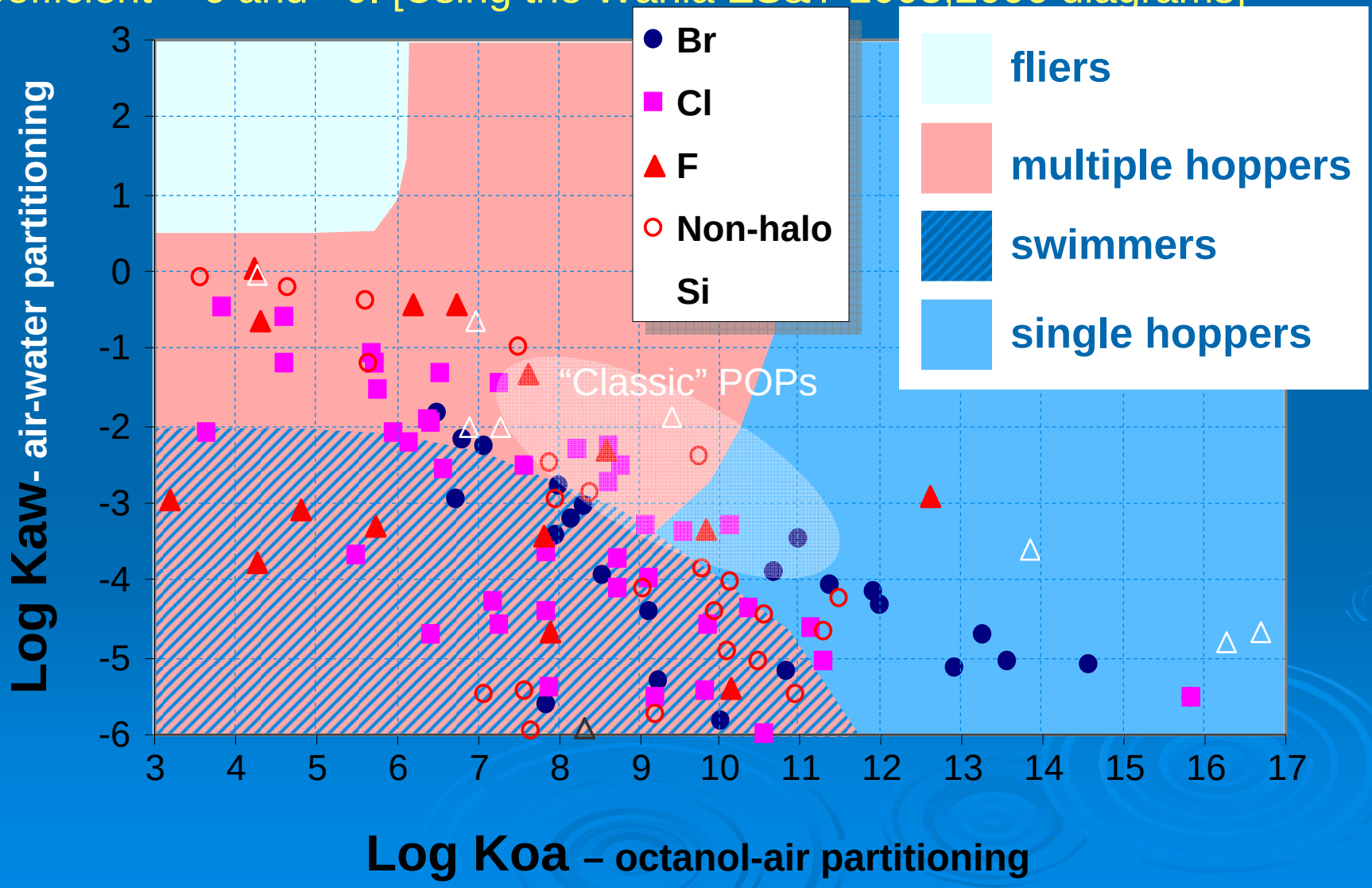
Information on measurement and analyzability of the 429 substances

Analysable	Well monitored in the GL region (ie. programs such as IADN & fish monitoring)	All chemical that may have been analysed in any GL measurement studies	Analysable using existing methods for neutral POPs or other neutrals such as pesticides	Phenols or carboxylates analyzable after derivatization or by LC-MS	Analysable by LC-MS/MS ESI mode (anionic) or positive CI mode (cation)	Analysable degradation product
Yes	**16**	**83**	**280**	**47**	**46**	**144**
No	**413**	**346**	**116**			
Maybe			**33**		**11**	

Are any of the 429 chemicals POPs?

Subset of 119 with the greatest LRT potential: 75% are halogenated

Predicted Atmospheric Oxidation t1/2 in air > 1 day, and log air-water partition coefficient >-6 and <0. [Using the Wania ES&T 2003;2006 diagrams]



Conclusions

- Screening of DSL and TSCA Inventory has yielded some interesting probable P&B substances
  - Most of the 400 identified are not currently analysed
  - Most are in commerce i.e. on TSCA IUR in past 10 yrs
  - Most could be analysed in environmental media although suitable analytical standards are not available for many
    - i.e. high proportion are halogenated; most with high log Kow and AOt1/2 >2 days indicating they would be extractable

Conclusions

- Uncertainties in this type of screening include:
  - possibility of false positives (e.g. readily degradable chemicals such as anhydrides; esters are screened in)
  - False negatives e.g. high MW compounds have low estimated BCF but may still be a concern if persistent e.g. in sediments
  - Lack of information on uses and actual emissions of the chemicals
    - some are chemical intermediates – may be entirely consumed in manufacturing process or present as residuals in products

Next Steps

- T Screens (i.e., ECOSAR, AIMS, ONCOLOGIC)
- Medium Production Volume Chemical Screens
- P2 Opportunity Analyses
- Fish and Gull Egg Archive Analyses (5 year trends)
- Possible ToxCast Nominations