Analysis of Untargeted Organic Chemicals of Interest in Environmental Samples Using GC×GC-TOF Mass Spectrometry

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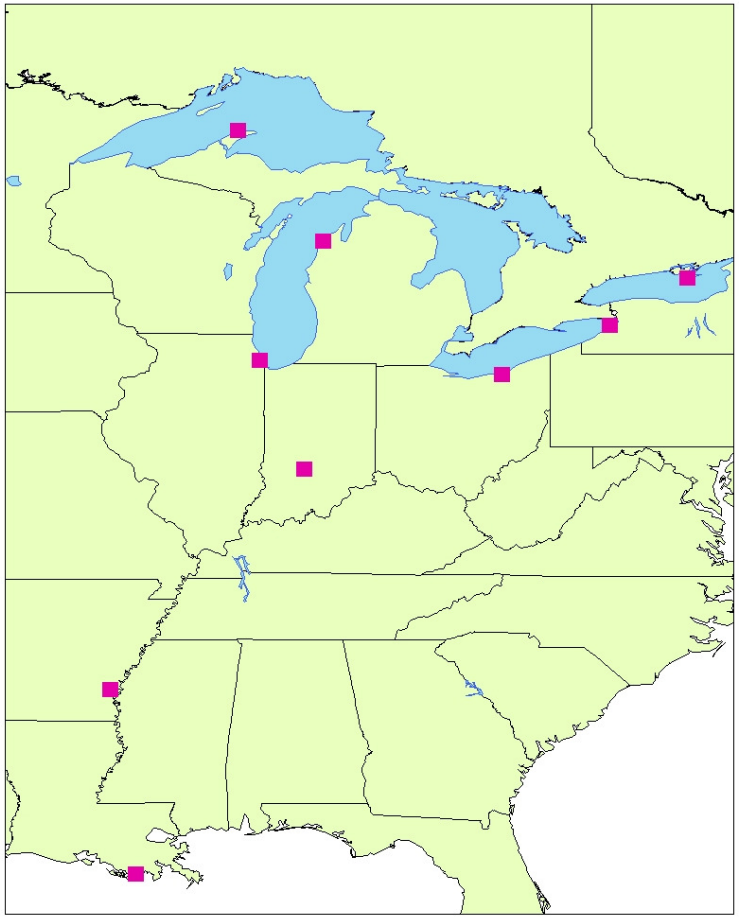
- Background: how I became interested in untargeted analytical method
- Challenges for environmental chemists
- What is untargeted analytical approach?
- Findings in dietary fish oil supplements
- Marine mammal exposure to mixtures of anthropogenic contaminants and foreign naturally occurring chemicals
- Impact of environmental tobacco smoke on PAHs in house dust
- Current & future works

Fate of Organic Contaminants (toxaphene, organochlorine pesticides, PBDEs) in atmosphere



Binational Atmospheric Monitoring: Integrated Atmospheric Deposition Network (IADN) sites (US EPA and Environment Canada)

- Air Sampling
- Chemical Analysis (GC/MS with SIM mode)
- Atmospheric Behavior
  - Concentration Comparison
  - Temporal/Spatial Trend
  - Source finding/ Backward air trajectories

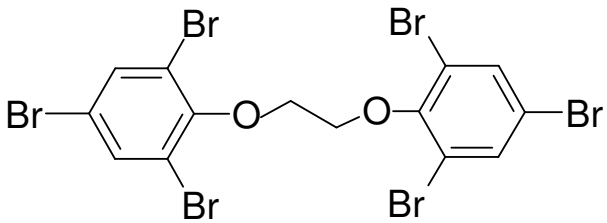
Unknown chromatographic peaks were detected during chemical analysis

Detection of unknown peaks in GC/MS chromatograms (air samples)

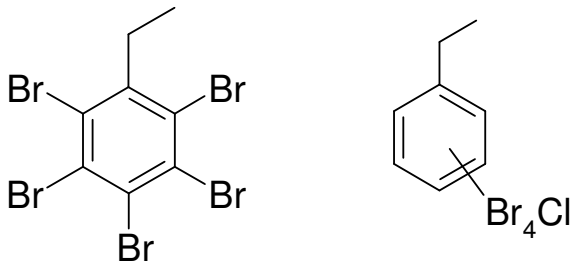
Full-scan mass spectra (EI & ECNI/ Search for potential chemicals)

Confirmation with authentic chemicals

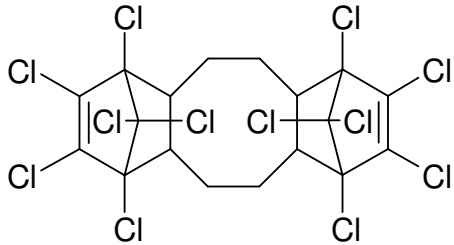
Analysis in environmental samples (air, sediment cores, and fish)



1,2-*Bis*(2,4,6-tribromophenoxy)ethane



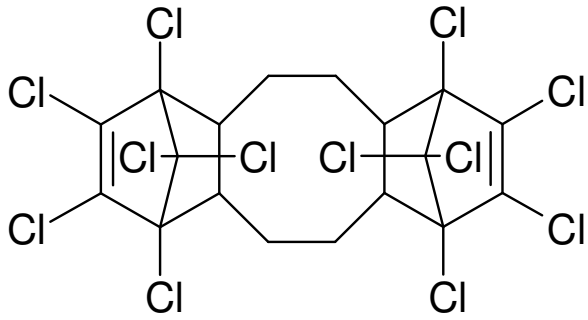
Pentabromoethylbenzene



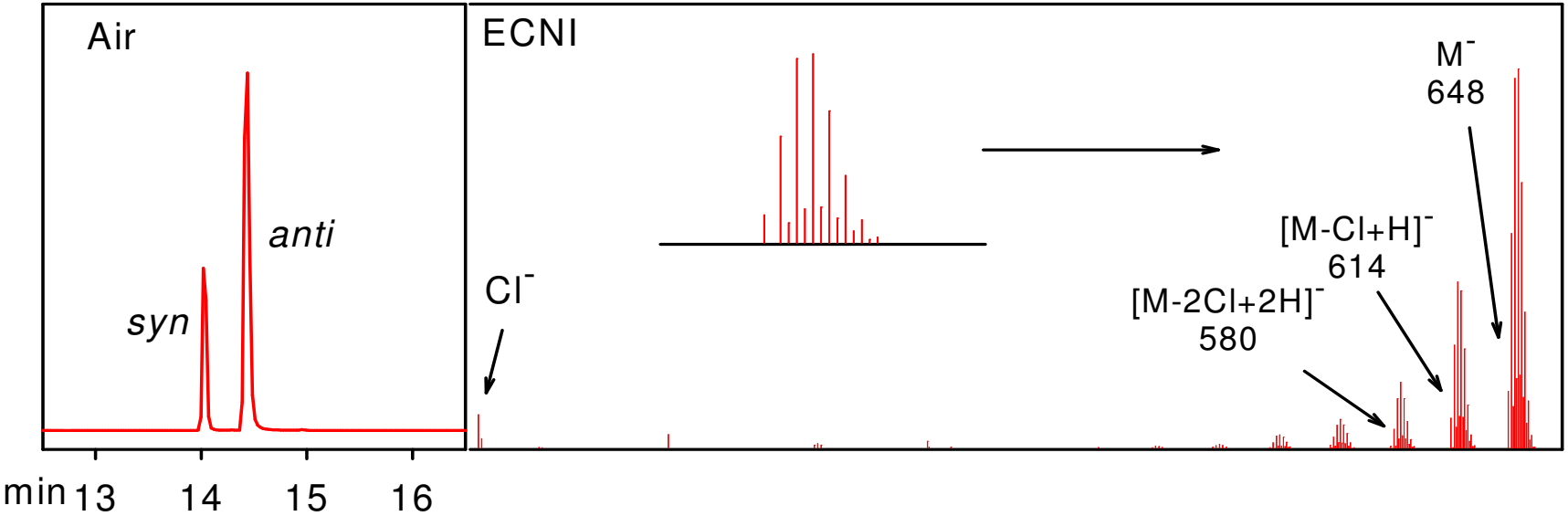
Dechlorane Plus

Discovery of Dechlorane Plus in Environment

- Two unknown chlorinated compound GC peaks found in air samples around the Great Lakes during brominated flame retardant analysis
- Verified by GC and EI and ECNI mass spectra using the commercial product ($C_{18}H_{12}Cl_{12}$, OxyChem)

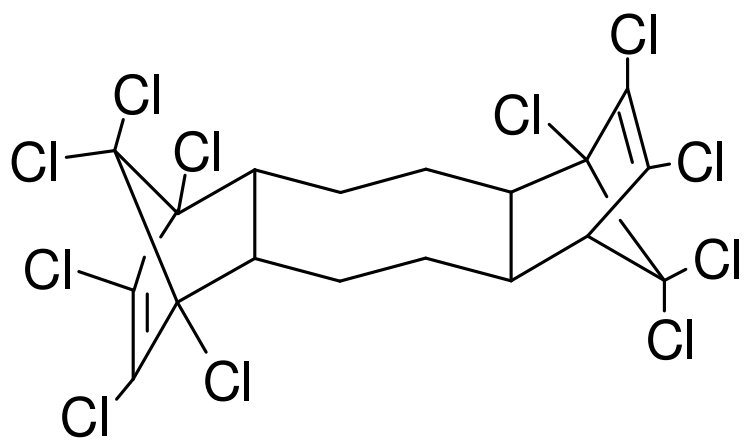


Dechlorane Plus (DP)

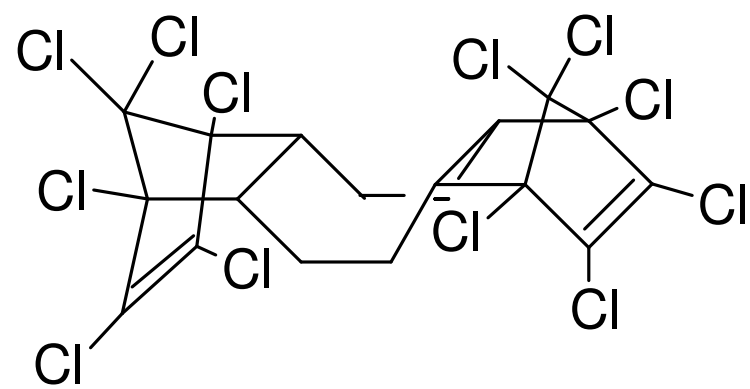


Introduction of Dechlorane Plus

- DP is a flame retardant that has been used for a long time, sometimes with Sb_2O_3, in several plastics
- Made by OxyChem (formerly Hooker Chemical manufactured Mirex called Dechlorane)
- Diels-Alder reaction: two stereoisomers (*anti*- and *syn*-)
- Two isomers are separated by thin layer chromatography and are identified by ^{1}H-NMR and reference NMR data (Garcia et al, *Tetrahedron Lett*. **1991**), *anti*: *syn* = 4:1 in commercial product

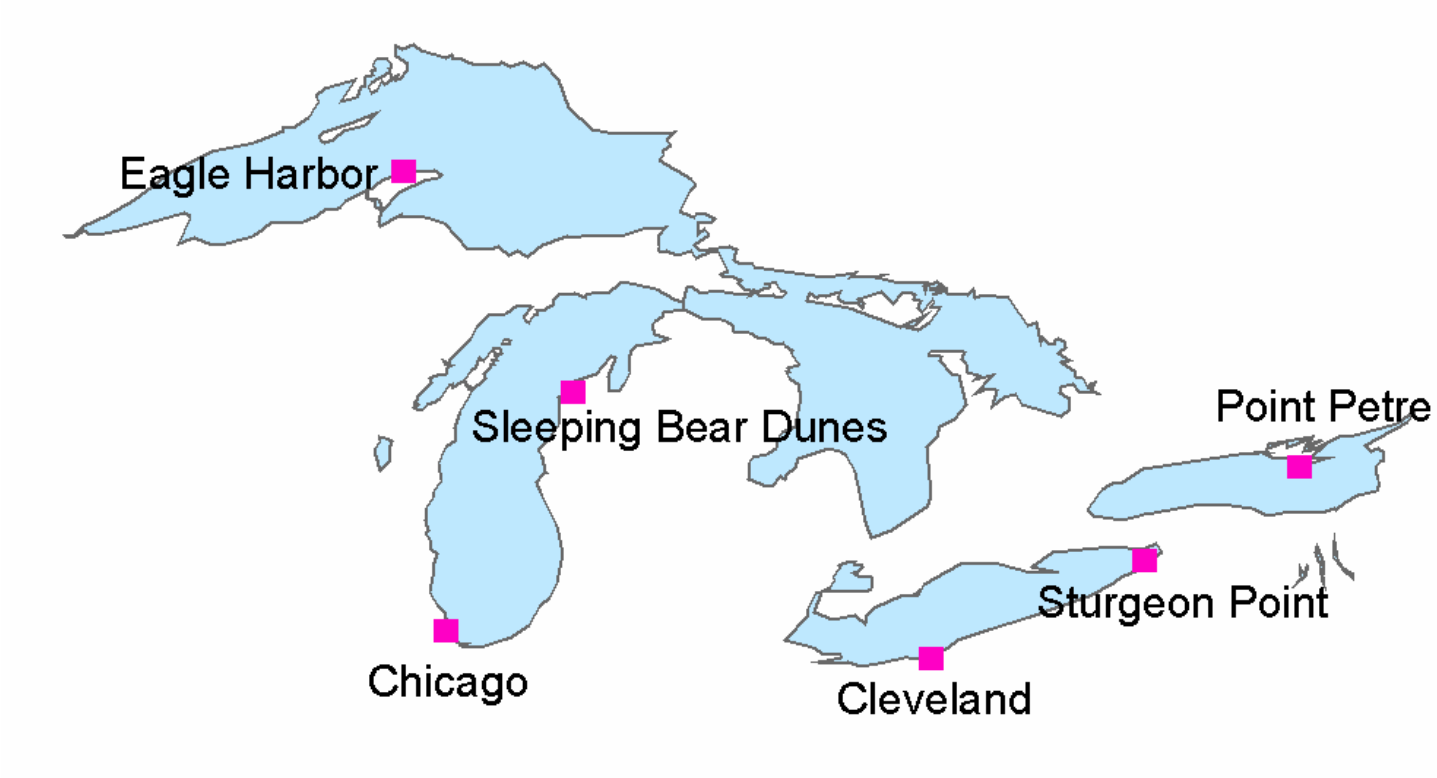


anti



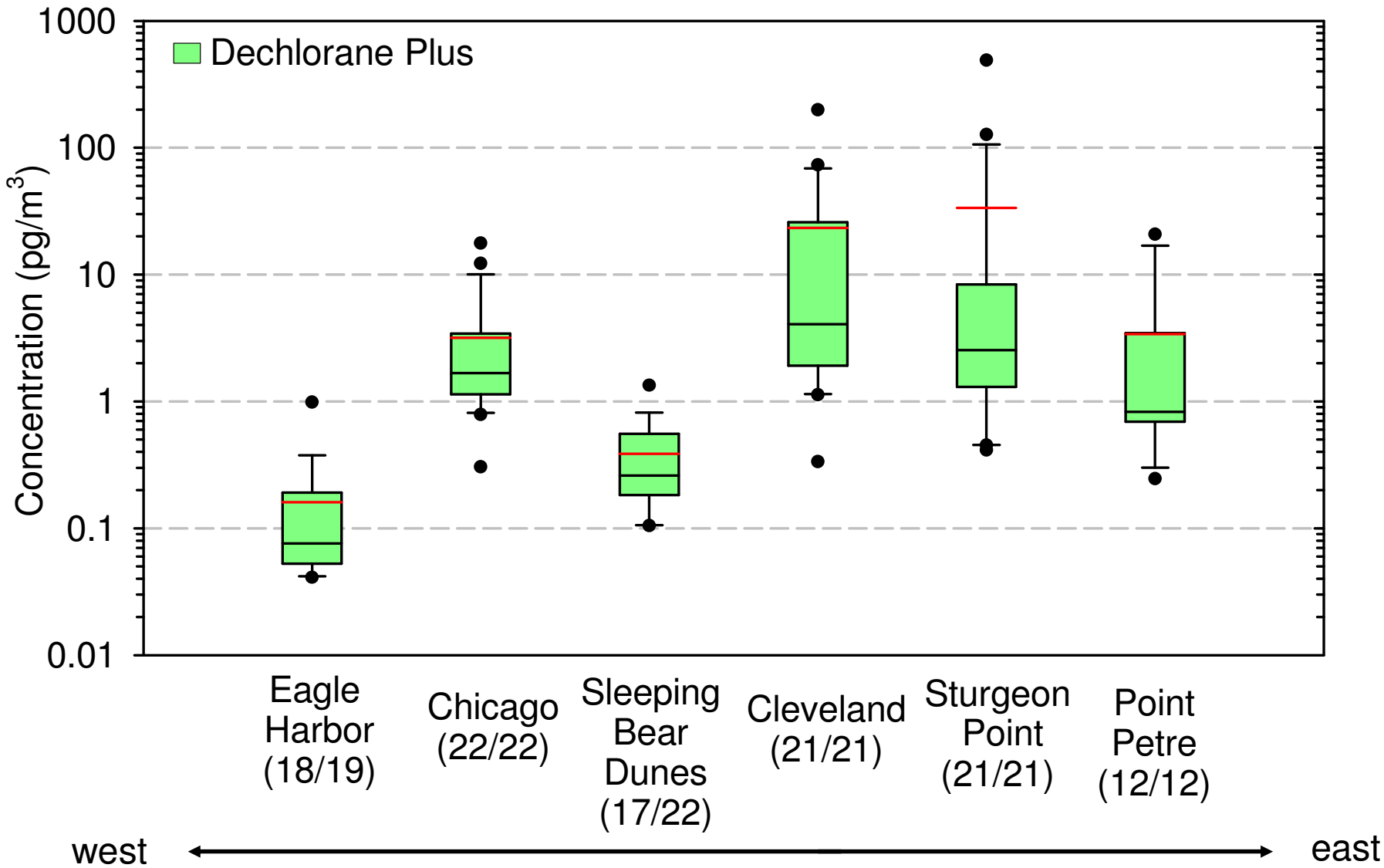
syn

Dechlorane Plus in the Atmosphere of Great Lakes



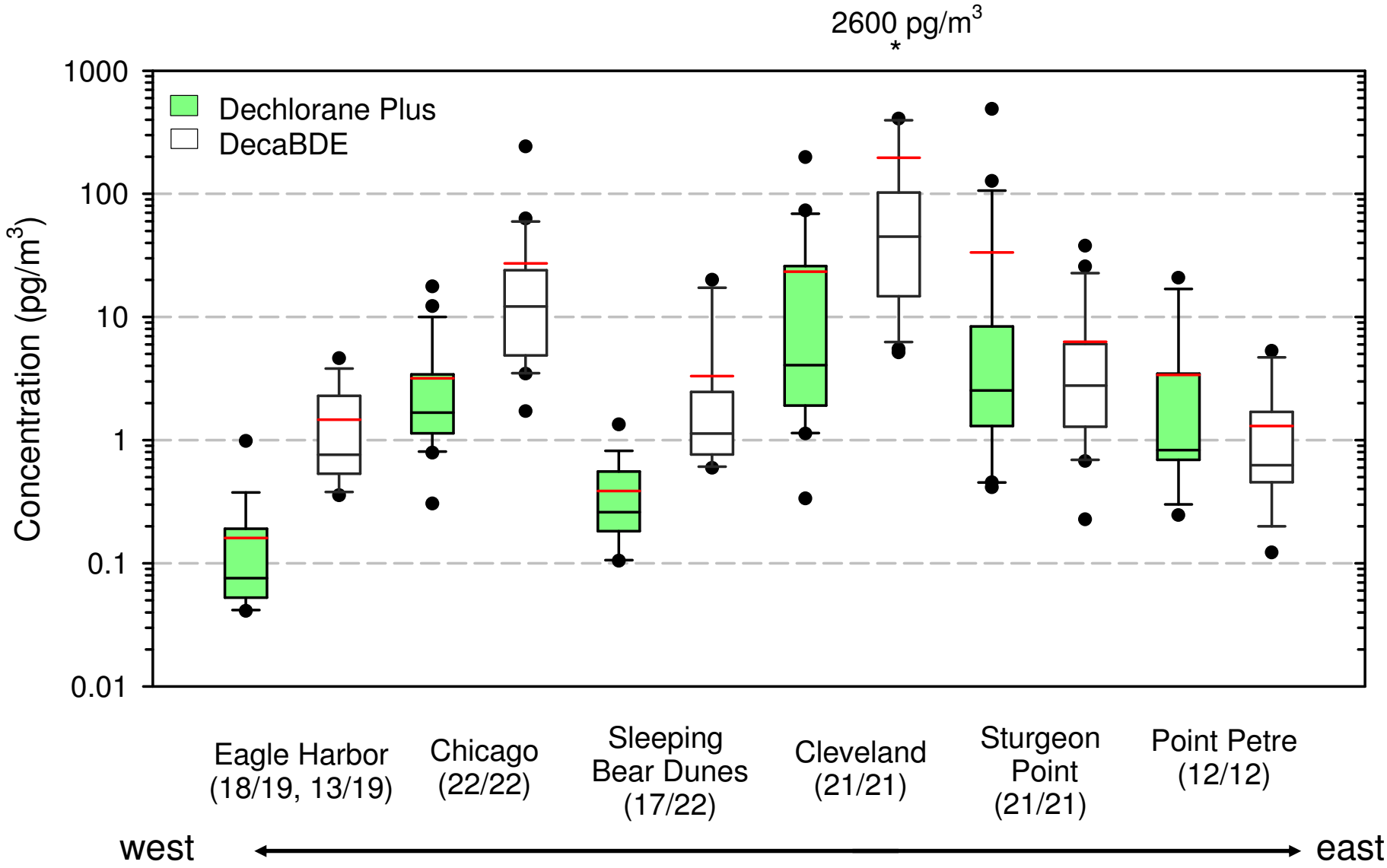
- Integrated Atmospheric Deposition Network (IADN) sites (urban, rural, and remote sites)
- High-volume air sampler (filter for particulates and XAD for vapor) during April – December in 2004
- Samples collected every 12 days
- Soxhlet extraction, and then GC/MS analysis

Atmospheric Dechlorane Plus (pg/m^3)



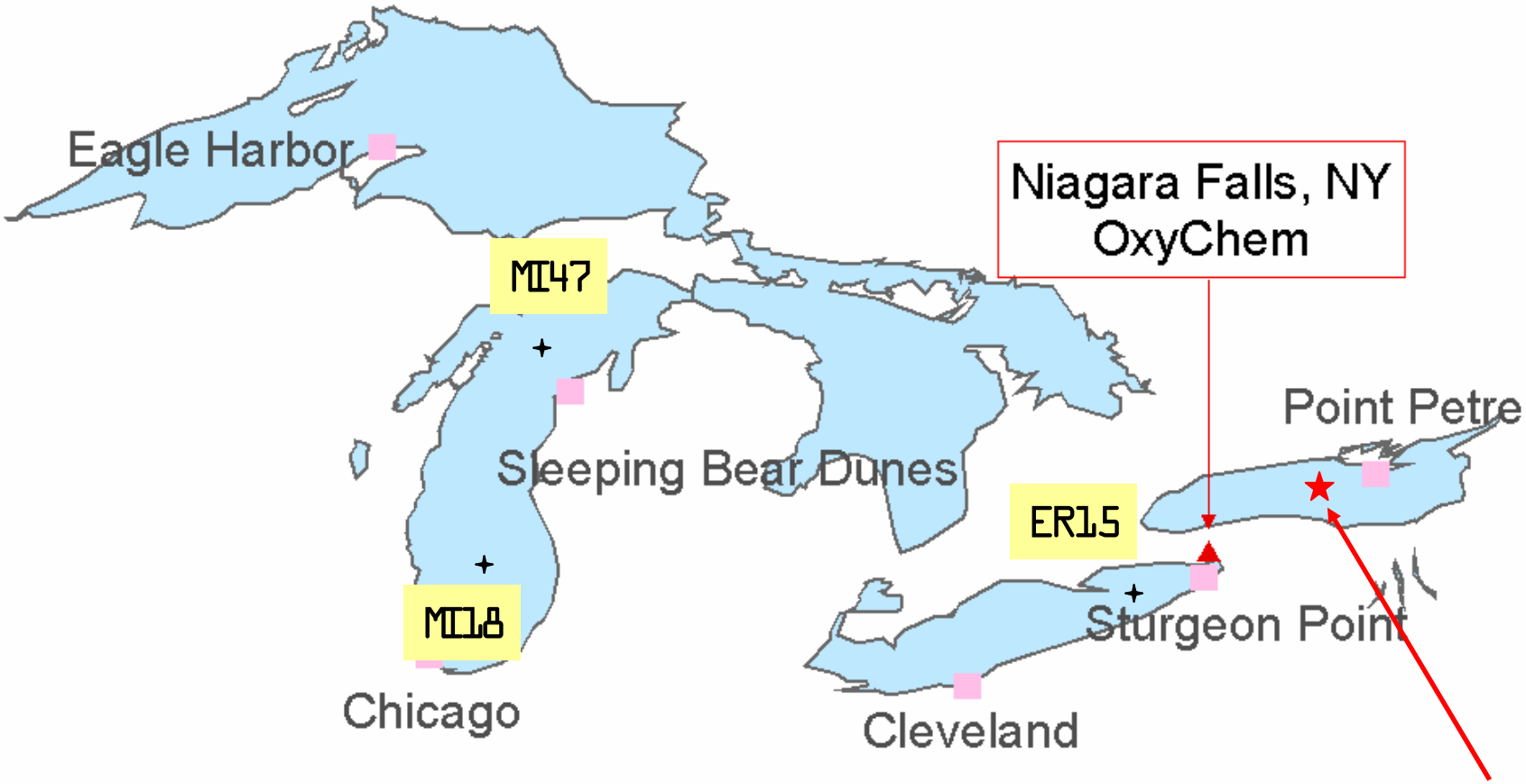
(number of samples above detection limit/number of samples for analysis)

Comparison with Decabromodiphenyl Ether

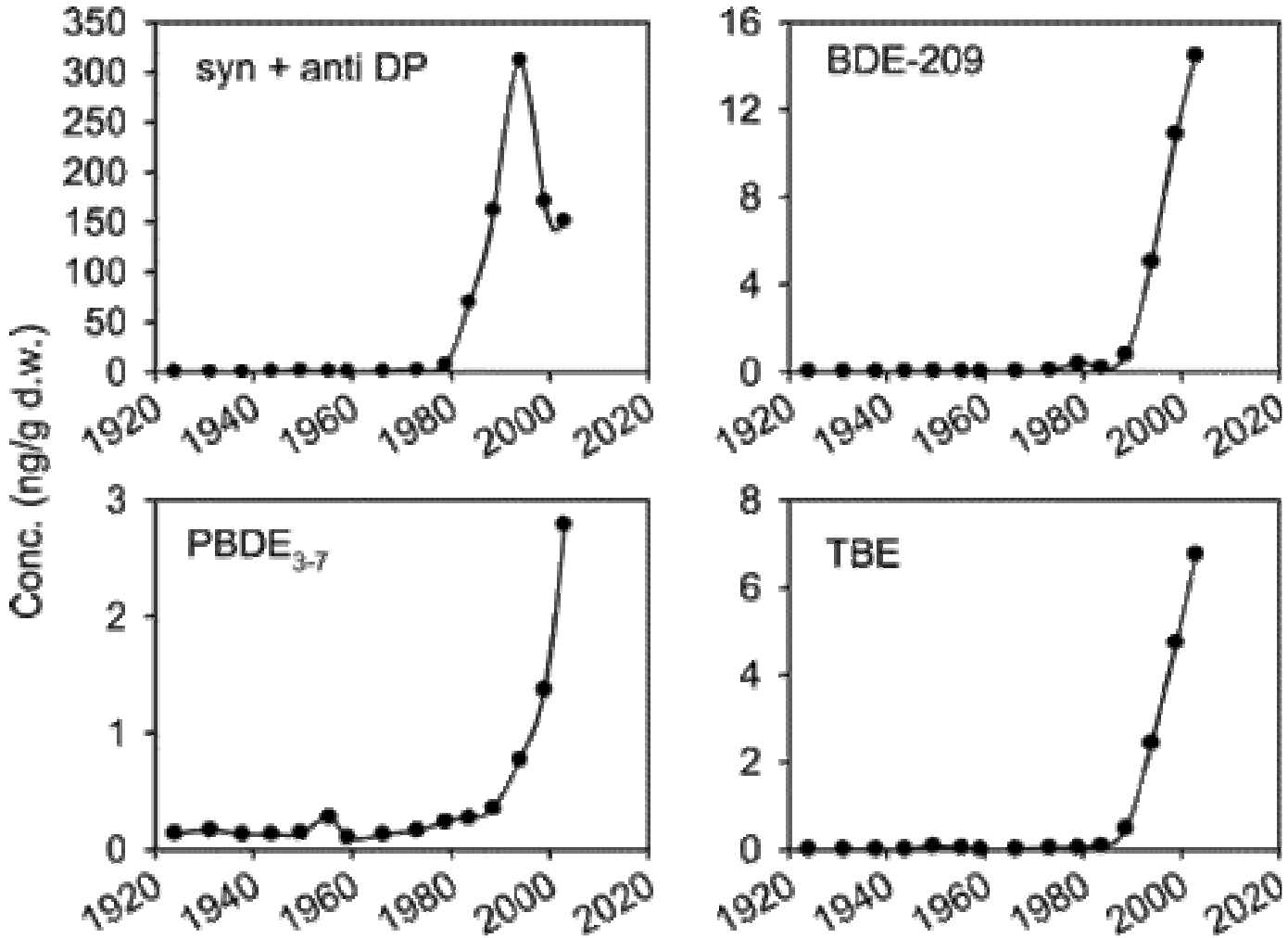


Manufacturing Plants of Dechlorane Plus

Hot Spot of Dechlorane Plus in Great Lakes: Lake Ontario



DP and other BFRs in a Sediment Core from Lake Ontario



Source: Qiu et al., ES&T 2007, 41, 6014-6019

Introduced in ES&T News: DP was detected in the environment for the first time >20 years later after its introduction

Environmental News

A new fl

"The identification of Dechlorane Plus in the environment, *so* many years after the introduction of the compound, really shows the importance of researchers going [after] new environmental contaminants," says Åke Bergman of

Researchers analyzed samples taken from the Integrated Atmospheric Deposition Network. The IADN sites where samples were taken are shown with a ■. The scientists analyzed archived sediment samples from sites shown with a ●. The location where OxyChem manufactures Dechlorane Plus is shown with a ★.

"I see this paper as a wake-up call," Birnbaum says. She says that the paper makes clear that

is indeed disturbing that new organochlorines are still to be detected in our environment, 40 to 50 years after the discovery of DDT in the environment," he adds.

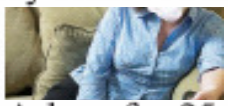
nology Branch. "My sense is that this paper will lead to other groups looking for this chemical," Harner concludes. —KELLYN S. BETTS

Old toxic flame retardant came back…

EDITORIAL

they concentrate in food chains and wind up in people, and aren't biodegradable. They discovered widespread use of a compound called tris(2,3-ibromopropyl) phosphate as a fire retardant in children's sleepwear. A mutagen and putative human carcinogen, it leeched into children's bodies. After a 1977 paper by Blum and Ames in *Science*, that use was banned. Well, the alert chemical industry quickly substituted a dichlorinated tris, which Ames and Blum also found to be mutagenic and was subsequently removed from sleepwear.

The history of residential fire risk is an interesting one, because it involves the tobacco industry. Remember them? They designed cigarettes that when dropped or put down, would smolder long enough to start a fire. For years, cigarette-lit fires were the greatest cause of fire-related deaths in the United States. After three decades of opposition from tobacco lobbyists, 22 states and Canada finally



was back at Stanford. I hadn't seen Arlene for 25 years or so, but a few months ago, she turned up with an extraordinary sequel to the tris story, which she tells of in a recent Letter in *Science*. Fire retardants are now widely used in furniture foam, and the second most-used compound is none other than chlorinated tris! In less than three decades, this highly toxic mutagen has moved from your child's nightgown to your sofa.

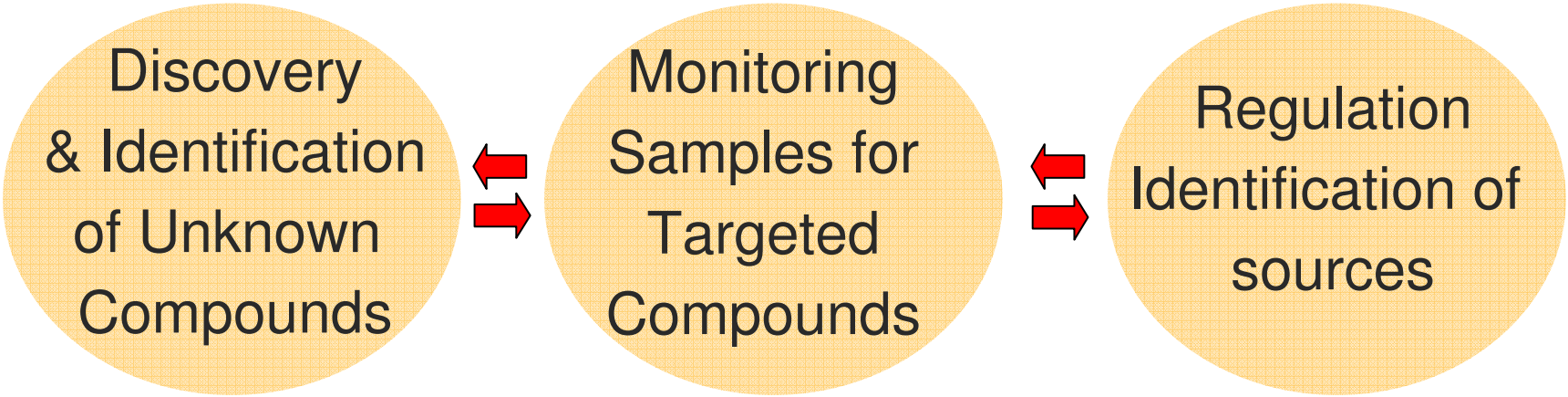
is about the same as that in states that do not regulate furniture flammability.

But the problem is a national one. The Consumer Product Safety Commission (CPSC) Reform Act (S 2045) toyed with a provision that would rush us into a national furniture flammability standard. That's premature, because it leaves no time to develop a safe way to reduce furniture flammability and puts potentially persistent toxic chemicals into U.S. homes. Congress should forget that approach. The real problem is that the U.S. regulatory system for toxic industrial chemicals is not effective and is a threat to public health.

In Europe, the chemical industry is required to establish safety before a product can continue to be marketed. The U.S. Toxic Substances Control Act (TOSCA) originally grandfathered existing chemicals, but none have been reexamined since the 1980s. Congress should abandon its attempt to attach a flammability standard to the CPSC, and instead turn to the real task of reforming TOSCA by introducing a real proof-of-safety provision. That would stop the chemical industry from continuing to make consumer protection look like a game of whack-a-mole.

– Donald Kennedy

Typical Monitoring Regulating Chemicals



- Newly identified previously unrecognized chemicals had been added to the list of the chemicals to monitor in IADN (PBDEs, Dechlorane Plus, TBE, HBCD etc).

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Are There Other Persistent Organic Pollutants? A Challenge for Environmental Chemists†

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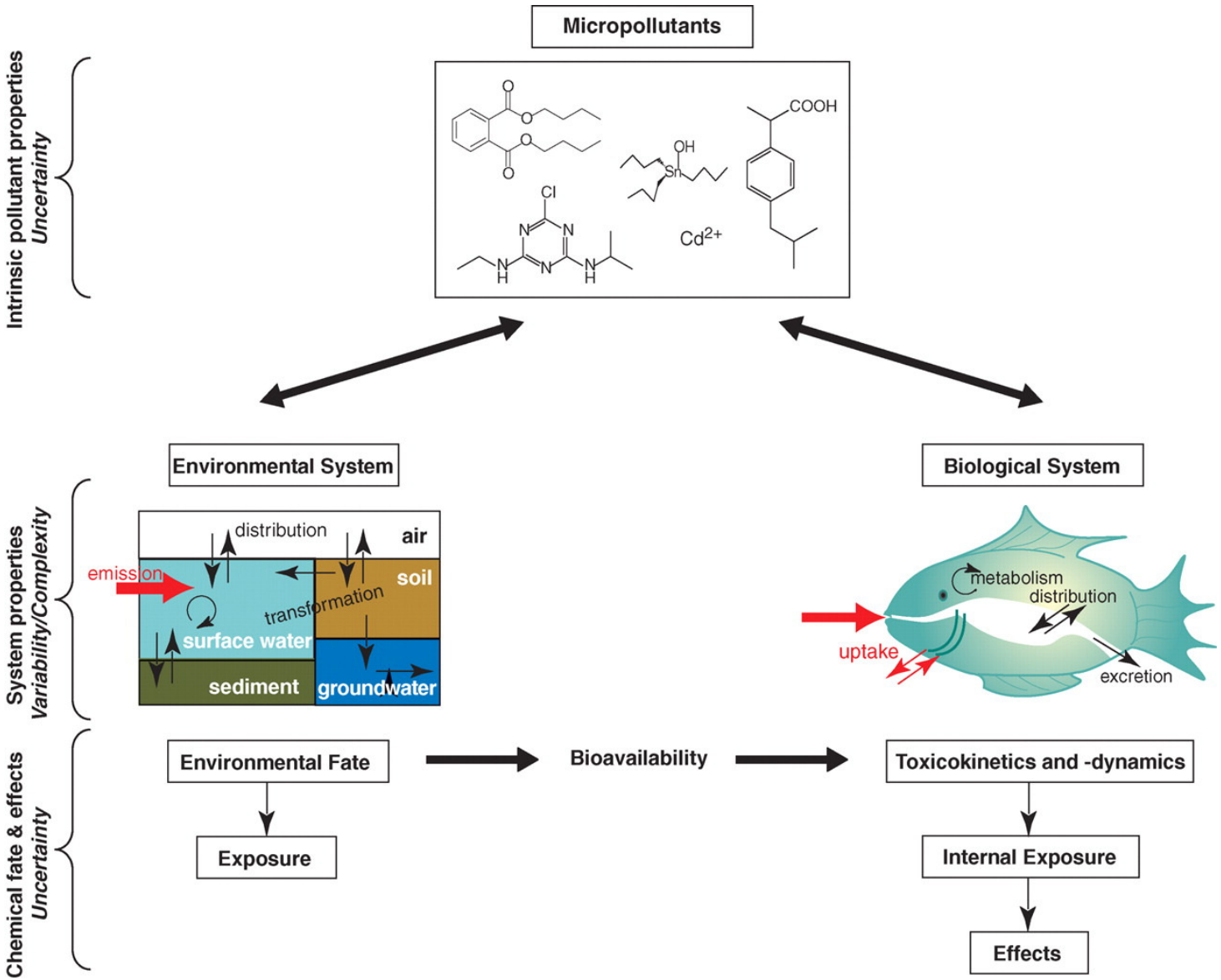
- Pro-active screening approaches have recently been suggested and studied. For example, environmental fate models have been used to screen hundreds of thousands of chemicals registered in a chemical database for their potential to act like POPs (Muir et al., ES&T 2006; Brown and Wania, ES&T 2008).

- This approach requires new analytical methods to cover such a wide range of chemicals (Muir et al., ES&T 2006).

- Furthermore, the ability to detect metabolites and environmental degradation products that do not appear in the database is critical.

The Challenge of Micropollutants in Aquatic Systems: Schwarzebach et al., Science 2006



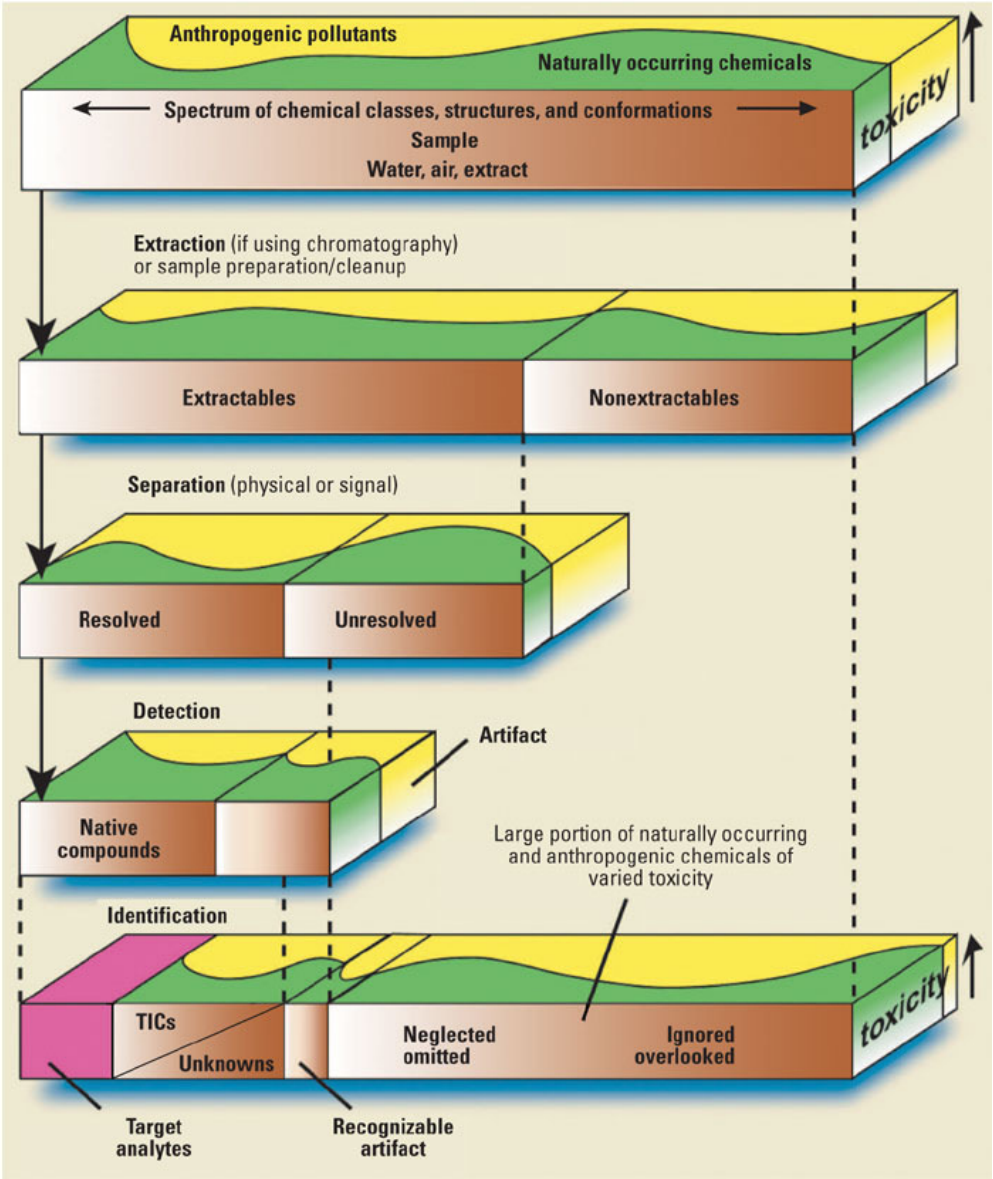
The Challenge of Micropollutants in Aquatic Systems: Schwarzebach et al., Science 2006

Scientific progress in aquatic micropollutant management clearly depends on interdisciplinary collaboration. Chemists and biologists must work together to harness the potential of new screening techniques for assessing the environmental impact of micropollutants; environmental chemists and engineers must strive to develop synergies between pathogen removal and the oxidation of micropollutants in water-treatment technologies. Furthermore, given the importance of chemicals in modern societies, sustainable solutions can only be found through active involvement of all stakeholders, including consumers, chemical manufacturers, politicians, and public authorities. This cooperation requires that pertinent topics in environmental chemistry, toxicology, and engineering be accorded a more prominent status in future curricula in chemistry, engineering, and the life sciences. With this article we hope to increase awareness of the urgency and global scale of the water-quality problems arising from micropollutants.

new compounds and other substances are constantly being incorporated into modern technology and hence into the environment, with insufficient thought being given to the implications of these actions. All of these issues assume added importance in urban areas, which concentrate flows of resources, generation of residues, and environmental impacts within spatially constrained areas. From a policy standpoint, reliable predictive models of material cycles could be invaluable in guiding decisions about . . . topics relating to human-environment interactions. . . .This grand challenge centrally encompasses questions about societal-level consumption patterns, since consumption is the primary force driving human perturbations of material cycles. (NRC 2001, p. 55)

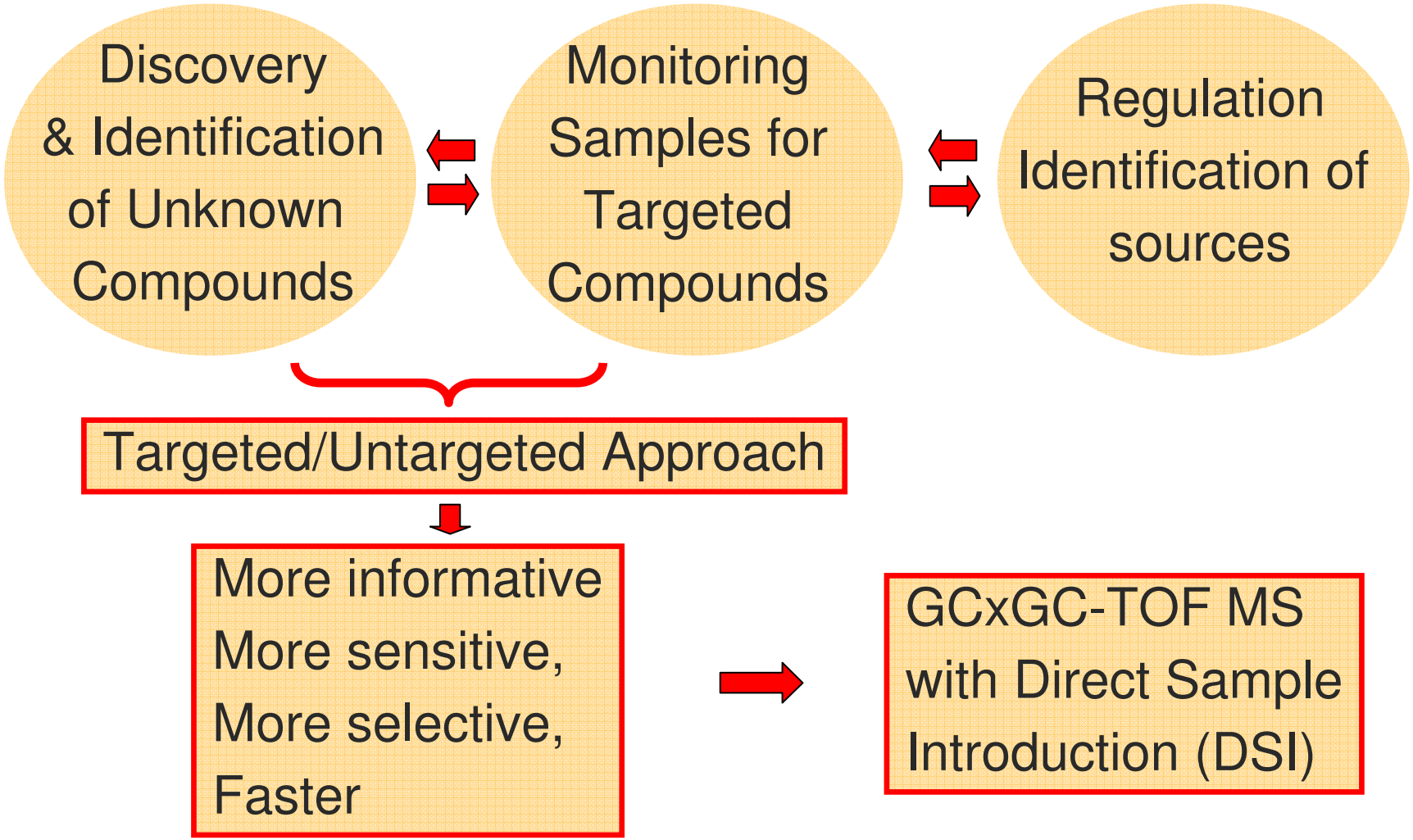
The chemical sea in which an organism develops, matures, and subsists comprises substances essential to life (nutrients) as well as those adverse to life-both naturally occurring xenobiotics and anthropogenic pollutants. The latter includes substances purposefully designed and synthesized (sometimes with the intent to adversely affect organisms, e.g., pesticides, antimicrobials) and those that are inadvertent (and sometimes hidden) by-products of manufacture, consumption, metabolism, and environmental transformation. This partial accounting of the potential chemical-exposure universe is immense, possibly comprising millions of substances. (Daughton JASM 2001)

Limitations and complexities of environmental chemical analysis



Source: C.G. Daughton, Environmental Health Perspectives, 111 (2003), 757.

Untargeted Analytical Approach for Organic Chemical Contaminants



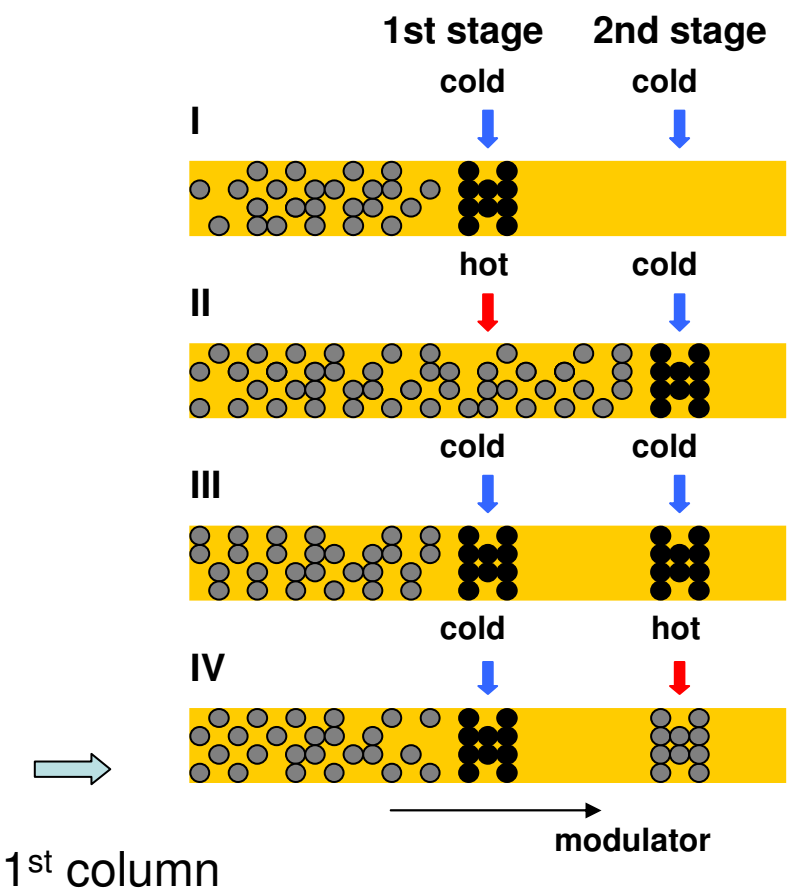
Objectives

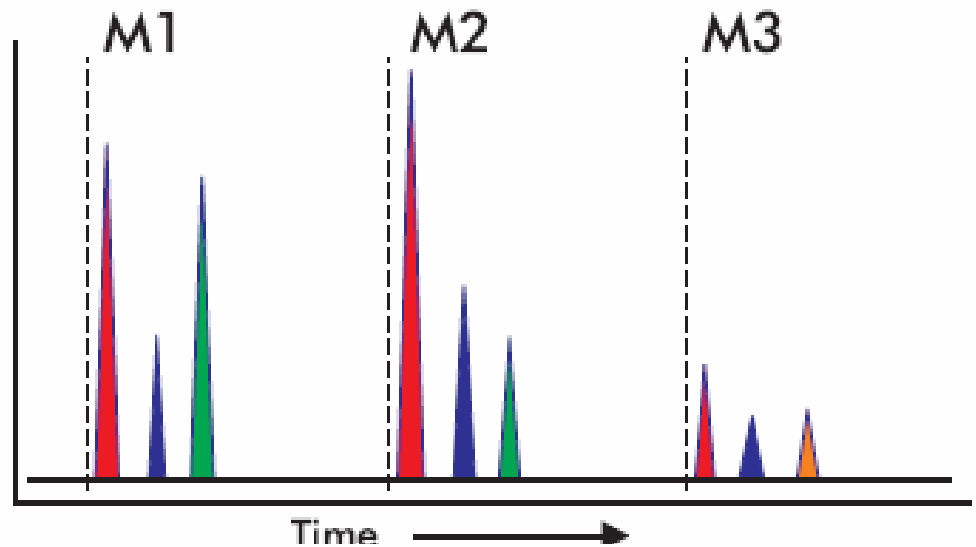
- Develop an efficient method using 2-dimensional comprehensive gas chromatography – time of flight mass spectrometry (GC×GC/TOF-MS) with direct sample introduction (DSI) that is able to identify and quantify many known, targeted persistent organic pollutants (POPs) in fish oils, and that also can identify unknown chemicals of interest.

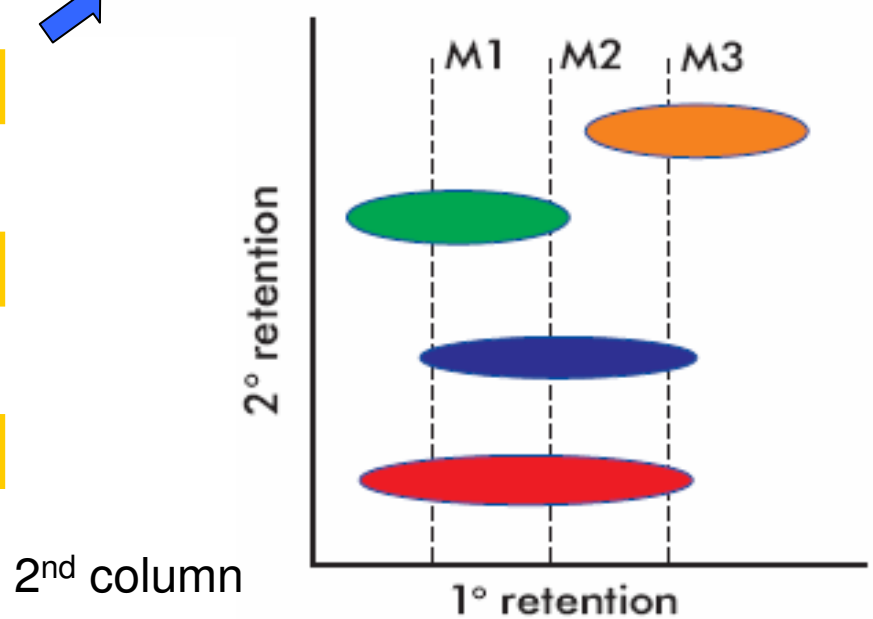
- Use this approach to analyze dietary cod liver oil supplement products and fish/dolphin oils from environmental samples.

- Obtain information for human and environmental exposure assessments.

2-D Comprehensive GC (GCxGC)







Ref: www.leco.com

Features of Time-of-Flight Mass Spectrometry (TOF-MS)

❖Full mass spectrum acquired
Powerful confirmation of compound in sample
❖Full mass range sensitivity
Low pg range for most compounds (GCxGC peaks)
❖Fast acquisition rates
Up to hundreds of spectra/sec
Defines narrow peaks from GCxGC
Range from 50-200 ms wide

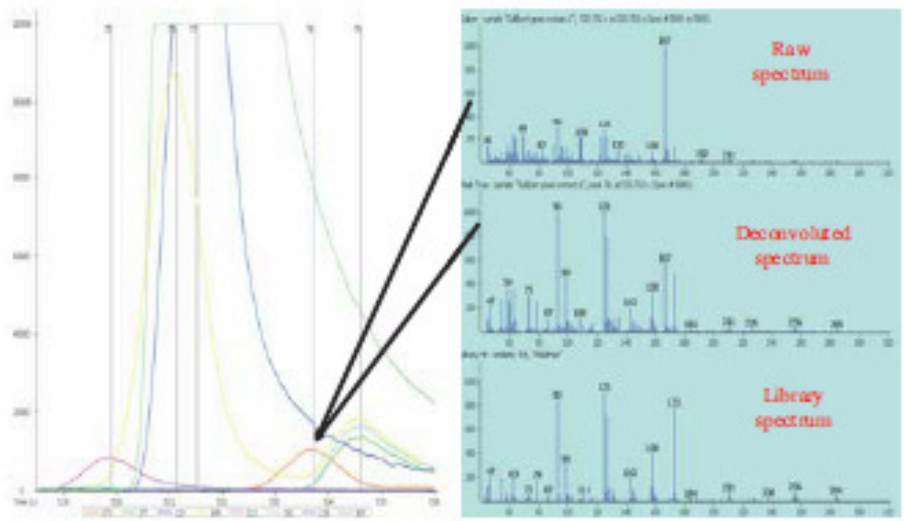


Figure 2. Chromatogram of 125 pg Malathion (orange peak) in an ash leaves extract plotted with ions representing the matrix. The raw spectrum taken at the peak apex for Malathion hardly hints that Malathion may be present. The deconvoluted TOF mass spectrum, even though it contains some residual 167 ion from the huge matrix interference, matches well with a library spectrum.

http://www.leco.com/resources/application_note_subs/pdf/separation_science/-258.pdf

❖Automated peak find
Find compounds buried beneath matrix
Locate non-target compounds spectral deconvolution
❖Produce quality, library searchable mass spectra from coeluting peaks

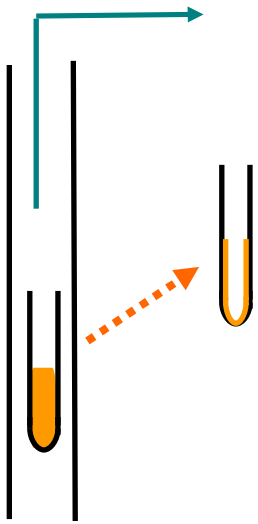
Direct Sample Introduction (DSI)

Originally invented by Amirav and colleagues

1) 10 μL of the sample placed in a microvial in a DSI liner:

Large volume injection up to 20 μL

2) The DSI liner is placed in the injection port



3) solvent evaporation (PTV)

4) analytes transferred to the GC column

5) The DSI liner *removed* together with *non-volatile matrix components*

DSI-GC×GC/TOF-MS advantages over conventional GC/MS

GC×GC	GC	Better resolution and sensitivity
TOF	Quadrupole	Full mass spectra with improved sensitivity Faster data acquisition Mass spectral deconvolution
DSI	Split/ splitless	Higher tolerance to dirty extracts Reduces sample preparation Expands analytical scope Enables large volume injection

METHOD

Materials: Three kinds of commercial dietary cod liver oil supplements (stored as liquid in bottles) and a dietary salmon oil (capsule type).

Instruments:

(a) LECO Pegasus 4D GCxGC/TOF-MS

(b) GL Science/ATAS/Leap Linex DSI

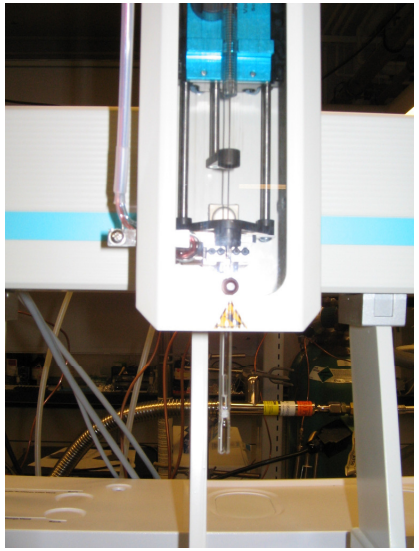
(d) J2 Scientific Automated Gel Permeation Chromatography

Instrument Conditions:

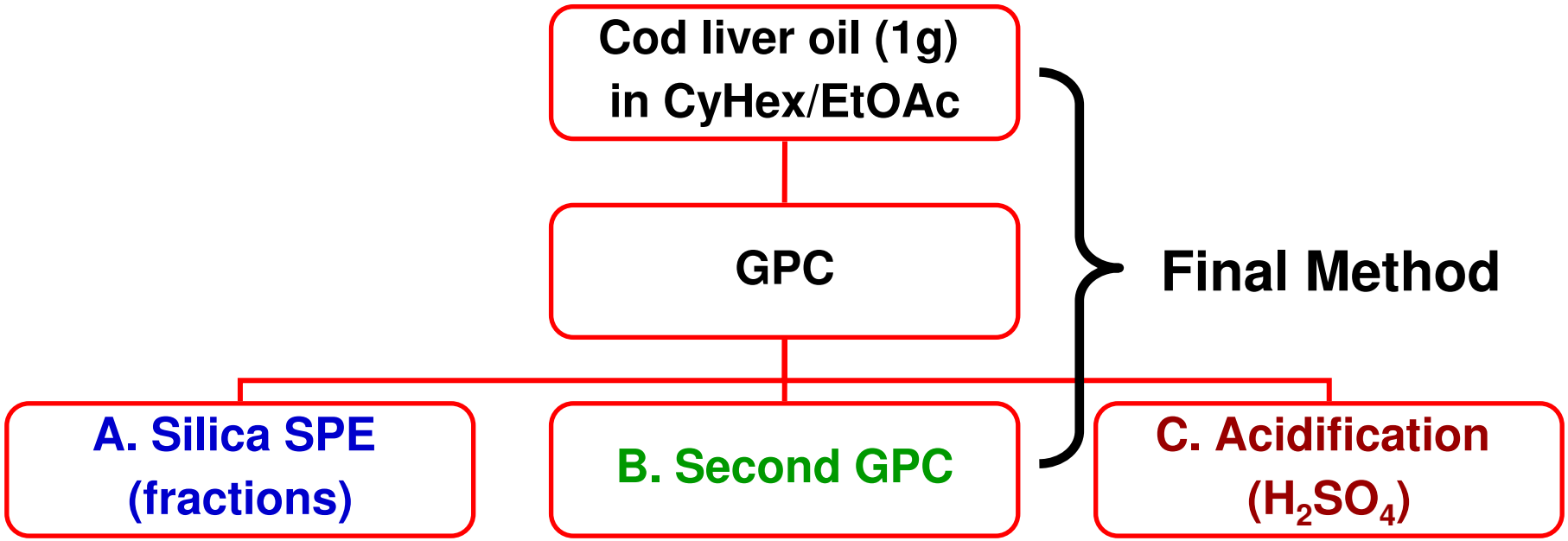
(a) GCxGC: 1D Restek Rtx-5Sil-MS (15 m, 0.25 mm i.d., 0.25 μm), 2D DB-17MS (2 m, 0.18 mm i.d., 0.18 μm), and 5-m guard column (0.25 mm i.d.). 3.5 sec modulation with 0.9 sec hot pulse

(b) TOF-MS: EI, 100 spectra/s in full scan

(d) DSI: 10 μL in automated DSI



Sample Cleanup Assessment



Cleaner but requires multiple injections	One injection for the multiple groups of POPs	Interferences from hydrocarbon breakdown products
Multiple injections required Fewer compounds detected	Largest number of untargeted halogenated compounds detected	Fewer compounds detected

Chemical separations were helpful to identify unknowns

Injection of the final cod liver oil extract after sample preparation

DSI-GCxGC-TOF MS

Peak find & NIST MS library search

Simultaneous analysis of multiple classes of POPs

PCBs, PBDEs,
Toxaphene, OCPs
(Chlordanes,DDTs, Mirex etc)
Hexabromobenzene
Tetrabromophthalic anhydride
Di/tri bromoindole

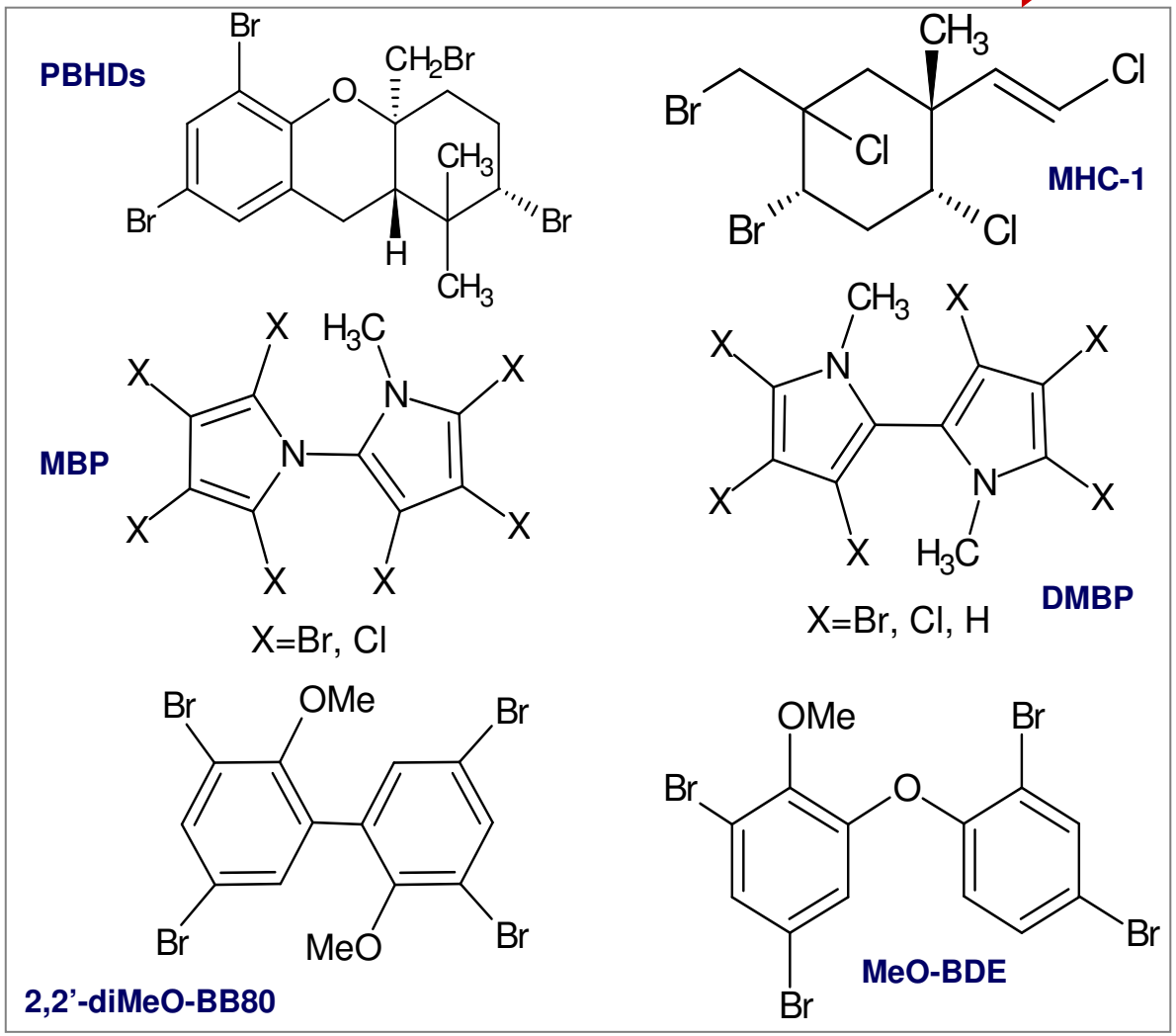
Untargeted Analysis

Unknown peaks of halogenated hydrocarbons using full MS & literature followed by confirmation with standards.
Identification of unknown peaks.

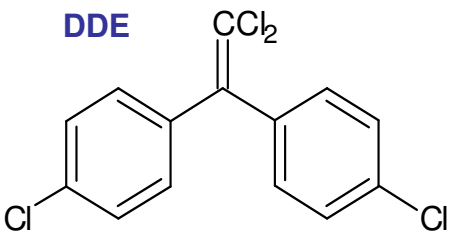
Degrees of Qualitative Analysis

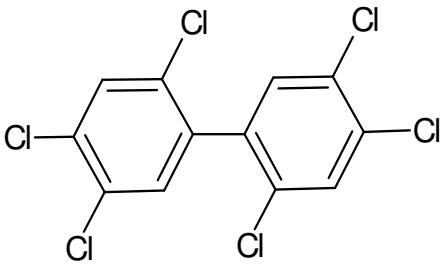
- Confirmation = two analyses agree with GC-MS identification vs. reference standards
- Identification = GC-MS match vs. ref. stds.
- Presumptive Identification = MS match vs. NIST spectral database
- Pretty Good Idea = MS match vs. description in the literature.
- Educated Guess = MW and isotope pattern?
- No Idea = gives a GC peak and MS

Some unknown peaks were identified to be halogenated natural products (HNPs) by comparing with authentic standards.



Some Known POPs





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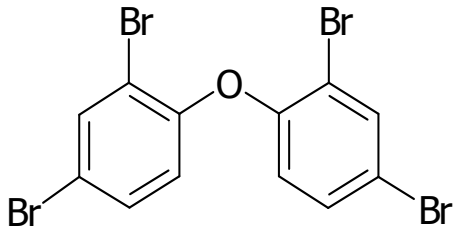
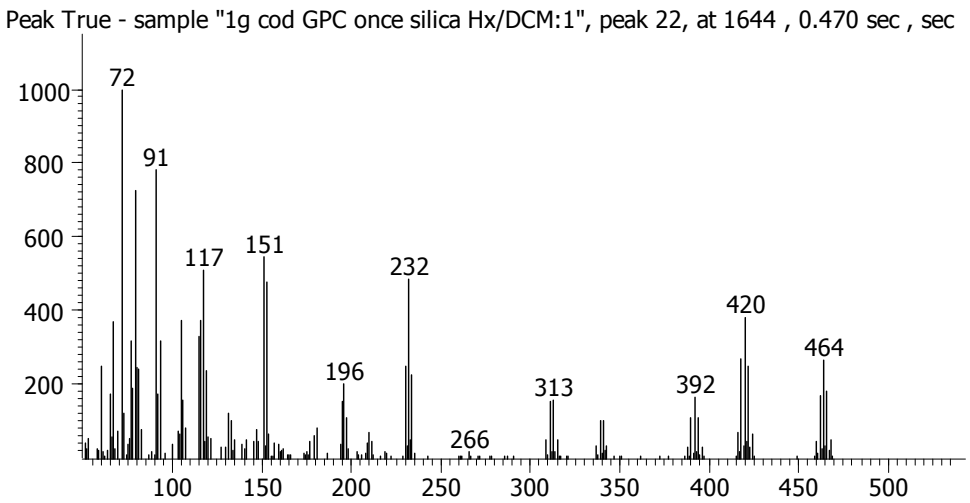


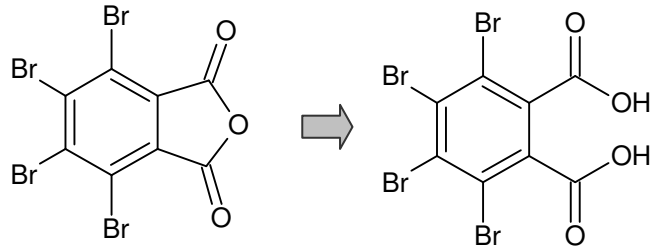
2,2',4,4'-tetrabromodiphenyl ether

BDE-47

Unexpected Compounds



NIST library search suggests

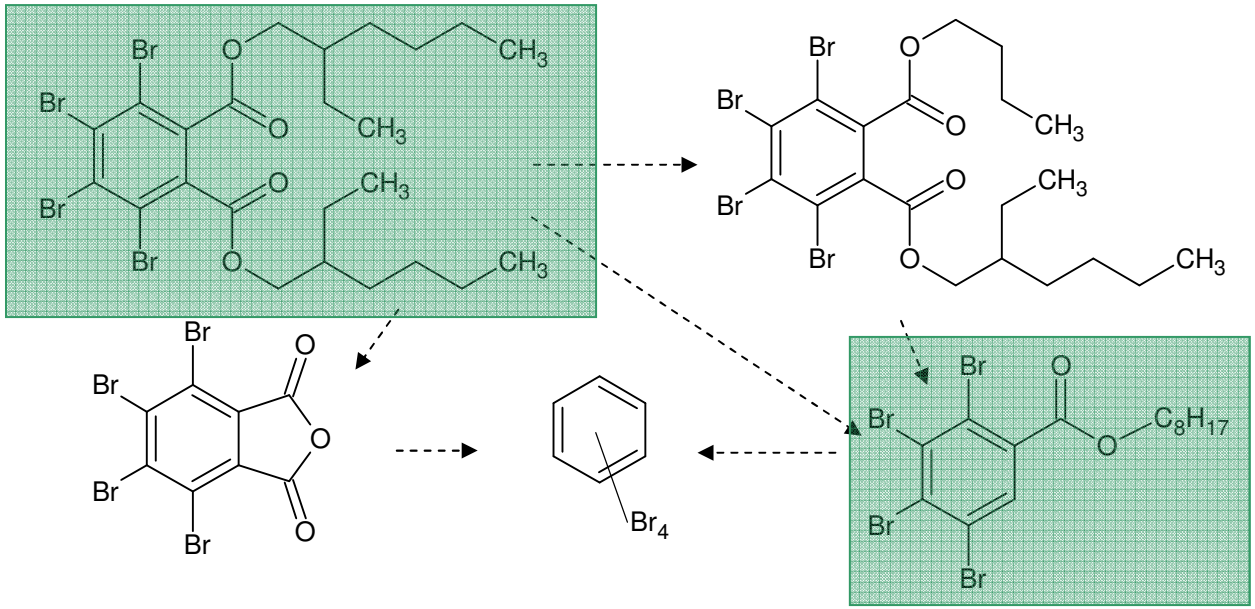


Log BCF=3.9 Log BCF=0.5

(bioconcentration factor)

<u>But its source</u>

Its Sources and Their Degradation Pathways



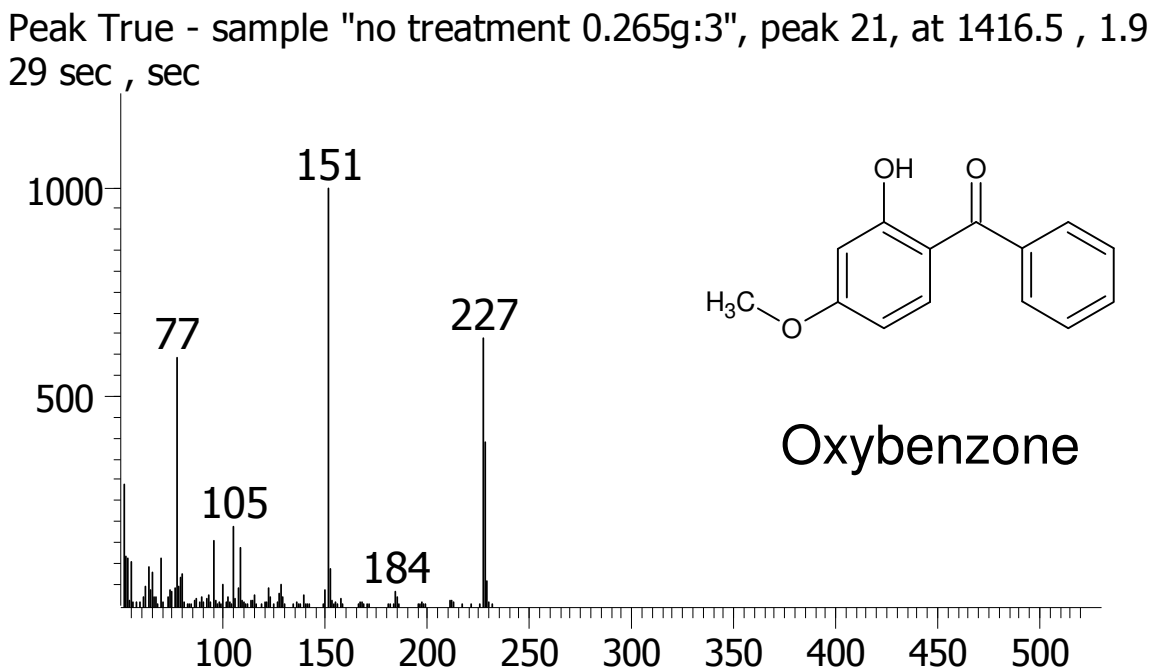
Major compounds in Firemaster 550 (flame retardant)

bis-(2-ethylhexyl)-tetrabromophthalate

2-ethylhexyl 2,3,4,5-tetrabromobenzoate

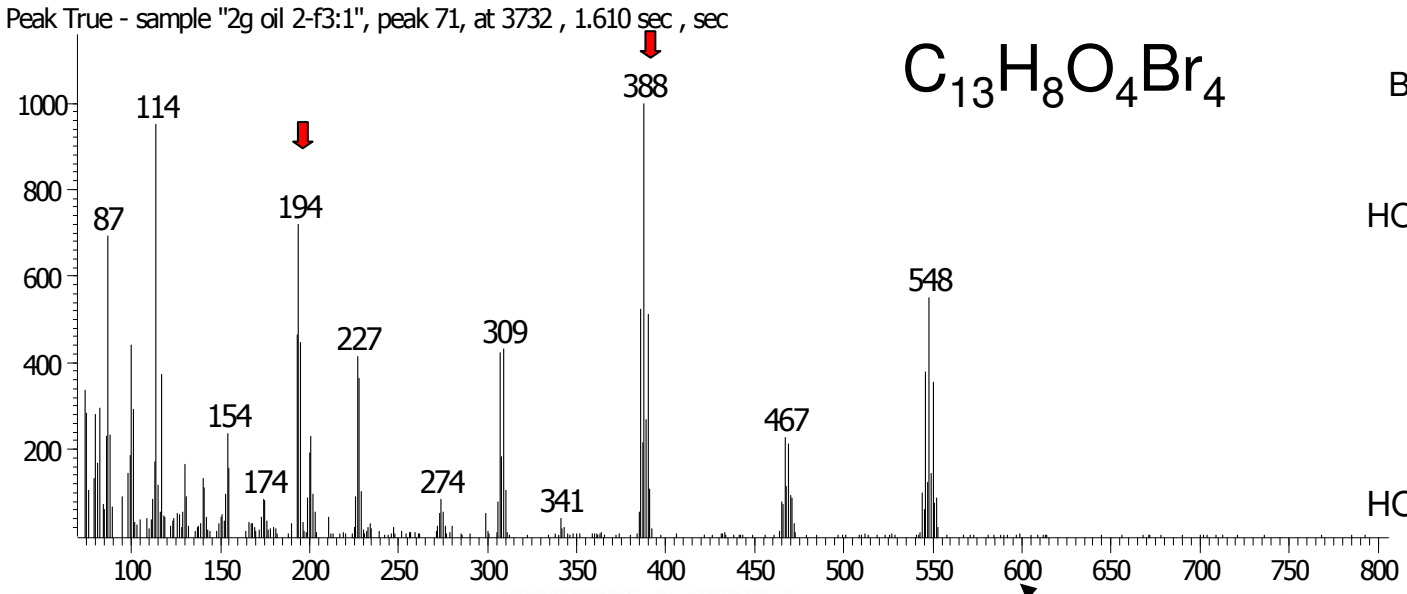
Source: GPC parts?

Unexpected Compounds

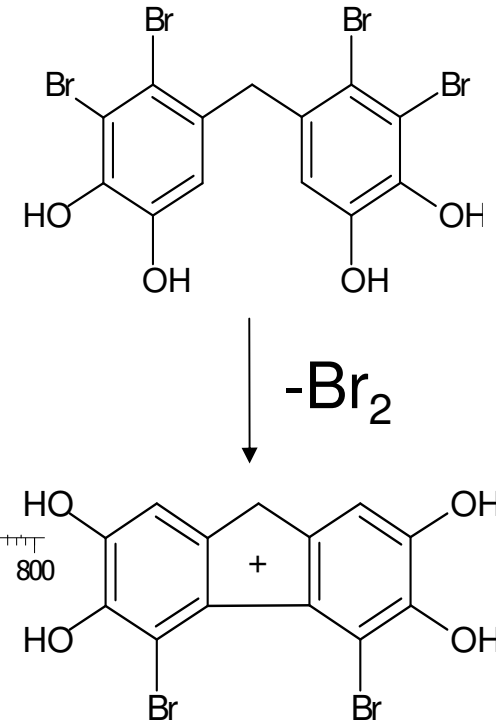


- Common sunscreen agent (toxic)
- Also called Benzophenone-3
- Possible source may be from packaging material containing oxybenzone as a UV stabilizer.

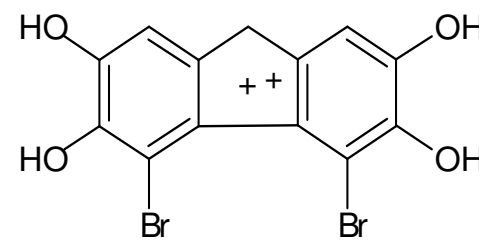
Some unknown peaks are presumptively identified based on their mass spectra.



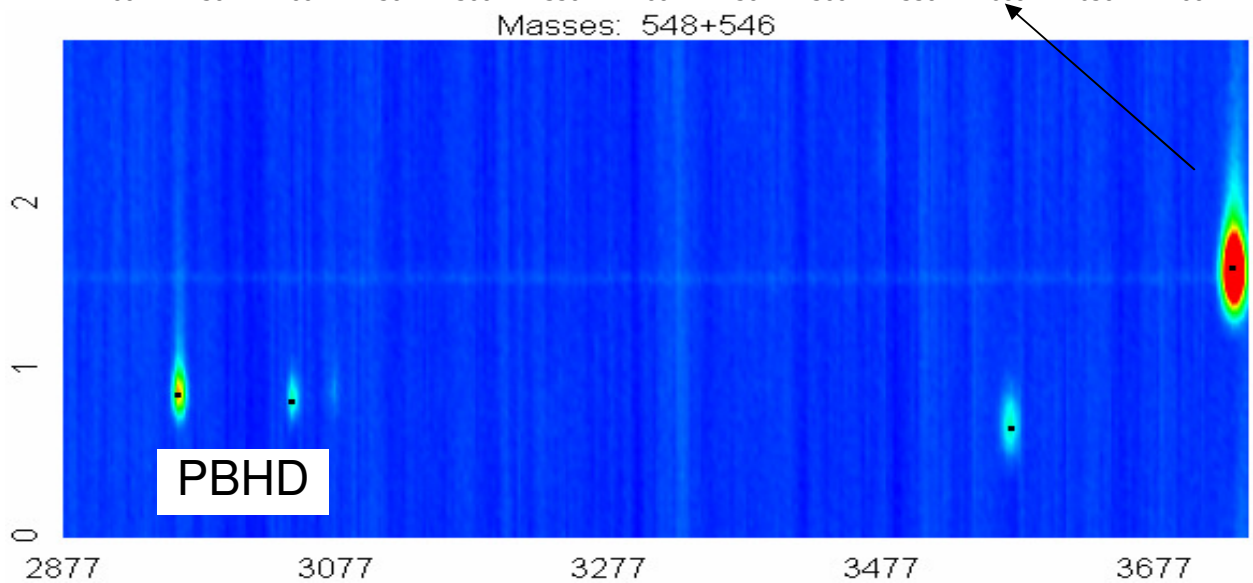
$C_{13}H_8O_4Br_4$



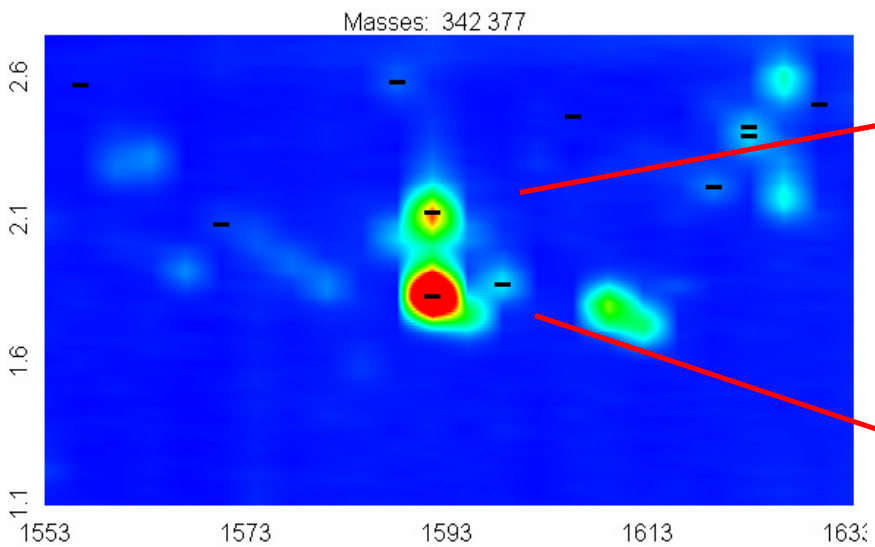
m/z 388



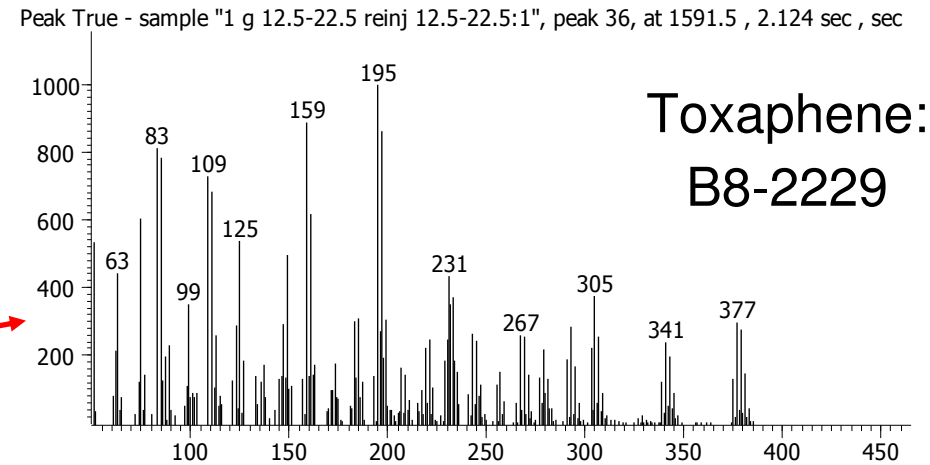
m/z 194

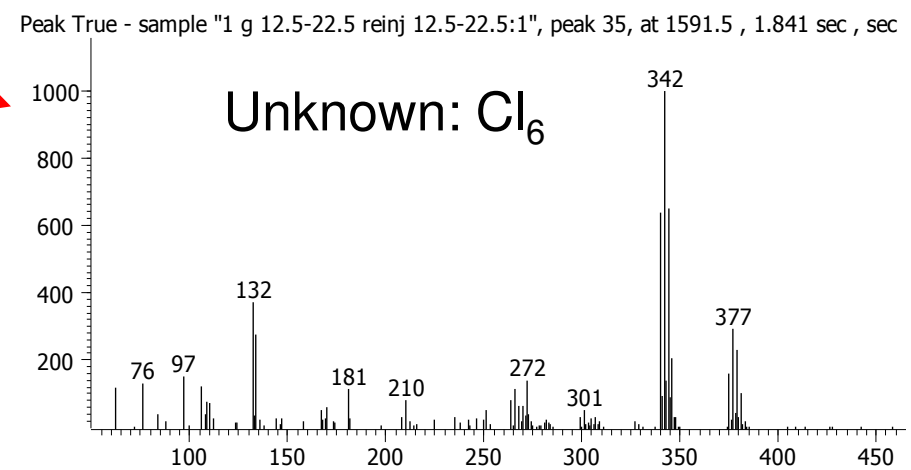


Some unknown peaks are presumptively identified based on their mass spectra.

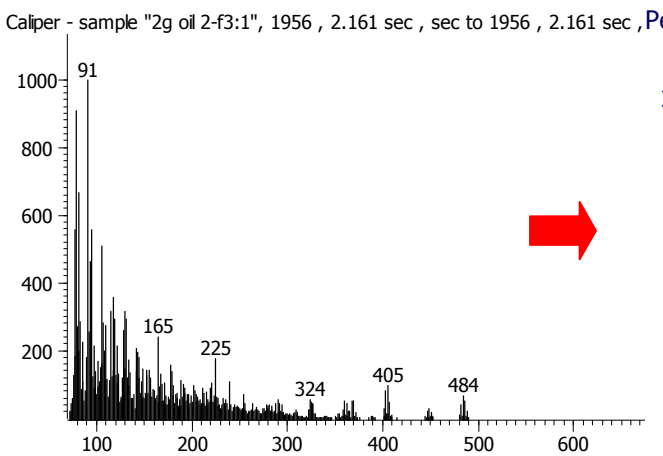


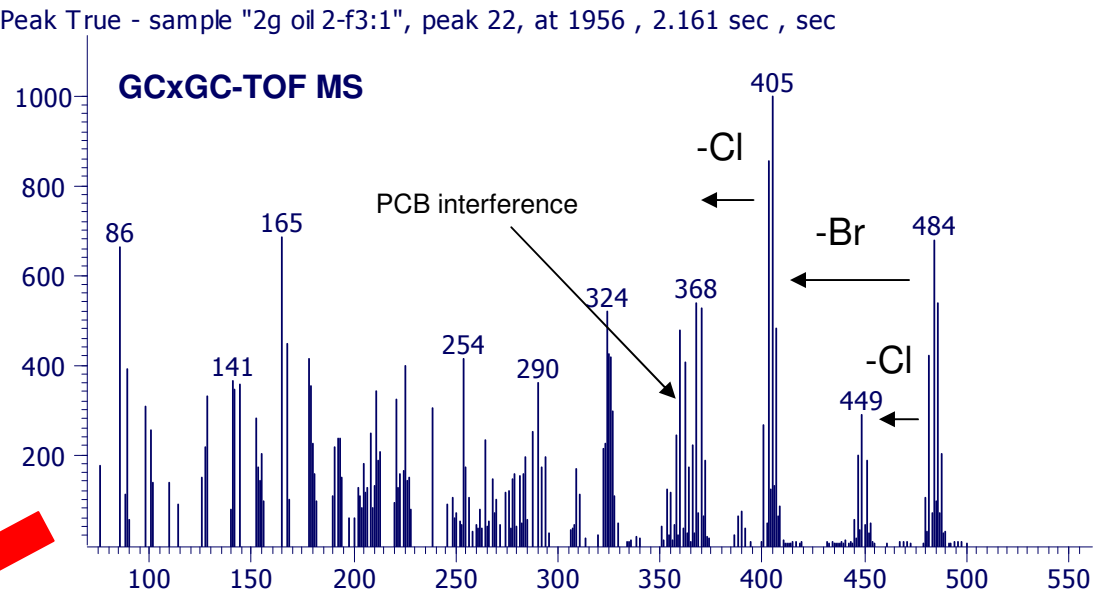
Separation by 2nd GC





Deconvoluted MS of Unknown Compounds



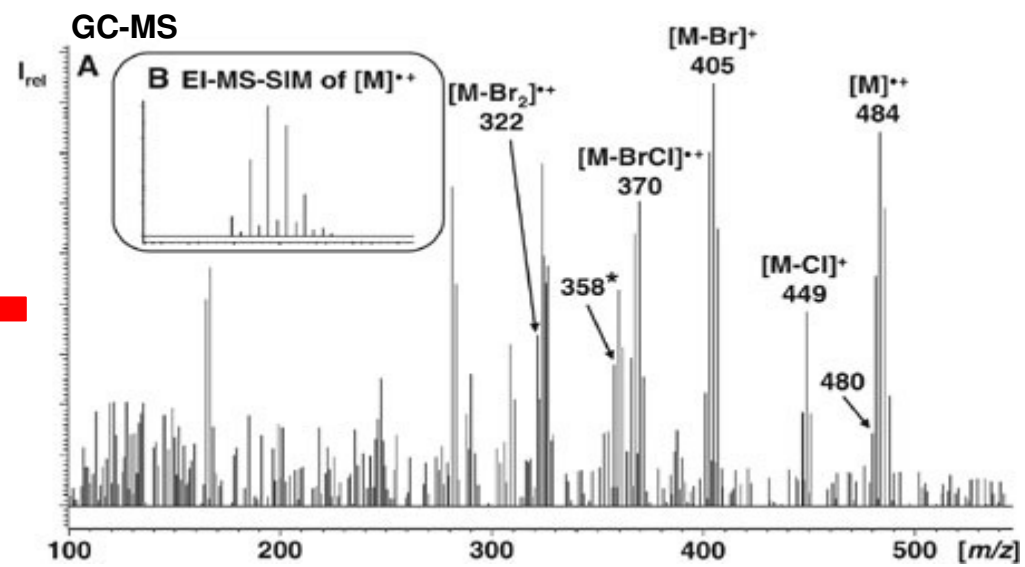


Br_4Cl:

$C_9H_5Br_4ClO$
$C_{10}H_9Br_4Cl$

Br_3Cl_3:

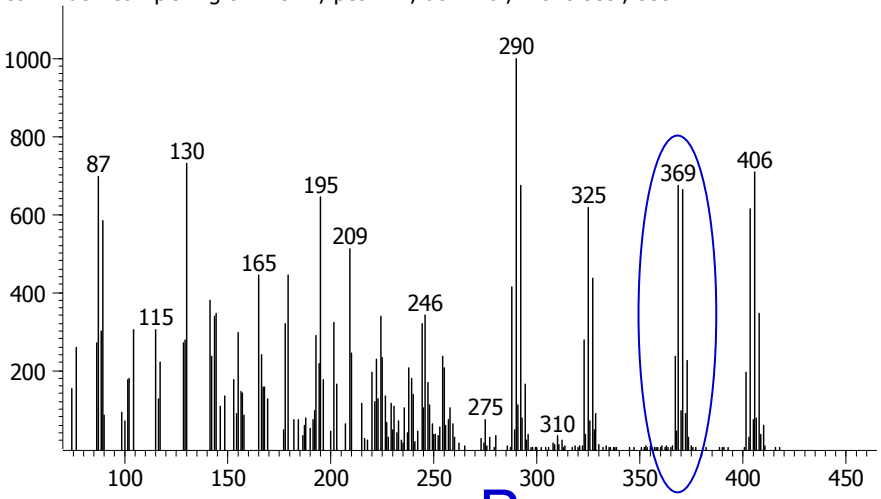
$C_9H_2Br_3Cl_3N_2$
$C_9H_{14}Br_3Cl_3O$
$C_{10}H_2Br_3Cl_3O$



Arch. Environ. Contam. Toxicol. 52, 512-518 (2007)

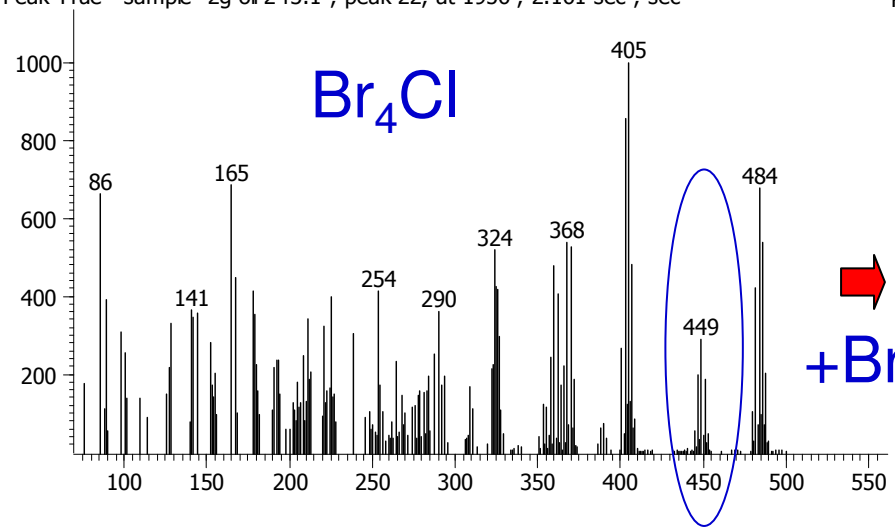
Its Related Compounds

Peak True - sample "2g oil 2-f3:1", peak 11, at 1776 , 1.820 sec , sec



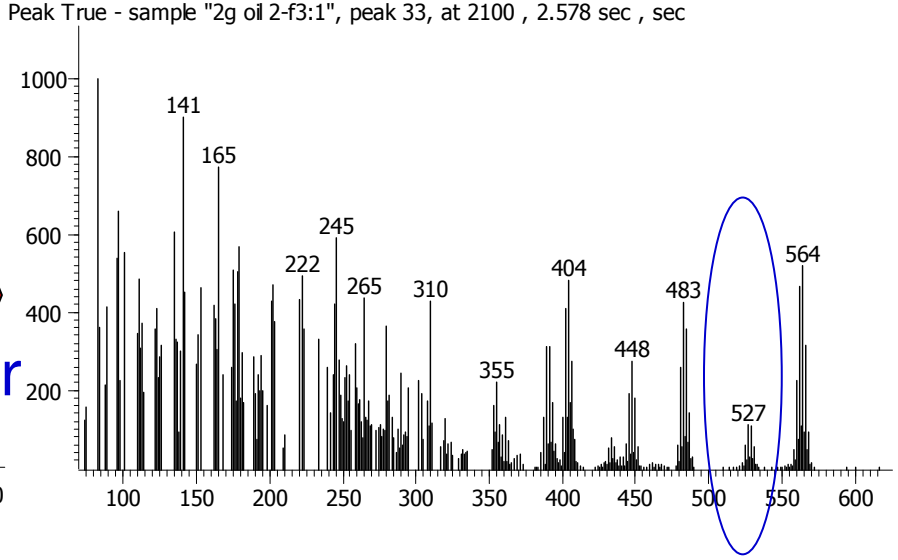
-Br

Peak True - sample "2g oil 2-f3:1", peak 22, at 1956 , 2.161 sec , sec

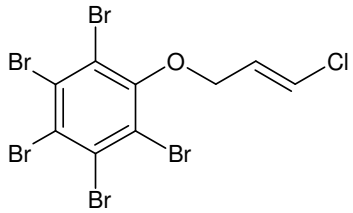


+Br

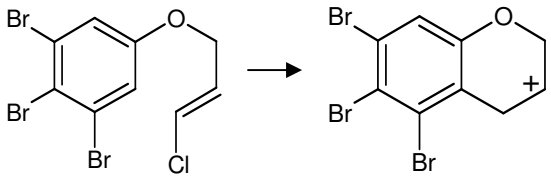
Peak True - sample "2g oil 2-f3:1", peak 33, at 2100 , 2.578 sec , sec



Possible chemical structures

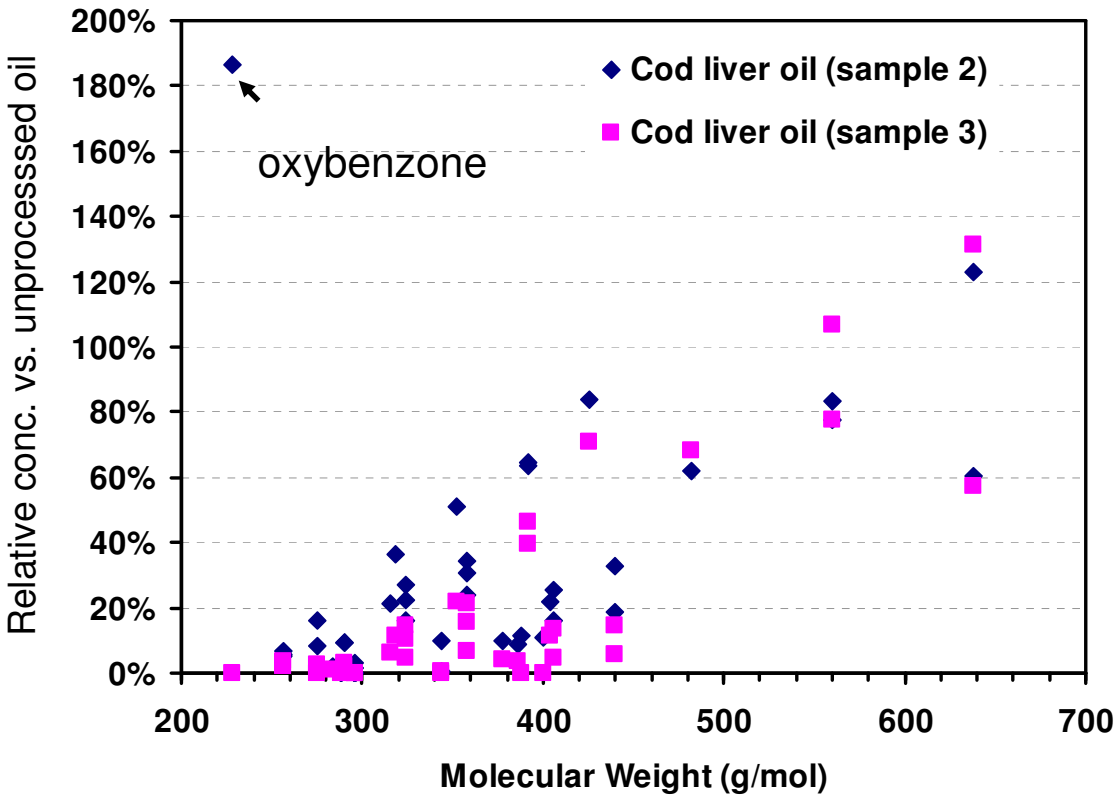


$C_9H_4Br_5ClO$



Processing of Cod Liver Oil Supplements

	Cod liver oil 1	Cod liver oil 2	Cod liver oil 3
Treatment	*No information*	*PCB and metal free*	*Moleculary distilled*
Origin	*Norwegian cod liver oil*	*Norwegian cod liver oil*	*Arctic cod liver oil*
Storage	*Liquid in amber plastic bottle*	*Liquid in amber plastic bottle*	*Liquid in amber glass bottle*
Brand	*A*	*A*	*B*
Oxybenzone	*370 ng/g*	*690 ng/g*	*nd*



- The commercial molecular distillation treatment used for removal of organic/inorganic toxic contaminants is only effective for the lighter organic contaminants.
- Oxybenzone might originate from its usage in the container as a UV stabilizer.

Human intake amount of POPs and HNPs per serving size (5 mL) of the cod liver oils

	Cod liver oil 1	Cod liver oil 2	Cod liver oil 3	Salmon oil
Treatment	*No information*	*PCB and metal free*	*Moleculary distilled*	*No information*
Origin	*Norwegian cod liver oil*	*Norwegian cod liver oil*	*Arctic cod liver oil*	*Wild Alaskan sockeye*
PCBs	602	177	92	334
OCPs	556	130	44	394
PBDEs	50.9	32.6	34.9	nd
HCB, octachlorostyrene, hexabromobenzene	42.1	1.03	0.34	115
Total POPs	***1250***	***341***	***171***	***843***
Dibromodimethoxybenzene, anisole, bromoindole, MHC-1	695	69.9	14.7	87
Q1 (MBP-Cl7)	14.8	1.72	nd	12.8
MBPs, DMBPs, methoxy-BDEs, BB-80, PBHDs	250	103	138	779
Total HNPs	***959***	***174***	***152***	***879***

Human intake: ~ 2.2 ug/serving size

Dolphin exposure to these mixture of contaminants?

- Dolphin is one of sentinel marine species.
- Oil extract from a blubber of a common dolphin (*Delphinus delphis*) which was fatally stranded in January 2006 in Orleans, Massachusetts, USA

Untargeted Analysis

Injection of the final dolphin oil extract after GPC cleanup

↓

DSI-GCxGC-TOF MS

↓

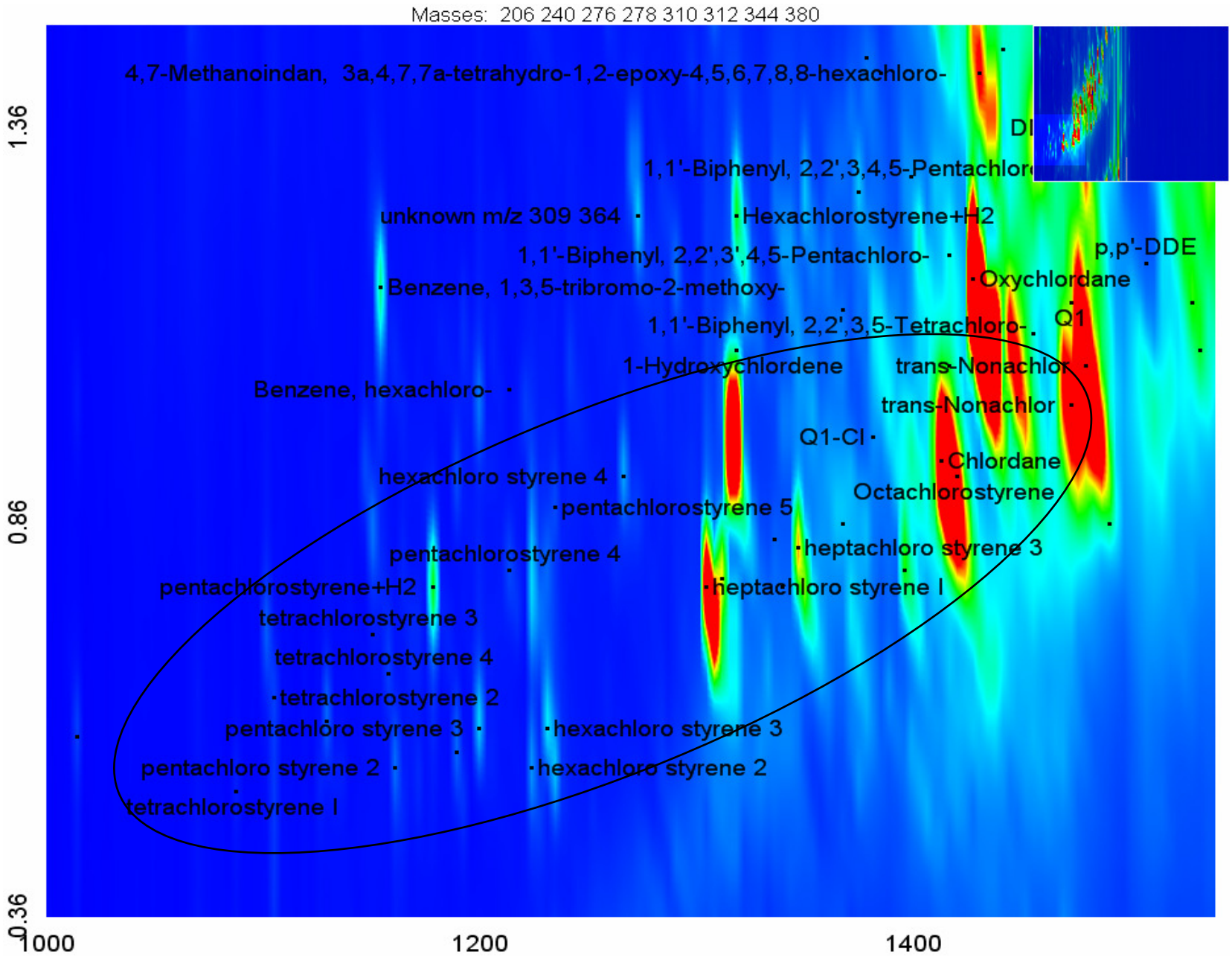
Peak finding of halogenated compounds &
NIST MS library search

↓

Well known POPs such as PCBs, DDTs, Toxaphene, Chlordanes, Heptachlor and Heptachloro epoxide, Mirex, and PBDEs were detected and confirmed with their authentic compounds.

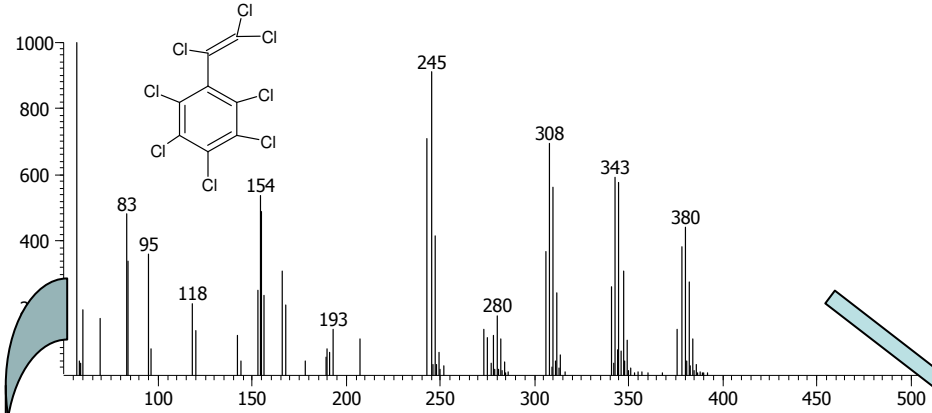
Other anthropogenic halogenated organic compounds and halogenated natural products were identified.

Octachlorostyrene and its related compounds

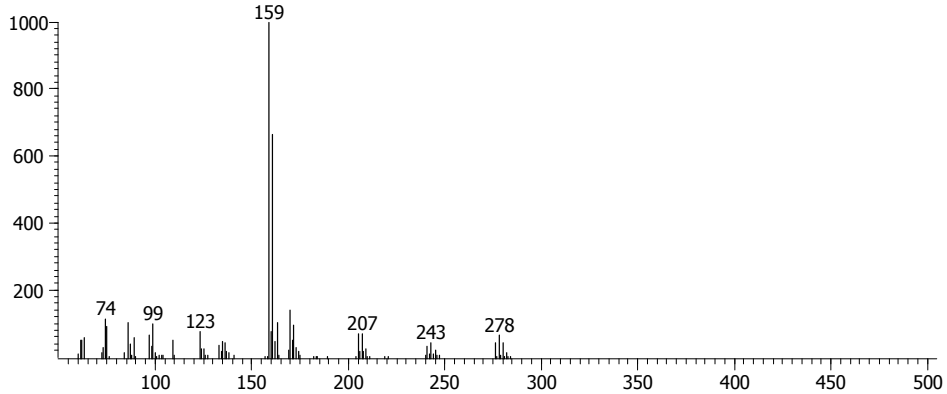


Some unknown peaks were identified to be polychlorostyrenes (trichloro – octachloro).

Peak True - sample "dolphin oil 1g GPC twice:1", peak 46, at 1420 , 0.920 sec , sec



Peak True - sample "dolphin oil 1g GPC twice:1", peak 11, at 1178.5 , 0.779 sec , sec

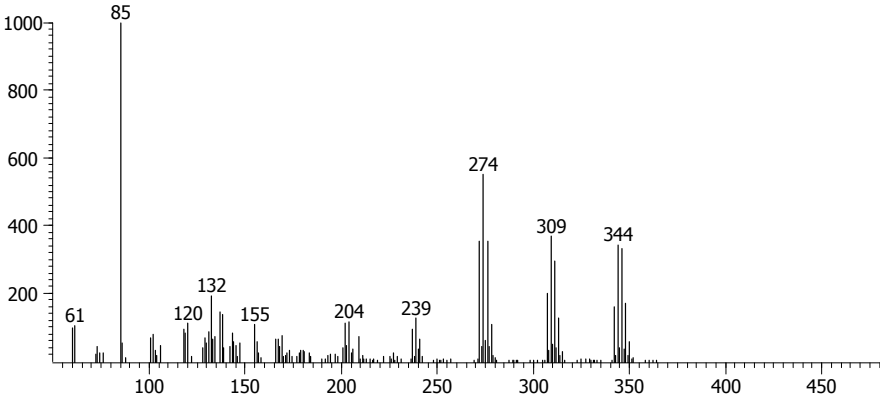


$-Cl_3$

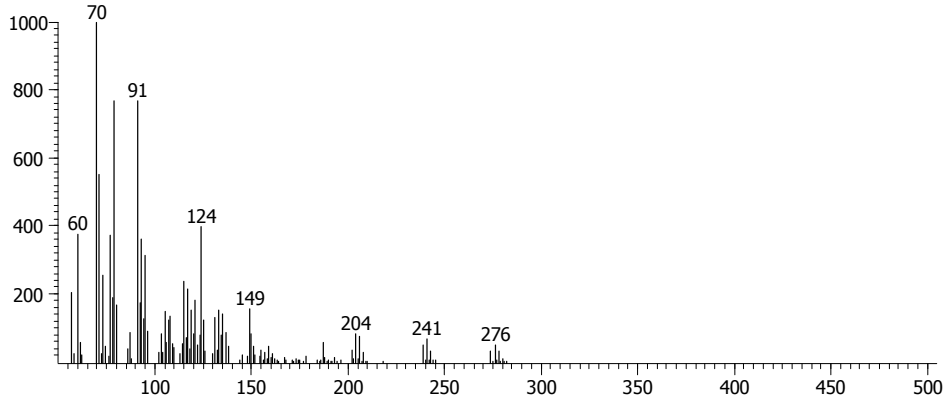
Hydrogenation?

-Cl

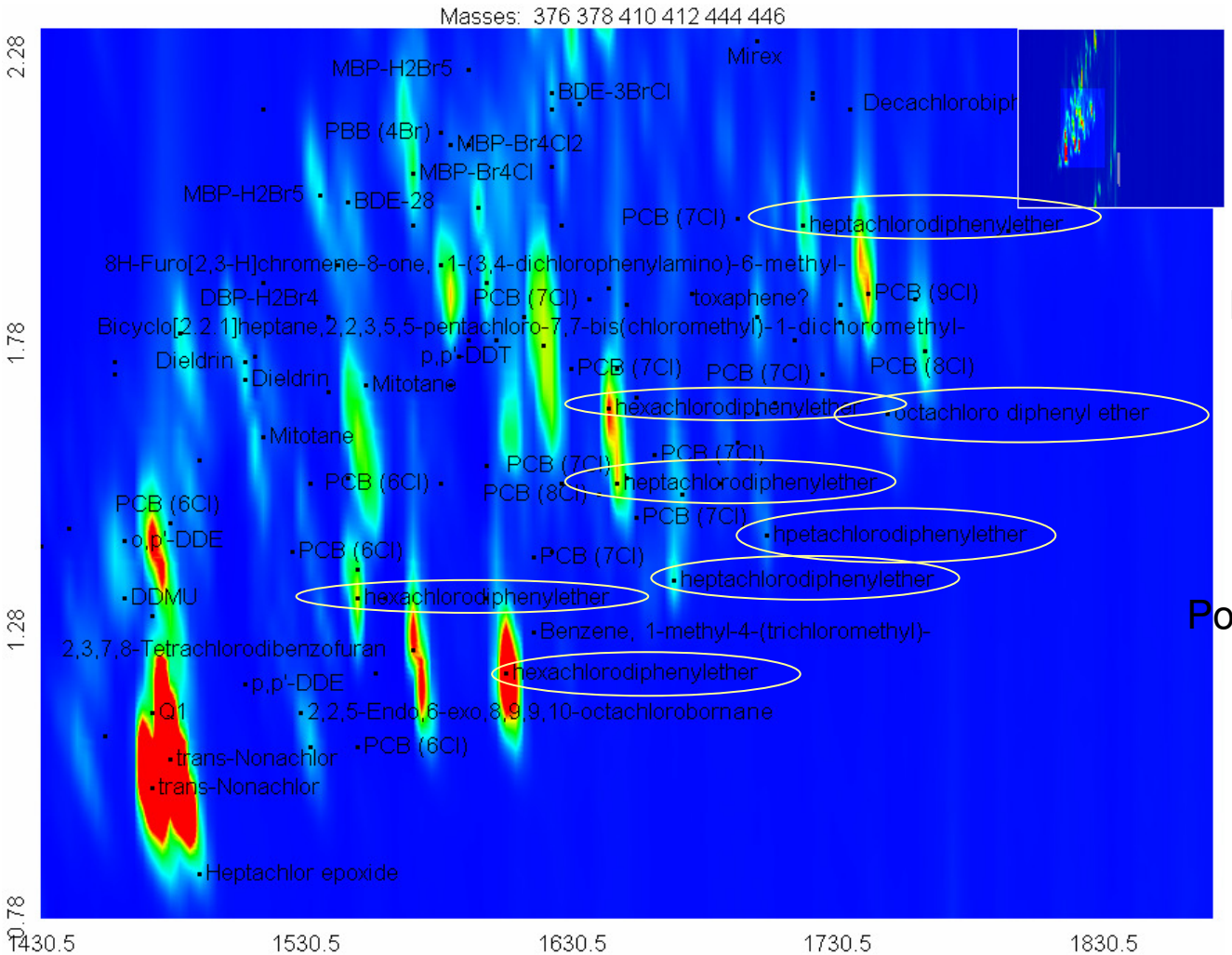
Peak True - sample "dolphin oil 1g GPC twice:1", peak 30, at 1346.5 , 0.830 sec , sec

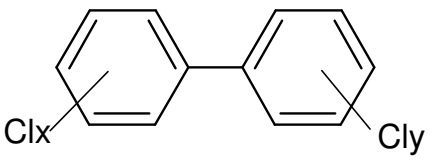


Peak True - sample "dolphin oil 1g GPC twice:1", peak 4, at 1129.5 , 0.617 sec , sec

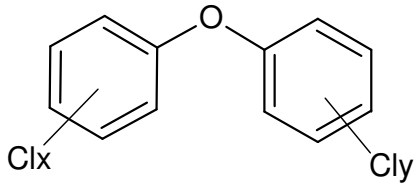


"Polychlorinated diphenyl ethers" are identified based on their mass spectra (hexa-octa: 12 congeners detected) and separated from PCBs



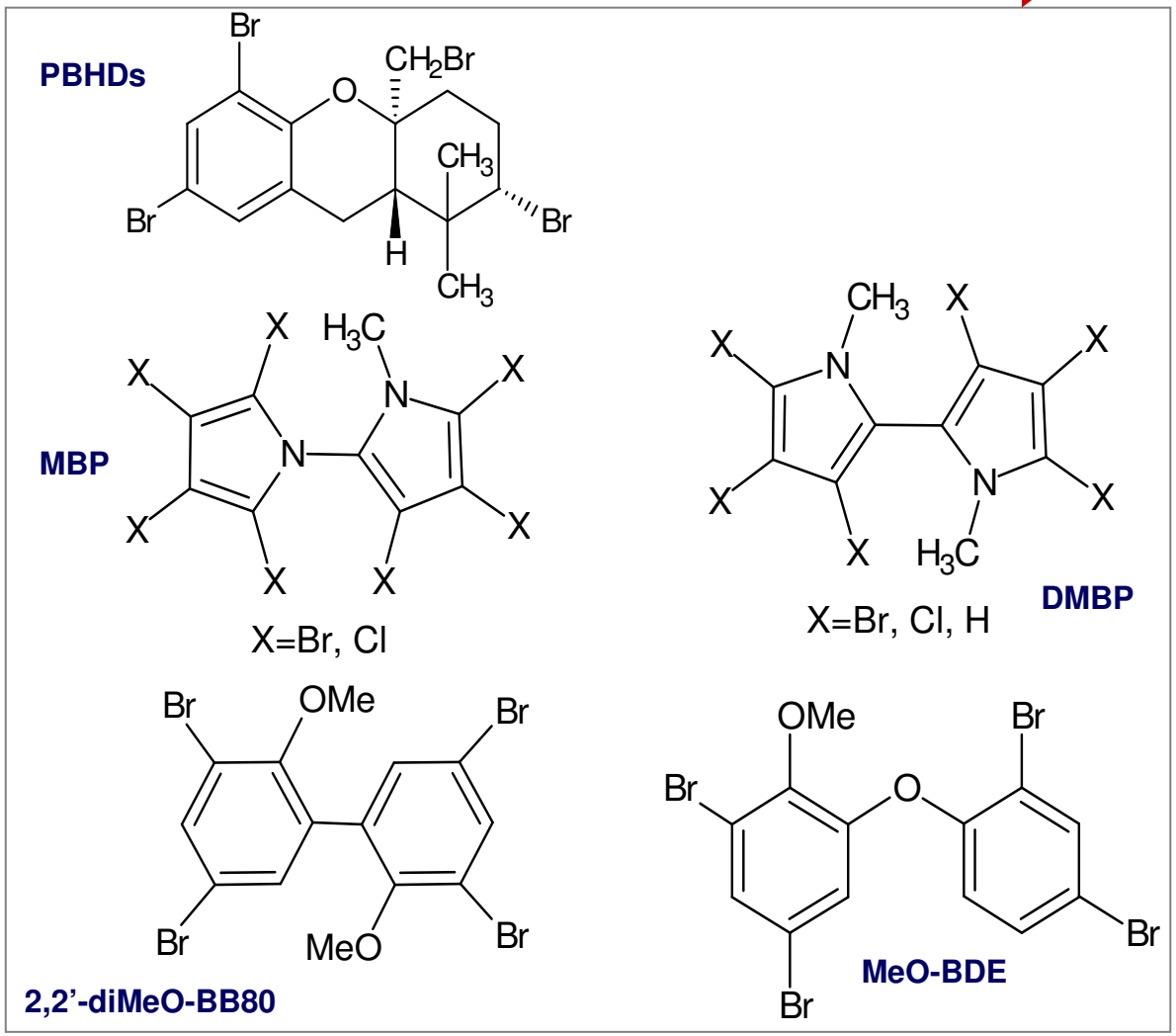


Polychlorinated biphenyl

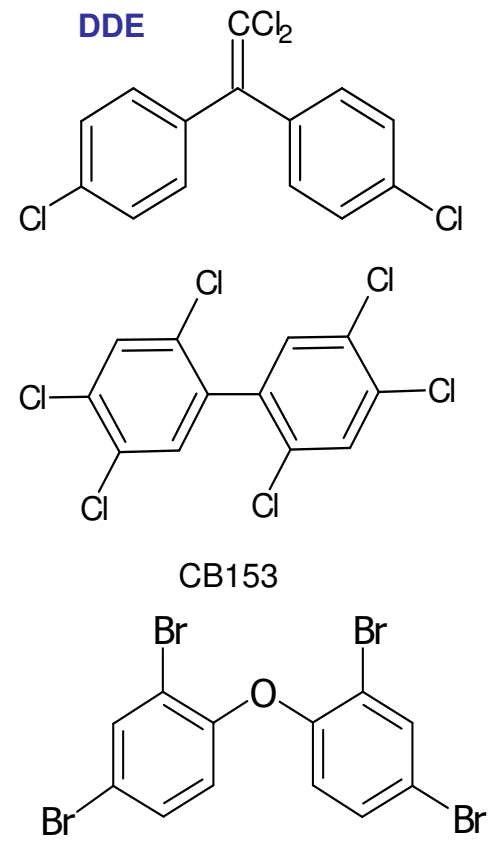


Polychlorinated diphenylether

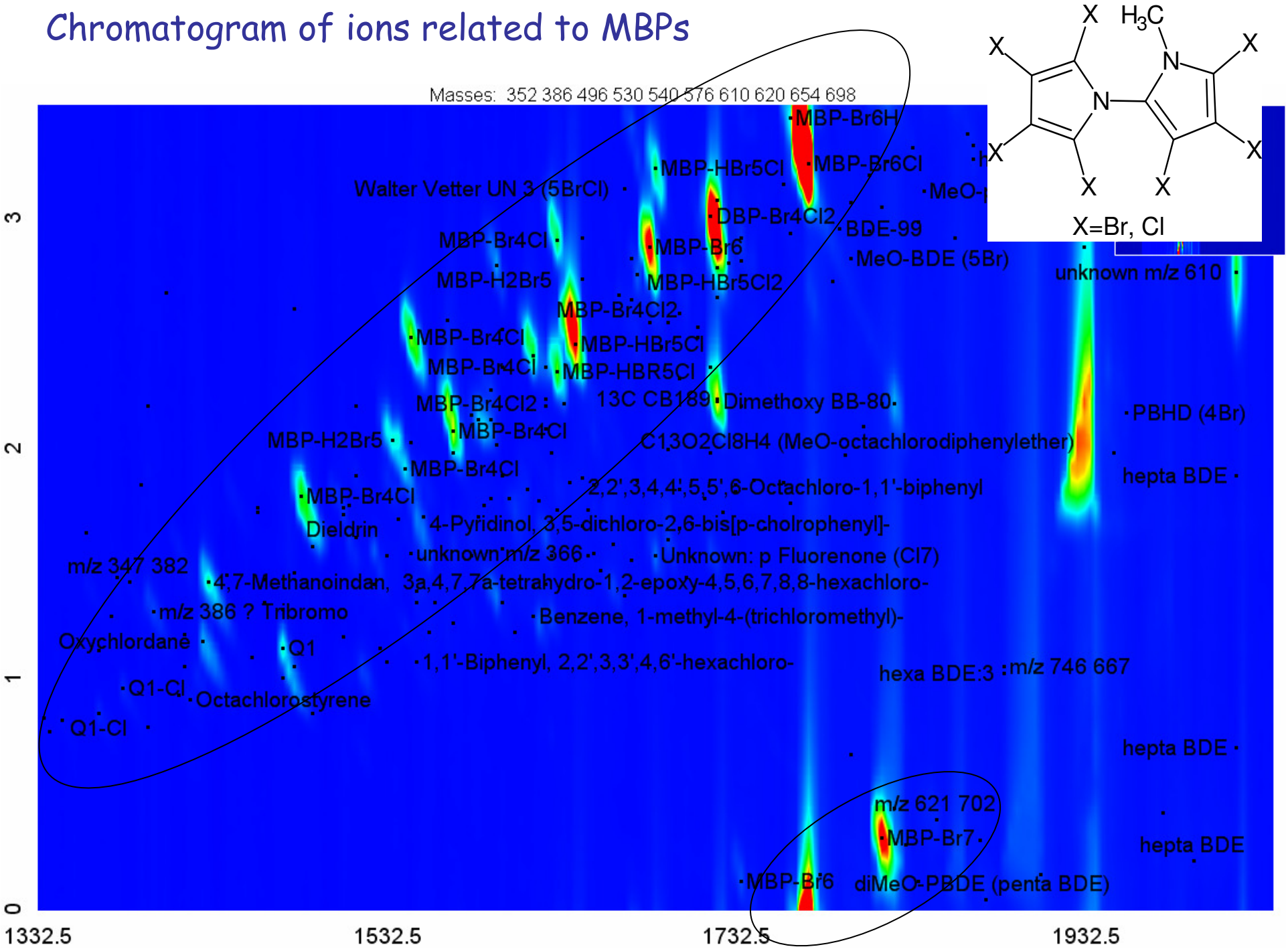
Some unknown peaks were identified to be halogenated natural products (HNPs) by comparing with authentic standards.



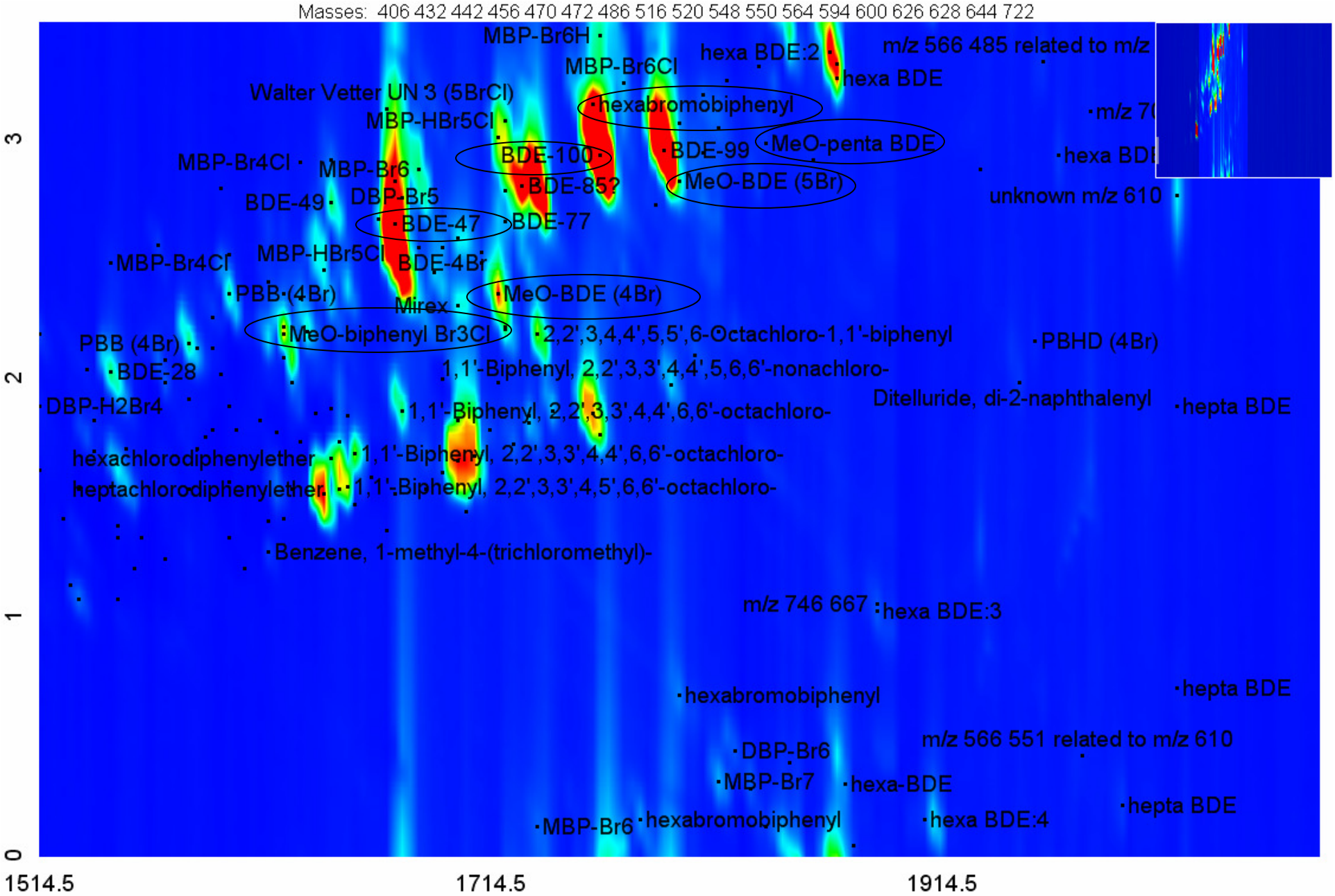
Some Known POPs



Chromatogram of ions related to MBPs



Chromatogram of ions related to MeO-BDEs, PBDEs, and PBBs

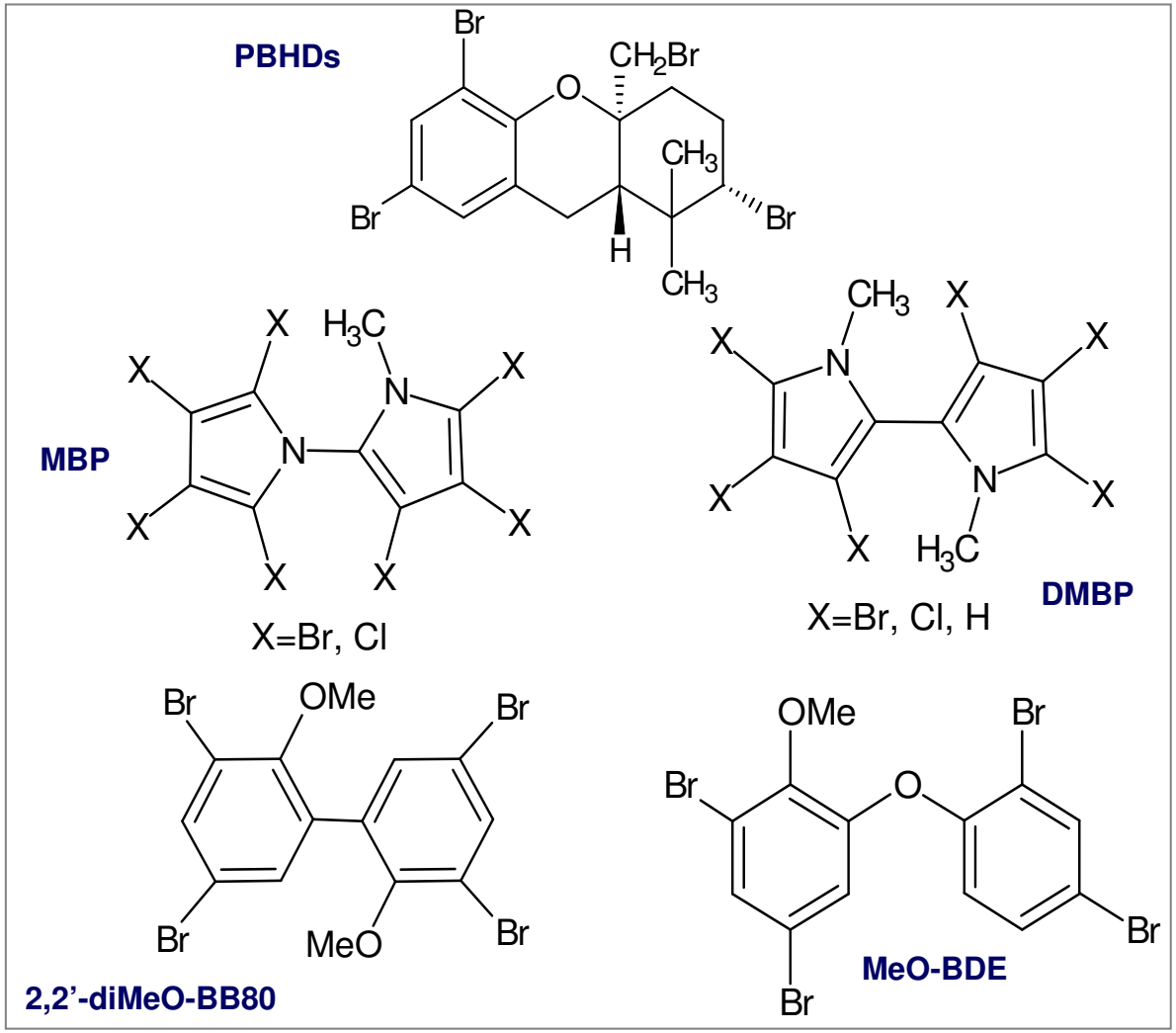


In the middle of quantitation of the contaminants: Accumulation of PBDEs and HNPs in the dolphin blubber

	Cod liver oil	Cod liver oil	Salmon oil	Dolphin oil
Type	*Dietary supplement*	*Dietary supplement*	*Dietary supplement*	*Extracted from blubber*
Treatment	*No information*	*Moleculary distilled*	*No information*	*No treatment*
Origin	*Norwegian cod liver oil*	*Arctic cod liver oil*	*Wild Alaskan sockeye*	*Massachusetts, USA*
PBDEs (ng/g)	11	7.6	1.7*	1300
Methoxy PBDEs (ng/g)	13	2.0	8.9	150
Q1 (MBP-Cl7) (ng/g)	3.9	nd	2.8	85
MBPs (ng/g)	0.51	0.063	0.52	4900
DMBPs (ng/g)	0.23	nd	160	170
2,2'-diMeO BB-80 (ng/g)	0.15	0.031	0.29	13
PBHDs (ng/g)	41	28	2.6	270

*Similar to blank level

What do we know about these halogenated natural products?



- Bioaccumulation
- Biomagnification
- Pathways of exposure
- Regional effect
- Temporal trend
- Sources
- Toxicological effect
- Ecological effect
- Human exposure
- Human health

Summary

- The novel approach using DSI-GC×GC/TOF-MS and a simple GPC clean up enables analysis of multiple groups of POPs simultaneously in fish oils.
- Several groups of halogenated natural products (HNPs) were identified in dietary cod liver oil by this approach as untargeted chemicals.
- Tetrabromophthalic anhydride and oxybenzone were surprisingly detected in the cod liver oil, but they probably did not originate from the environment.
- Further investigation for identification of the unknown halogenated compounds is required.
- Availability of HNP standards and update of NIST MS library for POPs and HNPs would be helpful.
- We found that the dolphin oil contained multiple classes of man-made and naturally occurring halogenated compounds. This suggests that the dolphin was exposed to the several groups of halogenated compounds not a single or few groups of chemicals.

Summary

- Our analytical approach was effective to detect and identify untargeted chemical contaminants (>200 compounds) in the dolphin oil extract in a single analysis.
- Octachlorostyrene and its related compounds (dechlorinated) were detected, and their peak intensities were comparable to well known organochlorinated pesticides.
- Due to GC×GC's better separation capacity, polychlorinated diphenyl ethers were separated from PCBs.
- Multiple classes of halogenated natural products (MBPs, DBPs, MeO-PBDEs, Dimethoxy BB-80, and PBHD) and their numerous congeners were detected, and their peak intensities were higher or comparable to PBDEs.
- Identifications of unknown peaks are in progress, and authentic standards are required for confirmation.
- Quantification of these multiple classes of halogenated compounds in the dolphin blubber is in progress.

Impact of Environmental Tobacco Smoke on Polycyclic Aromatic Hydrocarbons in Household Dust

http://www.babiestoday.com/articles/immunizations-and-health/third-hand-smoke-and-babies-6353/

- Environmental Tobacco Smoke:

  sidestream smoke plus mainstream exhaled smoke (called secondhand smoke)

  >4000 chemicals
- Tobacco smoke pollutants remaining in an indoor environment after a cigarette has been extinguished has been referred to as "residual tobacco smoke", or more popularly "thirdhand smoke (THS)"
- THS consists of a combination of semi-volatile compounds found in SHS that have sorbed on surfaces and dust or has become trapped in carpets, upholstery, fabrics, and other porous materials commonly found in indoor environments.
- PAHs are a part of environmental tobacco smoke and semi-volatile, so they are likely to be THS.

STUDY DESIGN of HEALTHY HOME PROJECT for Investigation of Residential THS

by Measurement and Evaluation Research Group in SDSU:

PI/Co-PI: Dr. Georg Matt/Dr. Jenny Quintana

Part 1: smokers and non-smokers with at least a child under 12 years old who had lived in their current home for at least 6 months and planned to move within the next month (smoker homes, n=94, non-smoker homes, n=50)

*criteria: "smoker homes", where residents had smoked 7 or more cigarettes/week inside the home during the week prior to study measures and smoked inside the home during at least 5 of the past 6 months including the current and most recent month, or "nonsmoker homes", where no cigarette smoking occurred inside the home.

Part 2:new residents were eligible if they were age 18 or older, spoke English or Spanish, had not smoked any cigarettes since they moved into the home, and if no visitors had smoked inside the home since the new residents moved in (25 former smoker homes and 16 former nonsmoker homes).

*After Part 1 residents confirmed they had moved, research assistants delivered or mailed up to 12 recruitment letters and flyers to the same homes, requesting that new residents contact the research office by telephone for eligibility screening.

**All participants were recruited in San Diego County

STUDY DESIGN of HEALTHY HOME PROJECT for Investigation of Residential THS

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Part 1.
Smoker homes (n=94),
non-smoker homes (n=50)

Part 2.
Formerly smoker homes (n=25),
Formerly non-smoker homes (n=16)

Environmental sampling and measurement:
House dust, surface wipe samples, air, finger wipe samples and urine samples from the adult residents and their children

Extensive interviews with participants:
Collecting information about house features, lifestyles, and behaviors

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16 PAHs in house dust samples in Part 1

Method: PAHs in house dust samples

- Dust Collection
  - Vacuumed at least 1m^2 of area using a High Volume Small Surface Sampler (CS3 Inc., Sandpoint, ID), size of the area was recorded, and sieved (150 µm)
- Extraction of PAHs
  - After sonication extraction, the extract was centrifuged, filtered and concentrated
- Analysis via GC/MS
  - Splitless injection, HP-5MS GC column, SIM mode
- QA/QC
  - Internal and Recovery standards
  - Calibration and Performance standards
  - Lab Blank and Matrix standards
- Data Analysis
  - SPSS 17.0 and Stata IC 10.0

PAH concentrations (ng/g) in household dust between smoker and non-smoker homes

Table 1a

PAH Concentration in house dust (ng/g)

PAH Compounds (ng/g)	Smoking Living Rooms n=88								Non-Smoking Living Rooms n=43								pvalue
	Geo Mean	95% CI LB	95% CI UB	Median	25%	75%	Min	Max	Geo Mean	95% CI LB	95% CI UB	Median	25%	75%	Min	Max	
Napthalene [a]	13.36	11.61	15.37	12.52	7.99	19.43	1.21	122.06	13.57	9.91	18.59	10.26	7.79	21.27	1.79	1406.87	0.530
Acenaphthlylene	6.46	5.36	7.78	4.36	2.65	8.43	0.10	64.55	5.05	3.86	6.61	3.15	1.79	7.10	0.07	50.52	0.162
Acenaphthene	5.97	5.03	7.09	5.44	3.02	9.12	0.15	31.93	6.43	5.46	7.57	5.45	3.47	8.47	1.34	24.66	0.841
Fluorene	13.63	11.98	15.51	12.19	8.09	18.57	1.75	101.94	12.69	10.79	14.92	10.22	7.67	15.11	5.05	76.39	0.362
Phenanthrene *	134.99	116.48	156.45	132.82	96.00	199.49	14.05	1158.85	103.71	86.41	124.47	94.46	67.84	135.27	24.56	393.00	***0.006***
Anthracene	11.90	9.84	14.39	12.52	6.07	22.45	0.17	78.50	10.77	8.77	13.22	9.55	5.41	14.61	1.95	72.49	0.262
Fluoranthene *	111.44	91.54	135.66	112.36	72.31	209.46	0.28	816.52	69.04	54.77	87.02	75.85	39.91	101.20	11.91	363.70	***0.000***
Pyrene *	115.55	93.80	142.33	128.02	78.69	213.01	0.28	626.40	80.74	66.30	98.33	79.75	50.80	121.20	19.91	300.90	***0.001***
Benz(a) anthracene * [b]	32.38	27.38	38.29	31.48	17.49	57.31	3.60	209.83	22.85	17.96	29.06	19.15	13.33	37.24	4.15	213.81	***0.009***
Chrysene * [b]	71.03	59.95	84.15	76.34	41.88	128.77	6.70	380.49	51.31	41.04	64.16	45.67	35.33	79.96	7.30	226.18	***0.014***
Benzo(b) flouranthene [b]	122.22	100.71	148.33	124.21	81.84	196.96	0.12	580.25	107.29	89.24	129.00	112.84	81.80	163.64	18.36	290.21	0.215
Benzo(k) flouranthene [b]	39.53	30.07	51.98	50.47	25.61	89.61	0.10	282.84	38.93	31.22	48.54	39.47	21.88	63.32	6.35	194.95	0.144
Benzo(a) pyrene [b]	32.89	24.29	44.54	48.70	19.30	88.10	0.13	282.44	30.15	20.44	44.46	40.75	24.01	68.72	0.15	129.41	0.294
Indeno [123-cd] pyrene * [b]	52.77	42.85	64.99	59.18	31.67	95.09	1.90	528.24	37.47	29.74	47.21	36.45	22.41	59.28	4.85	171.24	***0.027***
Dibenz [ah] anthracene [b]	9.71	7.90	11.93	9.66	4.08	17.17	0.05	126.88	7.89	6.18	10.09	7.10	3.70	10.75	0.10	51.82	0.232
Benzo [ghi] perylene	124.61	104.21	149.01	133.38	83.55	198.84	2.60	731.39	100.02	82.16	121.77	100.75	64.03	162.95	21.36	320.47	0.061
B2 PAHs *	538.09	458.80	631.08	429.37	268.99	684.53	32.52	1962.38	317.46	262.55	383.86	331.49	223.41	513.23	47.72	1024.81	***0.022***
Total PAHs *	1001.07	868.77	1153.51	1016.76	675.97	1594.81	180.98	4390.82	770.38	651.05	911.59	755.78	534.42	1035.13	209.47	2477.61	***0.010***

a Denotes PAH ranked as possible human carcinogen (Group C) by US EPA's IRIS

b Denotes PAH ranked as a probable human carcinogen (Group B2) by USA EPA's IRIS

* Denotes significant difference between the Smoking and Non-Smoking Livingrooms using Mann Whitney Rank Sum Test

PAH surface loading (ng/m^2) in household dust between smoker and non-smoker homes

PAH Compounds (ng/m2)	Smoking Living Rooms n=87								Non-Smoking Living Rooms n=43								pvalue
	Geo Mean	95% CI LB	95% CI UB	Median	25%	75%	Min	Max	Geo Mean	95% CI LB	95% CI UB	Median	25%	75%	Min	Max	
Napthalene [a]	20.92	15.64	27.99	18.56	11.75	48.53	0.45	1469.61	13.82	8.67	22.05	13.70	6.86	23.83	0.80	7062.47	***0.032***
Acenaphthlylene	8.25	5.73	11.86	7.97	2.48	21.67	0.18	763.53	3.89	2.25	6.75	3.99	1.88	10.02	0.02	149.51	***0.033***
Acenaphthene	7.64	5.49	10.65	7.63	3.54	19.02	0.07	774.65	5.97	4.19	8.51	5.90	2.78	13.86	0.58	67.12	0.385
Fluorene	21.69	16.11	29.18	19.19	11.67	47.63	0.68	3797.28	13.30	9.12	19.42	11.27	6.84	26.19	0.62	181.66	***0.038***
Phenanthrene *	231.89	173.64	309.69	230.72	107.89	478.79	10.66	8589.74	118.82	77.98	181.06	118.50	50.45	332.46	7.72	2128.85	***0.017***
Anthracene	17.12	12.00	24.42	17.03	7.06	45.34	0.07	1386.22	10.90	7.07	16.80	11.48	4.29	20.52	0.27	320.71	0.069
Fluoranthene *	186.23	134.89	257.11	221.95	84.01	394.00	0.53	8954.83	77.94	50.34	120.65	84.14	27.85	211.56	3.17	2927.82	***0.001***
Pyrene *	190.66	133.31	272.68	220.12	110.33	447.52	0.25	10027.85	91.73	60.33	139.47	108.71	31.36	274.54	5.03	2422.23	***0.003***
Benz(*a*)anthracene * [b]	53.33	39.43	72.12	60.63	19.48	123.62	1.41	2327.66	24.67	15.92	38.23	24.45	8.52	61.38	0.77	825.90	***0.004***
Chrysene * [b]	119.77	89.44	160.39	127.89	54.54	238.52	2.17	5387.35	57.18	37.67	86.78	60.28	21.59	130.88	2.46	1550.12	***0.004***
Benzo(*b&k*)flouranthene [b]	291.43	205.60	413.11	382.82	129.37	750.32	0.07	8725.02	169.63	114.14	252.08	163.16	70.39	443.27	16.74	3180.21	***0.012***
Benzo(*a*)pyrene [b]	85.56	57.17	128.04	63.44	20.38	185.34	0.20	3080.07	29.49	14.97	64.48	40.94	18.61	107.56	0.02	1041.72	0.193
Indeno(*1,2,3-c,d*)pyrene * [b]	87.24	61.83	123.10	94.96	35.96	259.76	1.35	3534.12	41.60	26.84	64.48	41.50	14.30	106.79	1.82	1378.51	***0.008***
Dibenz(*a,h*)anthracene [b]	13.36	9.38	19.02	17.10	4.32	39.76	0.15	552.26	7.19	4.50	11.51	7.35	2.29	17.98	0.30	273.29	***0.025***
Benzo(*g,h,i*)perylene	211.77	152.89	293.32	244.87	79.05	525.59	4.62	9555.27	114.79	77.42	170.20	99.02	49.47	248.90	4.98	2146.53	***0.016***
B2 PAHs *	926.07	686.36	1249.48	980.39	381.15	2265.00	14.74	33161.77	488.35	331.06	720.39	423.36	261.29	1254.92	27.08	10396.28	***0.008***
Total PAHs *	1726.69	1297.05	2298.64	1734.36	729.76	3592.06	74.77	68925.47	889.91	596.50	1327.63	796.10	438.70	2325.97	47.82	18686.21	***0.000***

a Denotes PAH ranked as possible human carcinogen (Group C) by US EPA's IRIS

b Denotes PAH ranked as a probable human carcinogen (Group B2) by USA EPA's IRIS

* Denotes significant difference between the Smoking and Non-Smoking Livingrooms using Mann Whitney Rank Sum Test

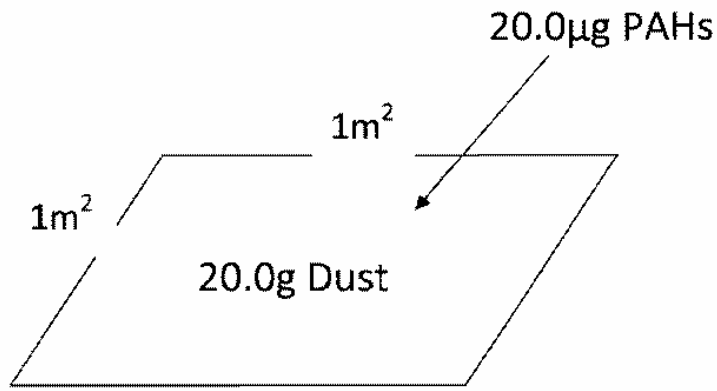
Concentration vs. surface loading:

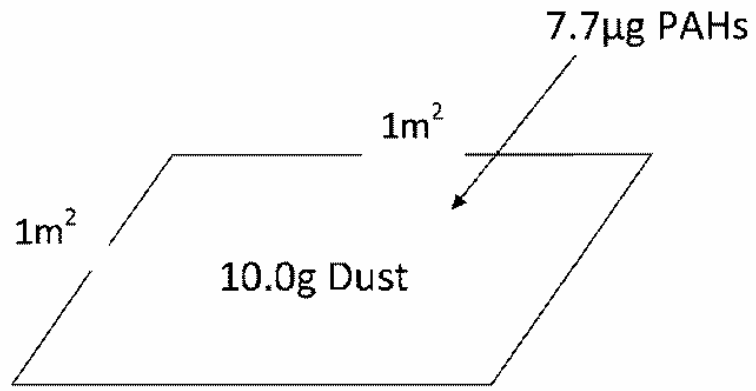
Concentration: micro or nanogram of toxin per gram of dust

- » Does not take into account the amount of pollution in the home
- » May not adequately predict exposure

Dust Loading: micro or nanogram of toxin per cubic meter of area

- » Allows calculation of the amount of pollution in the home
- » More predictive of exposure





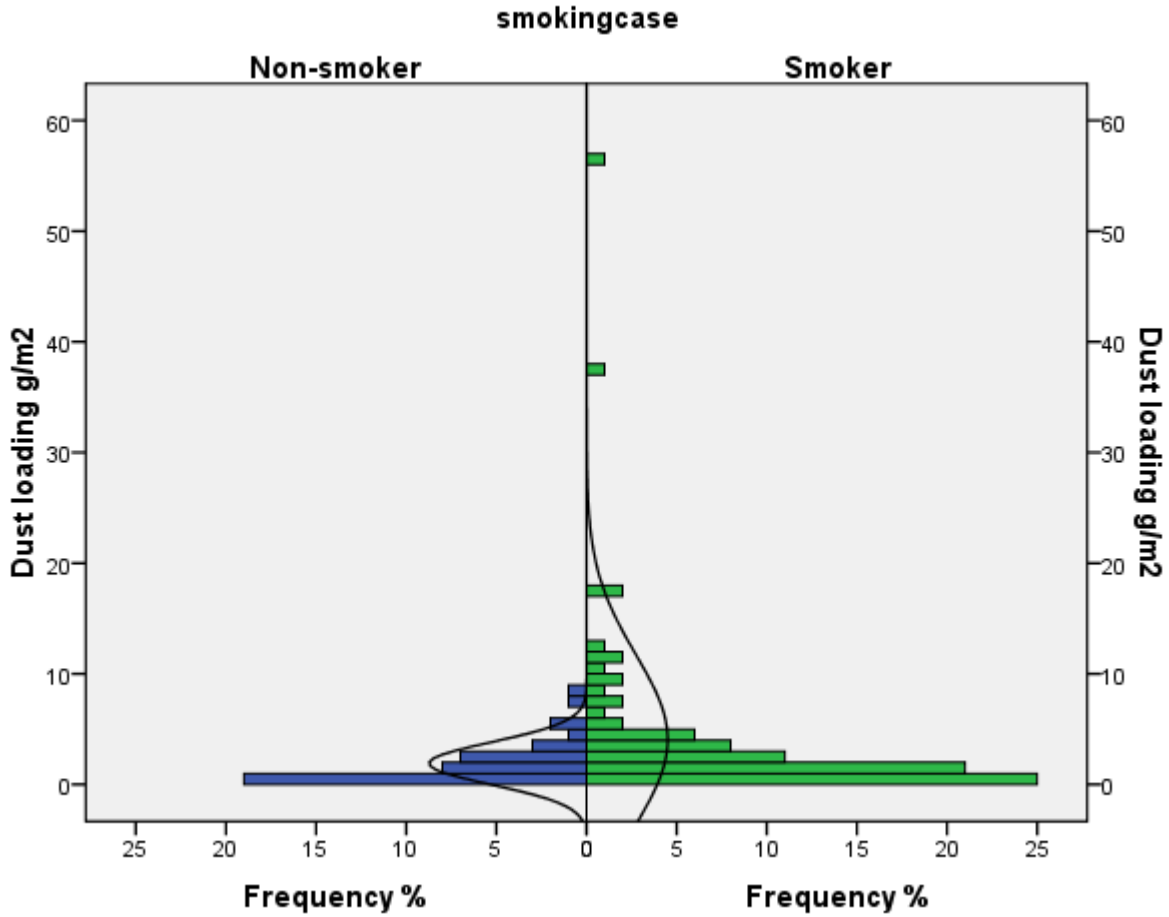
[PAH] = 20.0µg PAH/20.0g Dust = 1.0µg/g Dust

PAH Loading = 20.0µg PAH/$1m^2$ = 20µg/m^2

[PAH] = 7.7µg PAH/10.0g Dust = 0.77µg/g Dust

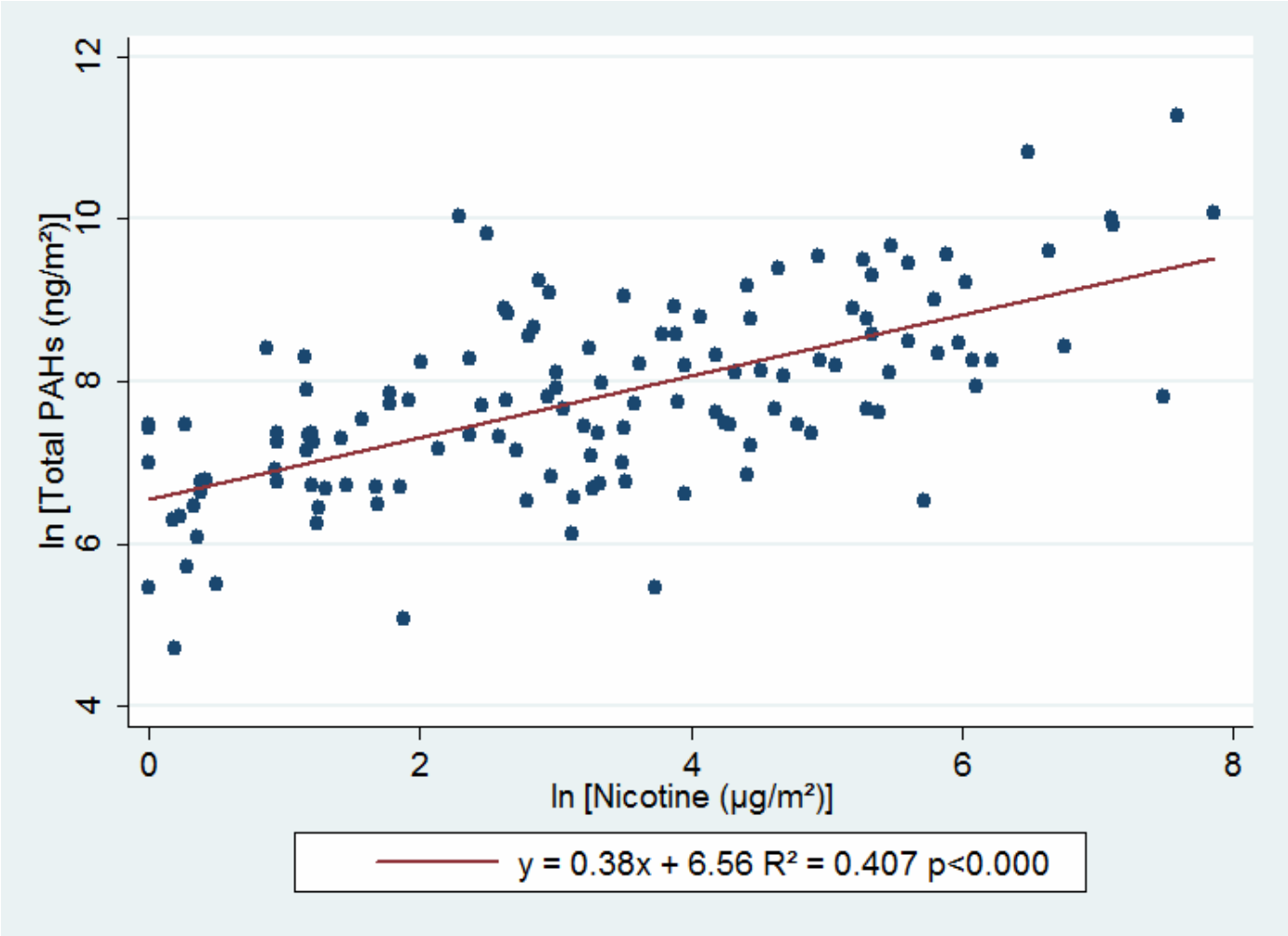
PAH Loading = 7.7µg PAH/$1m^2$ = 8µg/m^2

Dust loading comparison non-smoker homes vs. smoker homes

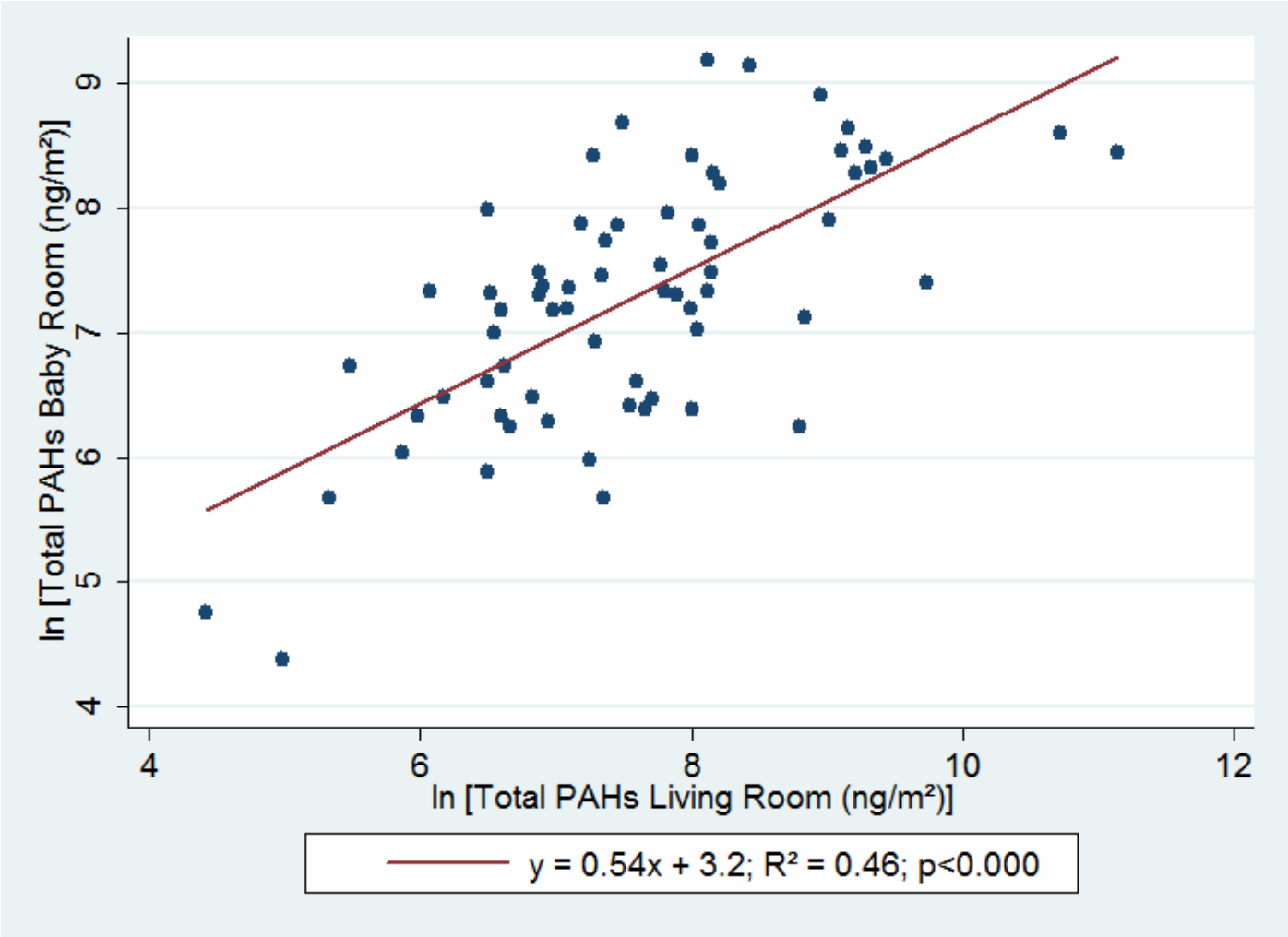


Dust loading was significantly higher in the smoker homes (p=0.07).
Smoker homes are dustier-> smoking contributes dust or smokers do less cleaning?

Significant positive association between PAH surface loading in dust, nicotine surface loading in dust.



Significant positive association between PAH surface loading in dust from living rooms and baby's rooms of smoking homes.



Comparison of the PAH levels with other studies

PAH (geomean: µg/g)	This study	Wilson	Wilson	Chuang	Chuang	Lebowitz	Mukerjee	Chuang	Chuang	Chuang
Location	San Diego, CA	North Carolina	North Carolina	North Carolina	North Carolina	Arizona	Texas	Kentucky	Washington	Ohio
number of samples	n=256	n=13	n=10	n=24	n=13	n=22	n=2	n=3	n=10 †	n=24
Napthalene	0.013	0.009	0.006	0.145	0.045	0.035	0.238	0.055	Not Measured	0.384
Acenaphthlylene	0.006	0.005	0.004	0.055	0.027	0.009	Not Measured	0.076	Not Measured	0.110
Acenaphthene	0.006	0.010	0.009	0.035	0.032	0.015	0.014	0.017	Not Measured	0.216
Fluorene	0.013	0.012	0.009	0.076	0.043	0.021	0.019	0.053	0.073	0.396
Phenanthrene	0.117	0.121	0.145	0.359	0.170	0.103	0.211	0.243	1.045	5.673
Anthracene	0.011	0.016	0.017	0.072	0.036	0.021	0.071	0.108	0.109	0.571
Fluoranthene	0.091	0.184	0.234	0.429	0.296	0.153	0.256	0.314	0.946	9.610
Pyrene	0.099	0.122	0.191	0.356	0.272	0.131	0.218	0.243	1.112	7.259
Benz(a) anthracene	0.027	0.047	0.095	0.172	0.156	0.061	0.092	0.18	0.488	3.384
Chrysene	0.058	0.098	0.149	0.279	0.174	0.115	0.168	0.248	0.887	4.860
Benzo(b & k)flouranthene	0.154	0.098	0.114	0.469	0.300	0.216	0.232	0.435	1.451	9.031
Benzo(a) pyrene	0.033	0.076	0.139	0.197	0.081	0.066	0.119	0.164	0.699	5.284
Indeno [123-cd] pyrene	0.042	0.096	0.034	0.180	0.077	0.099	0.124	0.179	0.579	3.996
Dibenz [ah] anthracene	0.008	0.040	0.018	0.072	0.028	0.026	0.029	0.071	0.195	1.092
Benzo [ghi] perylene	0.109	0.100	0.034	0.212	0.102	0.091	0.116	0.186	0.628	3.535
B2 PAHs	0.463	0.469	0.583	1.421	0.843	0.606	0.764	1.281	4.340	29.06
Total PAHs	0.862	1.073	1.292	3.487	1.972	1.232	1.953	2.716	8.116	62.39

Summary

- There is a measurable and significant difference in the PAH concentration and surface loading in dust between smoking and non-smoking homes.
- This study is the first study to measure PAH dust loading between smoking and non-smoking homes.
- The significant difference in surface loading coupled with the positive correlation between nicotine and PAH loading, suggests that ETS is a significant contributor to PAHs in dust.
- Smoking in one area of the home impacts PAH loading in dust throughout other areas of the home, including children's rooms.
- The PAH concentrations in the house dust of San Diego homes are relatively lower than those in other areas of the country.
- Part 2 samples are in the middle of data analysis, which will investigate the long-term house contamination of thirdhand smoke.
- Potential sources of PAHs such as traffic density and house features will be considered as variables with nicotine to conduct multi-regression model.
- The untargeted analytical approach will be applied to these house dust samples to assess human exposure to known toxicants and unrecognized/unexpected chemicals.

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