

Non-targeted analysis update

John Kucklick

National Institute of Standards and Technology

Hollings Marine Laboratory

Charleston, SC

Collaborators:

Jacki Murray, NIST

Denise Greig, MMC

Eunha Hoh, SDSU

Nate Dodder and Keith Maruya, SCCWRP

Motivation for Project

- Predictions that some chemicals in use have significant bioaccumulation potential but are not monitored
- Recognition that there may be unmeasured contaminants in samples missed by targeted analysis

New Candidates: Howard and Muir 2010 (Environ. Sci. Technol. 44:2277)

- 22263 organic chemicals in use in Canada and US were screened
- 610 compounds were possibly P&B
- 62% were halogenated
 - 181 fluorinated
 - 116 chlorinated
 - 10 iodidated
- 148 measured or detected

Identifying New Persistent and Bioaccumulative Organics Among Chemicals in Commerce

PHILIP H. HOWARD*[†] AND
DEREK C. G. MUIR[‡]

*SRC, Environmental Science Center, 6502 Round Pond Road,
North Syracuse, New York, and Aquatic Ecosystem Protection
Research Division, Environment Canada, 867 Lakeshore Road,
Burlington, Ontario*

Motivation for Project

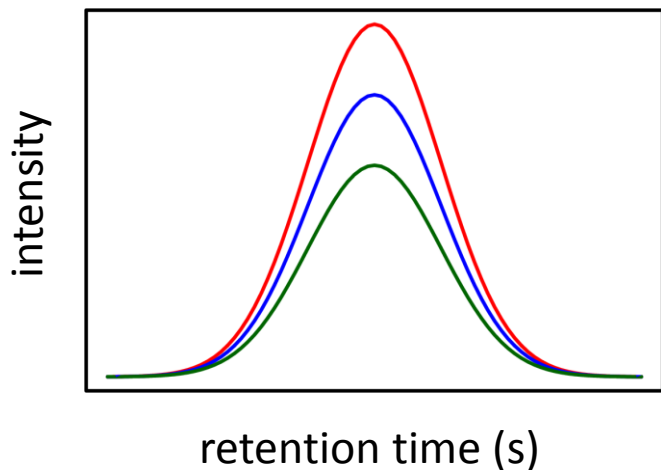
- Predictions that some chemicals in use have significant bioaccumulation potential but are not monitored
- Recognition that there may be unmeasured contaminants in samples missed by targeted analysis

Tools Facilitating Untargeted Analysis

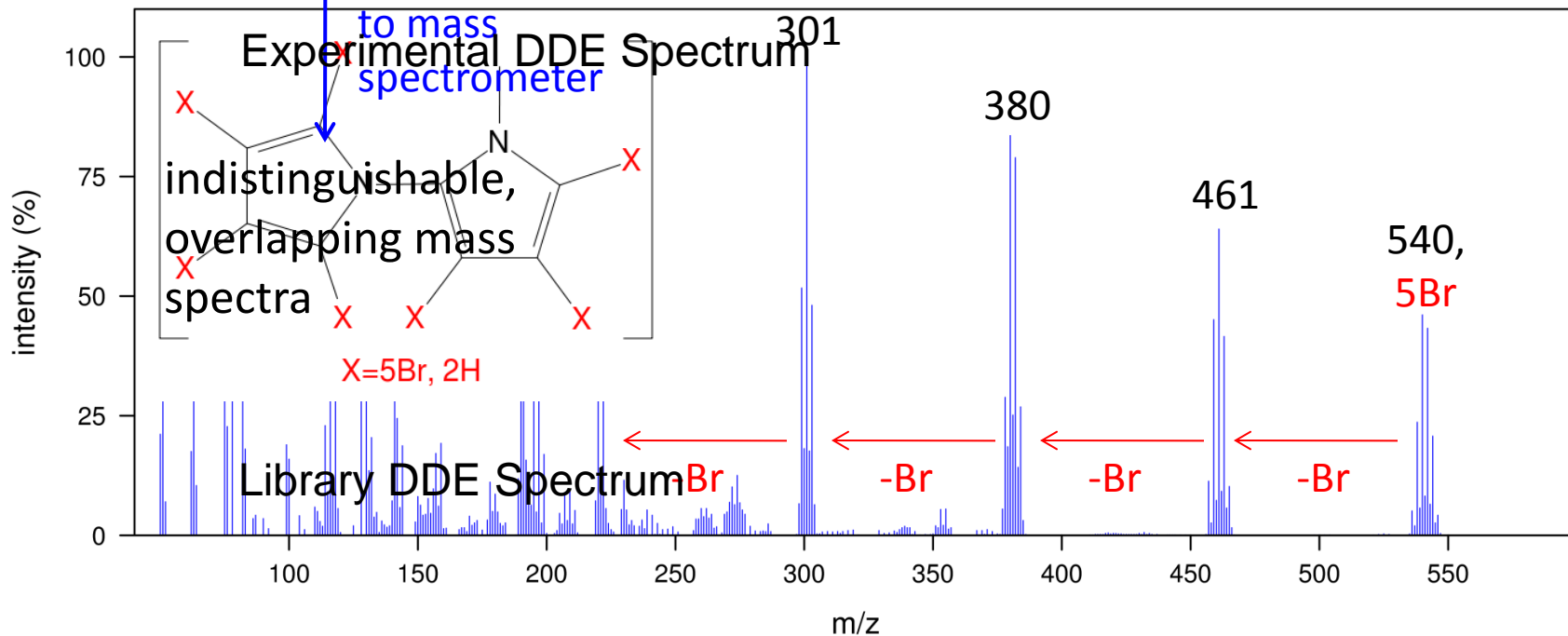
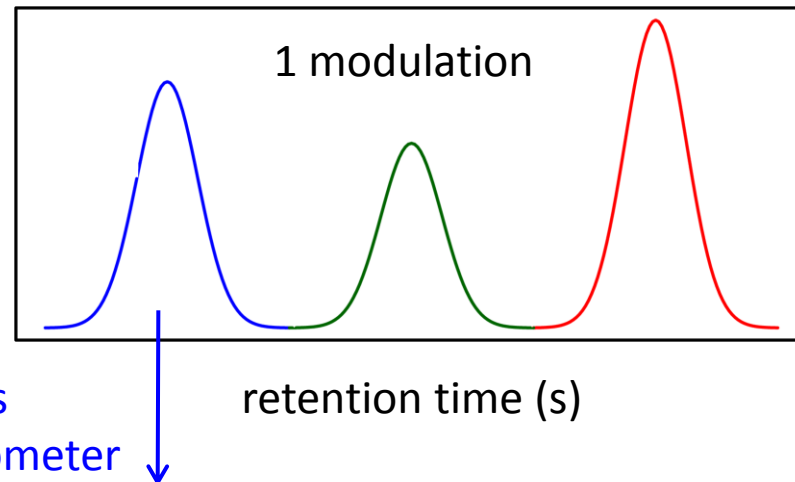
- Lists of chemicals with bioaccumulation potential
- Comprehensive mass spectral libraries (e.g. NIST Mass Spectral Library)
- GC x GC Time of Flight Mass Spectrometry

Instrumental Method: GC×GC-TOF (Simplified Description)

co-eluting peaks 1st GC column



separated peaks 2st GC column

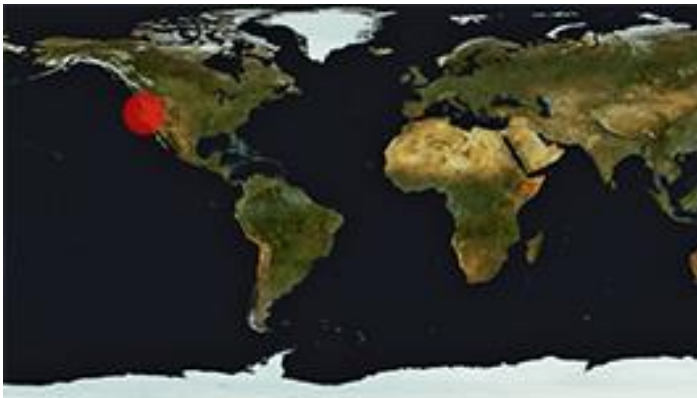


Pros and Cons

- Pros
 - GC x GC and spectral deconvolution produces high-quality spectra
 - Very high ability to resolve complex mixtures
 - Library searching using NIST MS library
- Cons
 - Misses polar compounds and those not amenable to electron impact ionization
 - Data handling is labor intensive
 - Library incomplete for many contaminants
 - Bias toward halogenated compounds

Objectives

- Provide information to San Francisco Bay water managers so that contaminants can be further studied
- Identify not routinely monitored contaminants in a higher trophic organism



Harbor Seal Blubber Samples

Age	Sex	Location	Inside or Outside Bay
Pup and Adult	M	Fitzgerald Marine Reserve	Outside
Adult	F	Limantour Beach (Point Reyes National Seashore)	Outside
Adult	F	Baker Beach	Inside
Adult	M	Angel Island	Inside
Adult	F	Richmond Marina	Inside
Adult	M	Alaska	Outside



Sample (1 g of seal blubber)



Pressurized Fluid Extraction (Dionex ASE)

Dichloromethane (DCM) extract



Size Exclusion Chromatography (600 mm x 25 mm PLGel)

Lipid reduced extract



Size Exclusion Chromatography (300 mm x 7.5 mm PLGel)

Lipid reduced extract



Fractionation by Si/Al column

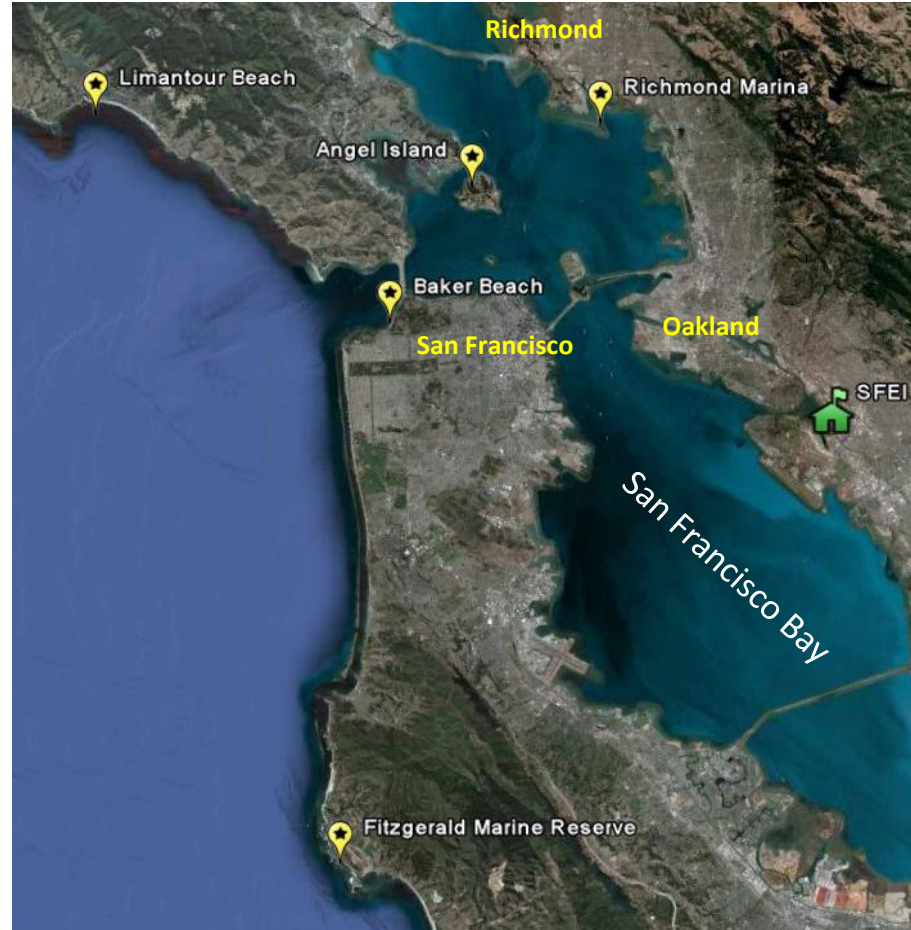
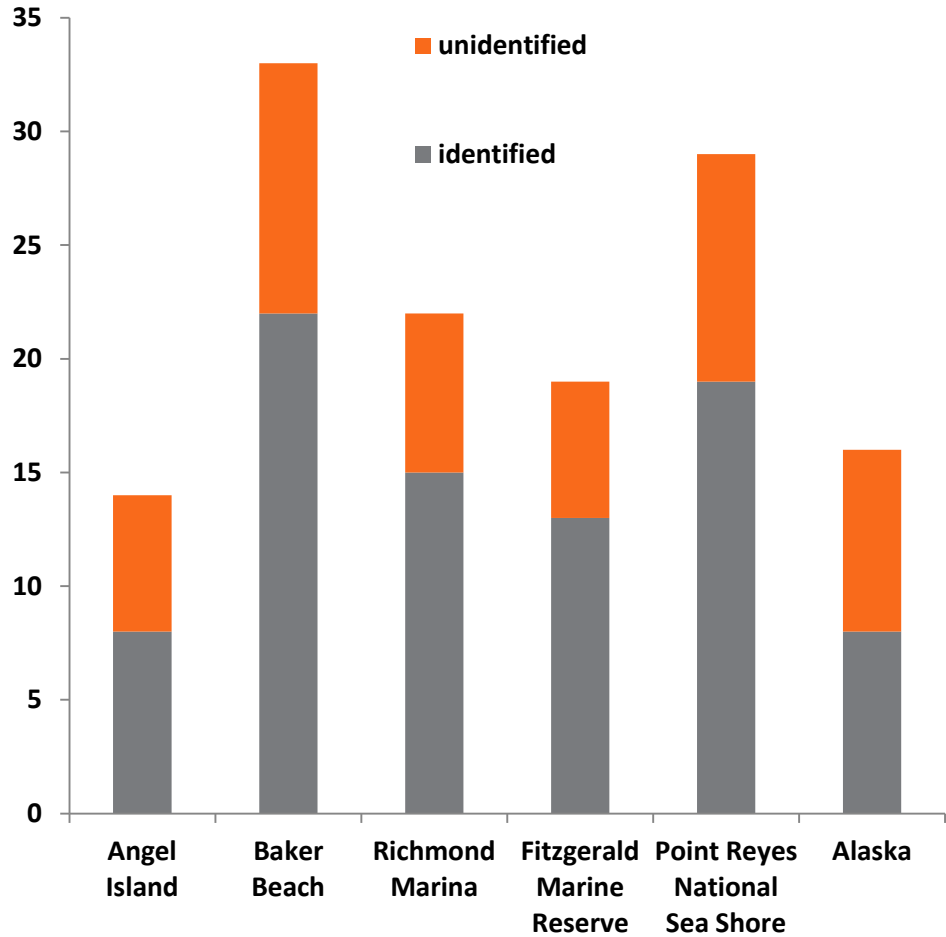
Non polar extract Mid polarity extract More polar extract



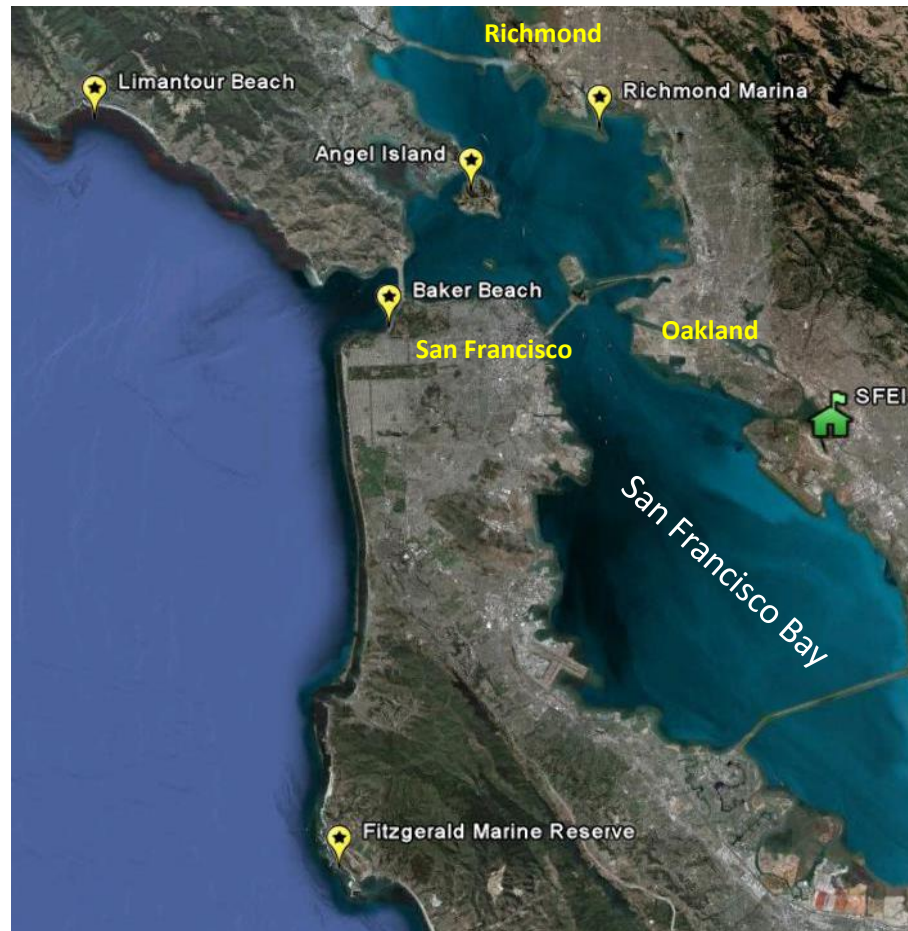
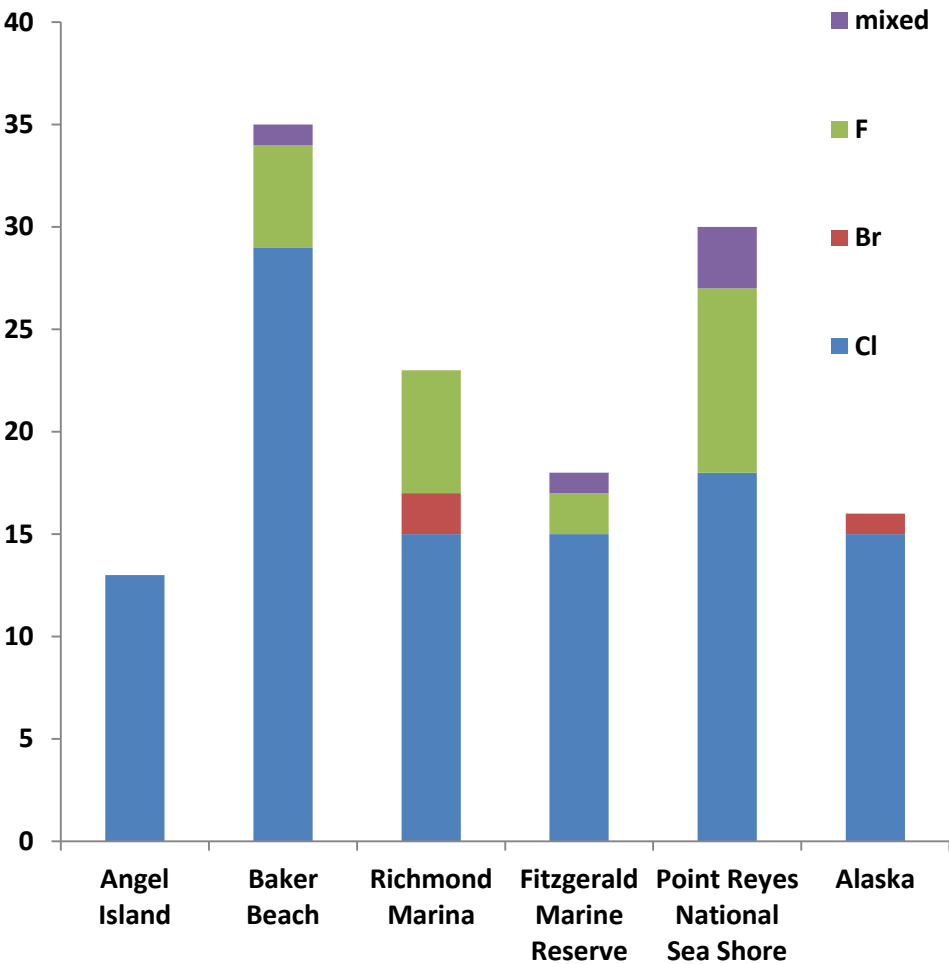
GC x GC TOFMS (LECO Pegasus)



Total compounds found per location

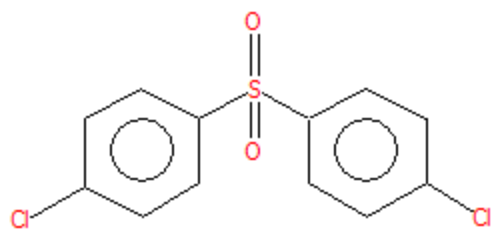


Compounds type versus collection location

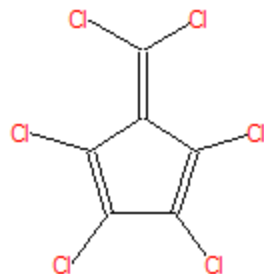


Chlorinated Compounds

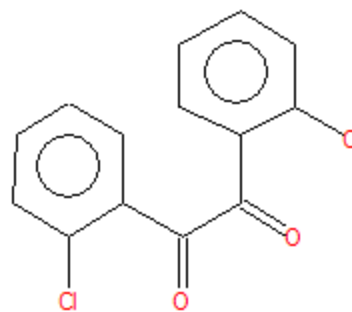
Compound	CAS#	Comments
Dechlorane 602	31107-44-5	flame retardant
p,p'-Dichlorodiphenyl sulfone	80-07-9	polymer starting material for "Udel"
Hexachlorofulvene	6317-25-5	polymer use?
Dichlorobenzil	21854-95-5	dyes, resins, disinfectant?
Dichlorobenzophenone	5293-97-0	?
Dichloroanthracene	605-48-1	combustion product?



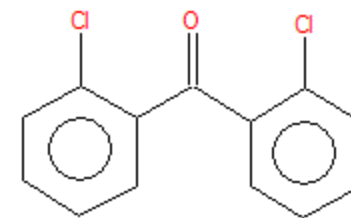
Dichlorodiphenylsulfone
On Howard and Muir List



Hexachlorofulvene



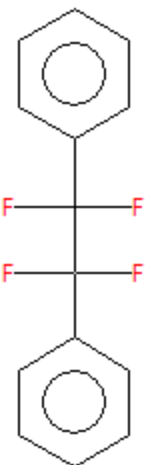
Dichlorobenzil



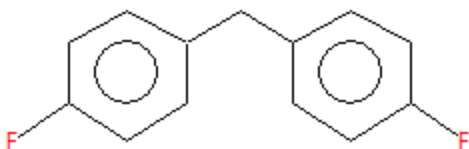
Dichlorobenzophenone

Fluorinated Compounds

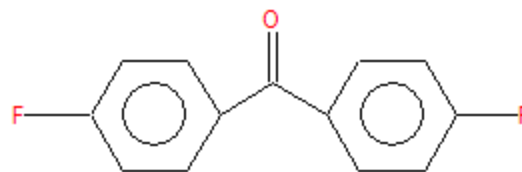
Compound	CAS#	Comments
octafluorodecane	--	degradation product?
1,1,2,2-Tetrafluoro-1,2-diphenylethane	425-32-1	
4,4'-Difluorodiphenylmethane	457-68-1	polymer subunit
Difluorobenzophenone	345-92-6	polymer use?
Monofluorobenzophenone	345-83-5	polymer use?



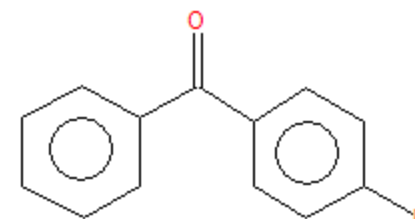
1,1,2,2-Tetrafluoro-1,2-diphenylethane



4,4'-Difluorodiphenylmethane

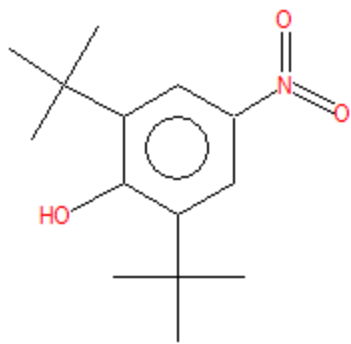


fluorobenzophenones

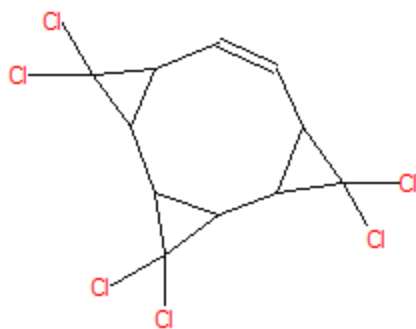


Miscellaneous Compounds

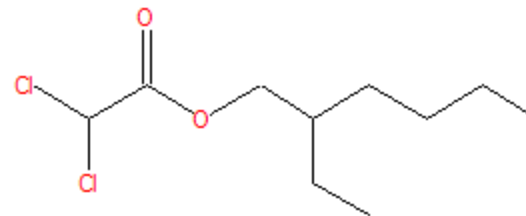
Compound	CAS#	Comments
Haloacetate esters	68144-72-9 (e.g.)	possibly wastewater origin?
Chlorinated Hydrocarbons	--	Below chloroparaffin MW range
Bayer 28,589	728-40-5	musk-like
tetrabromobiphenyl	16400-50-3	



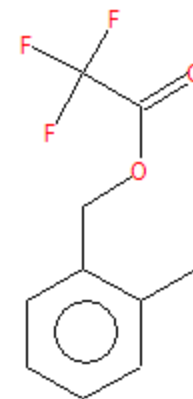
Bayer 28,589



Chlorinated Hydrocarbons

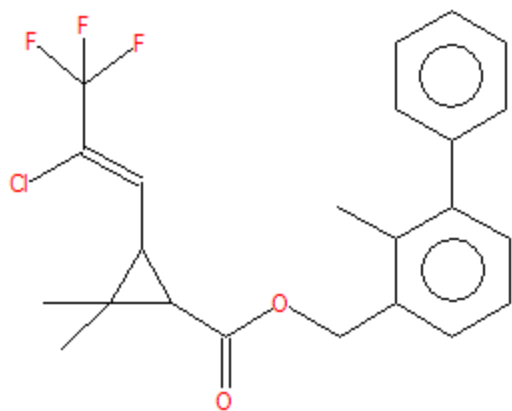


Haloacetate esters

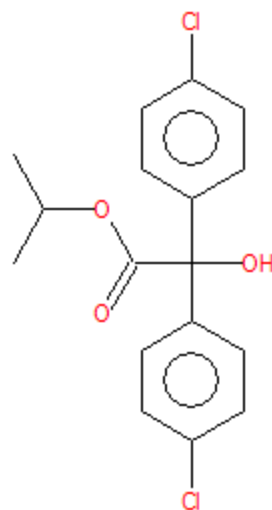


Pesticides

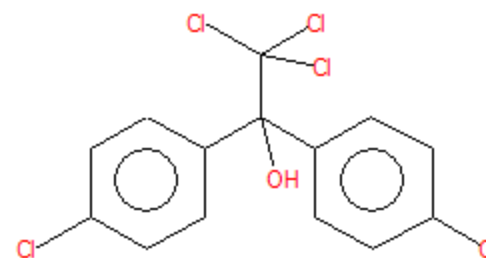
Compound	CAS#	Comment
Bifenthrin	82657-04-3	Pesticide, stable
Chloropropylate	5836-10-2	pesticide, miticide
Dicofol	115-32-2	Pesticide, cotton, citrus



Bifenthrin



chloropropylate



Dicofol

Next Steps

- Verify identified compounds
- Identify unknowns with help of Ed White from NIST
- Run halogen filters developed by Hilton
- Written summary report

Available Samples

ID	Age	Sex	Location	Tissues
HS-2118	Weaner	M	Fitzgerald Marine Reserve	Liver, Serum, Whole Blood
HS-2120	Adult	M	Angel Island	Liver, Serum, Whole Blood
HS-2028	Adult	F	Pt. Reyes Nat. Seashore	Liver
HS-2122	Adult	M	Fitzgerald Marine Reserve	Liver, Serum, Whole Blood
HS-2125	Adult	F	Richmond Marina	Liver, Serum, Whole Blood
HS-10	Adult	M	Alaska	Liver

General Approach

Extraction

- Blood--Focused Microwave Extraction
- Liver—Pressurized fluid extraction

Cleanup

- Size exclusion only

Derivatization

- Derivatize with MSTFA to create TMS derivatives

Time Line

- Verify Compound and Compound ID (in progress)
 - Spring/Summer 2012
- Liver and blood analysis (in progress)
 - Spring/Summer 2012 chemical analysis
 - Summer/Fall 2012 data analysis
- Mussel tissue samples
 - Fall 2012/Winter 2013
- First manuscript
 - Winter 2103