Analysis of Organic Iodine in Drinking Water

The use of TOI and a proposed TOX_{LCMS} Parameter

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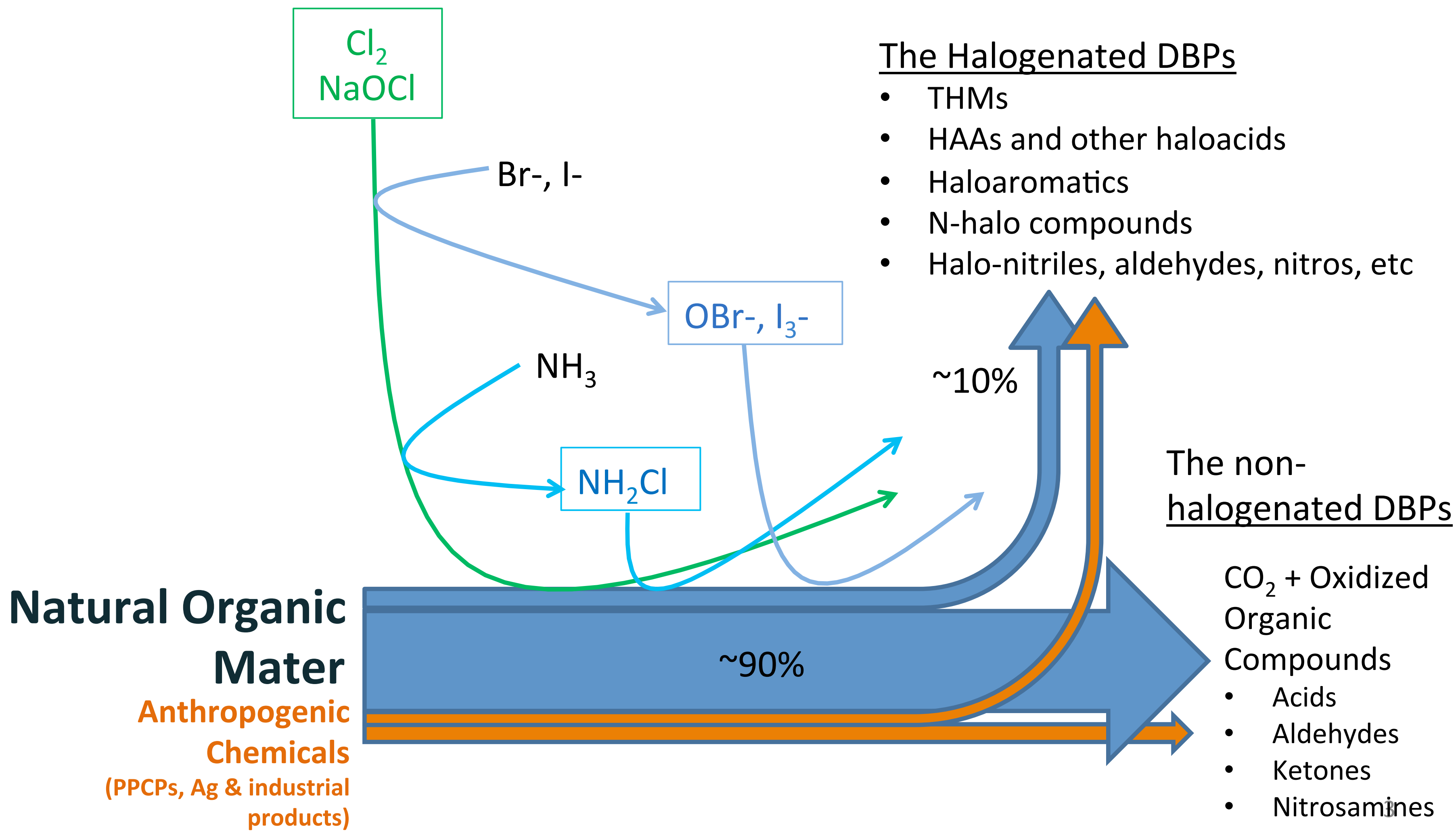
Outline

- Formation in Drinking Water
- Public Health Concerns
- TOX
  - Current Method
  - Relationship to the DBP issue
- Indirect Data on TOI
  - Lab Tests from high-I waters
  - Field Data on I-THMs & others
- Some Direct Data on TOI
  - Method using ICP/MS
  - Results to date
- Alternative TOI Approaches
  - LC/MS/MS
  - LC/QTOF
- Conclusions & where do we go from here?

It's one of my favorite recipes. I call it Total Organic Iodine

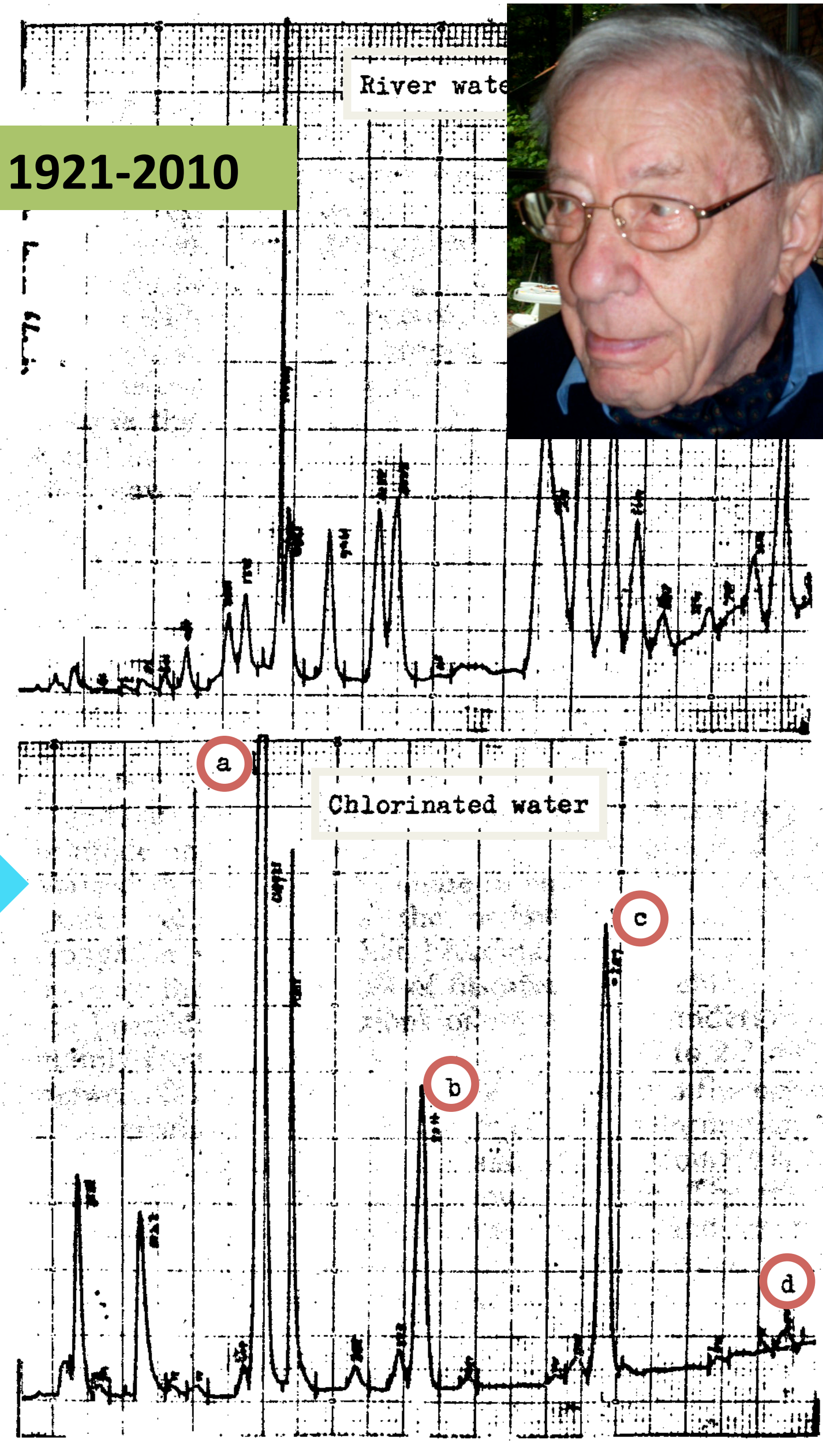
Formation of Cl_2-driven DBPs



John Rook & DBPs

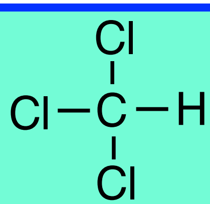
- Found DBPs and brought them to the world's attention
  - Brought headspace analysis from the beer industry to drinking water
  - Found trihalomethanes (THMs) in finished water
    - Carcinogens !?!
  - Published in Dutch journal <u>H2O</u>, Aug 19, 1972 issue
  - Deduced that they were formed as byproducts of chlorination
  - Proposed chemical pathways

Rook, 1974, <u>Water Treat. & Exam.</u>, 23:234

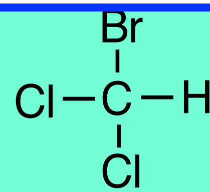


The first,
and currently regulated DBPs

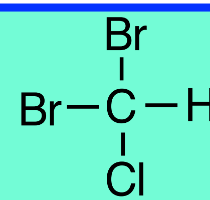
The THMs



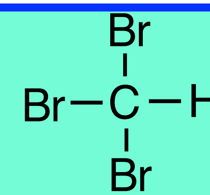
Chloroform



Bromodichloromethane

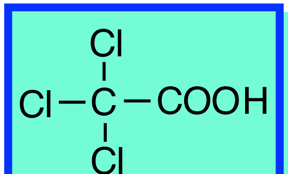


Chlorodibromomethane

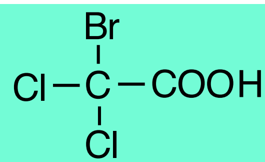


Bromoform

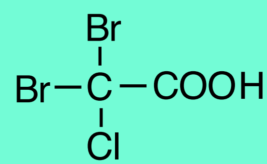
- The HAAs



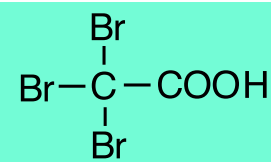
Trichloroacetic Acid *(TCAA)*



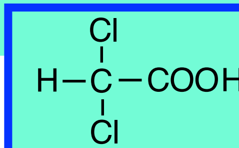
Bromodichloroacetic Acid



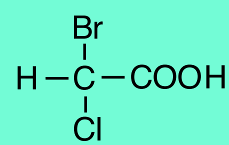
Chlorodibromoacetic Acid



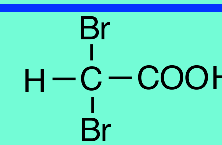
Tribromoacetic Acid



Dichloroacetic Acid *(DCAA)*



Bromochloroacetic Acid



Dibromoacetic Acid

HAA5 only

DBP Epidemiology

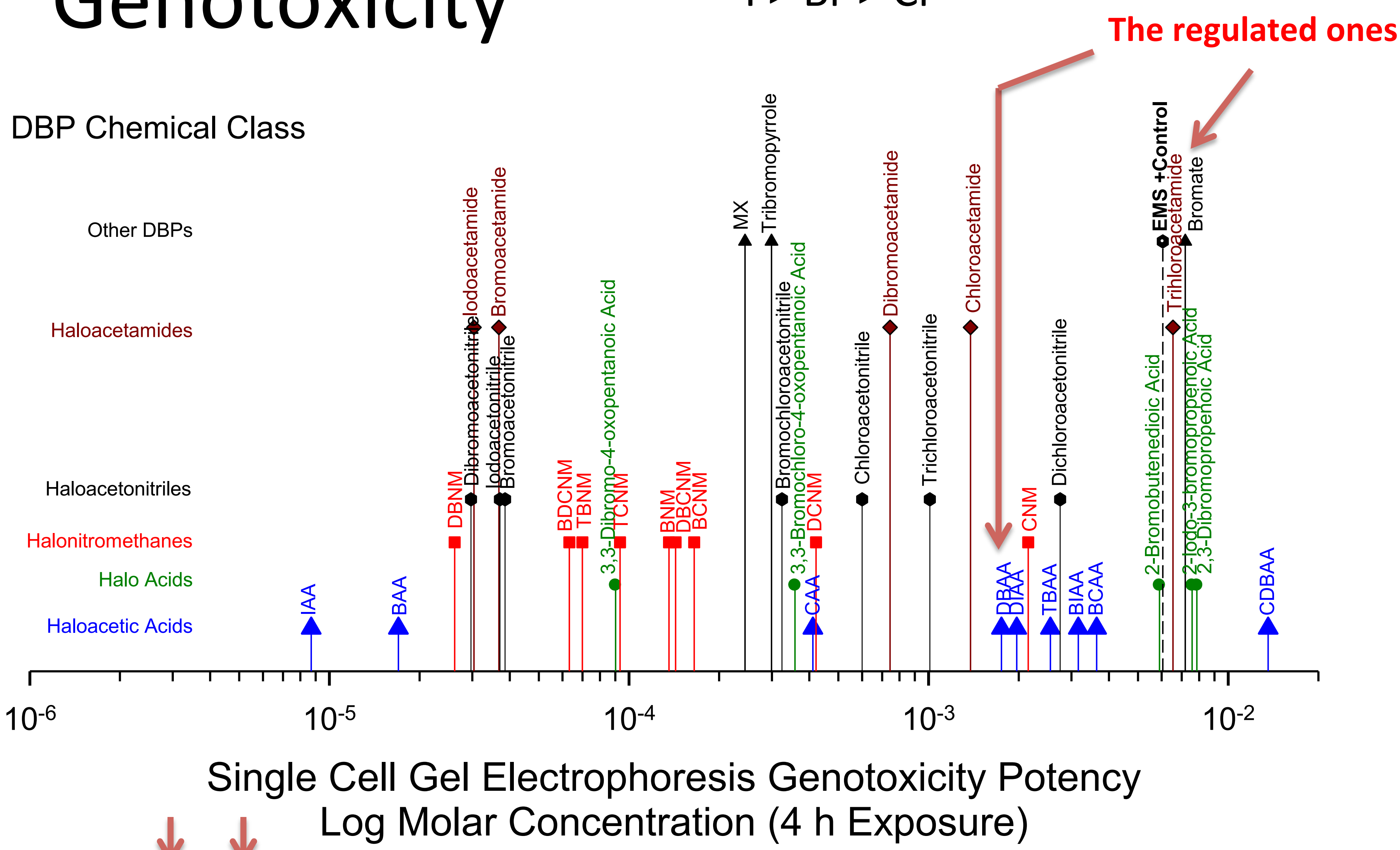
Epidemiology is not supported by Toxicology of known DBPs

- Bladder Cancer
  - DBPs linked to ~10,000 US cases every year
- Other Cancers
  - Rectal, colon
- Reproductive & developmental effects
  - Miscarriages & Low birth weight
  - Birth Defects
    - e.g., Cleft palate, neural tube defects
- Other
  - Kidney & spleen disorders
  - Immune system problems, neurotoxic effects

← **Basis for current EPA regulation**
80 µg/L THMs
60 µg/L HAAs

Genotoxicity

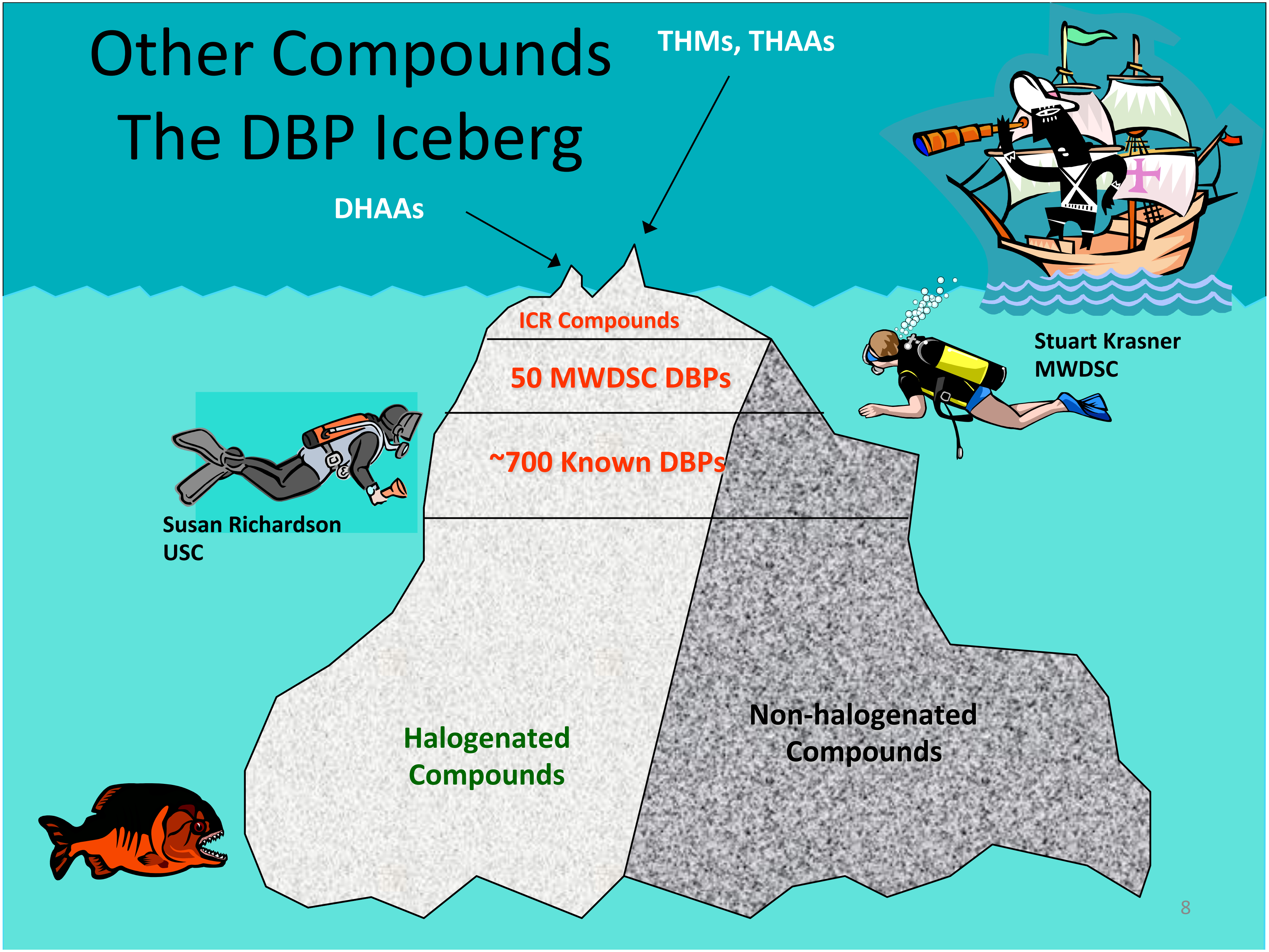
- Mono-X > Di-X > Tri-X
- I > Br > Cl



Not Genotoxic: DCAA, TCAA, BDCAA, Dichloroacetamide,
3,3-Dibromopropenoic Acid,
3-Iodo-3-bromopropenoic Acid, 2,3,3,Tribromopropenoic Acid

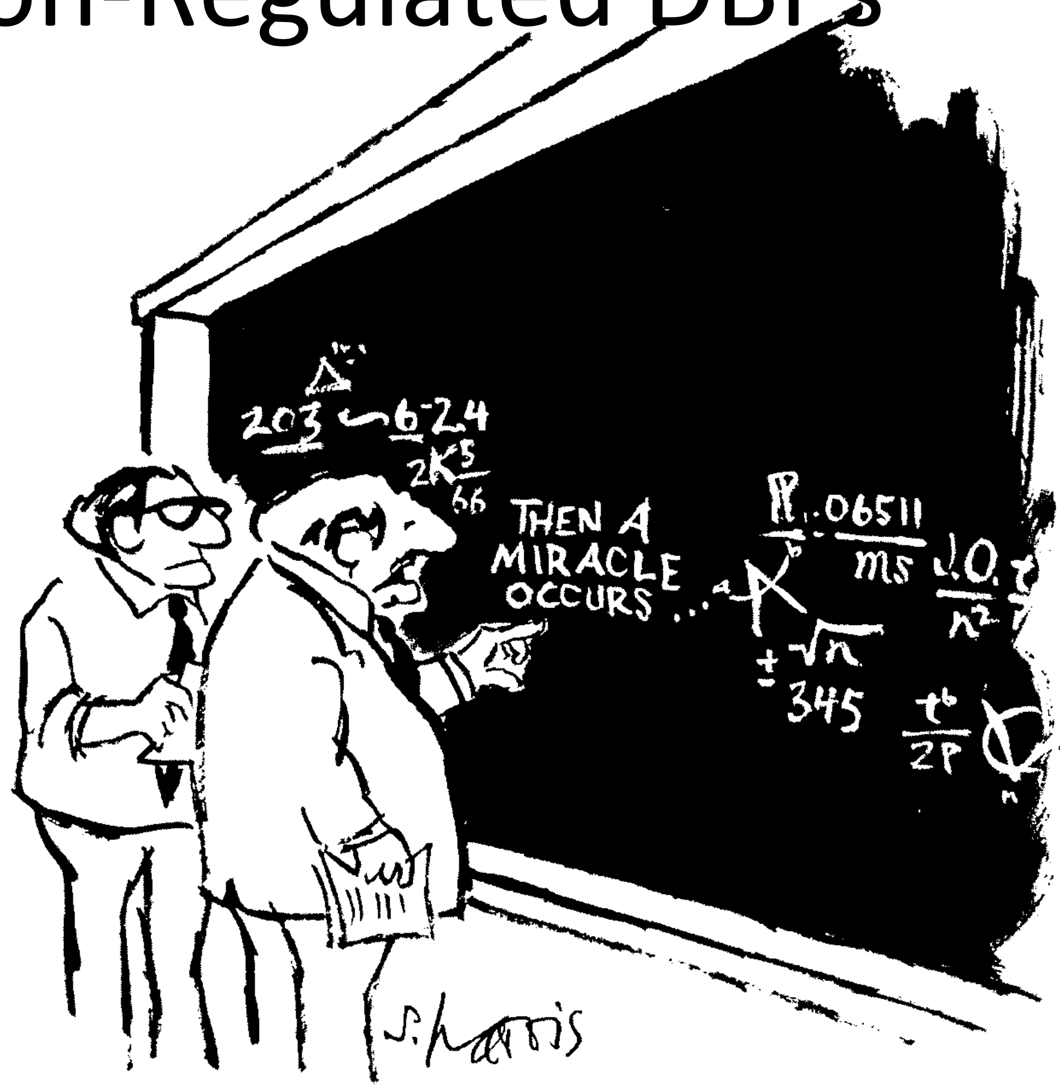
From Plewa & Colleagues

Other Compounds
The DBP Iceberg



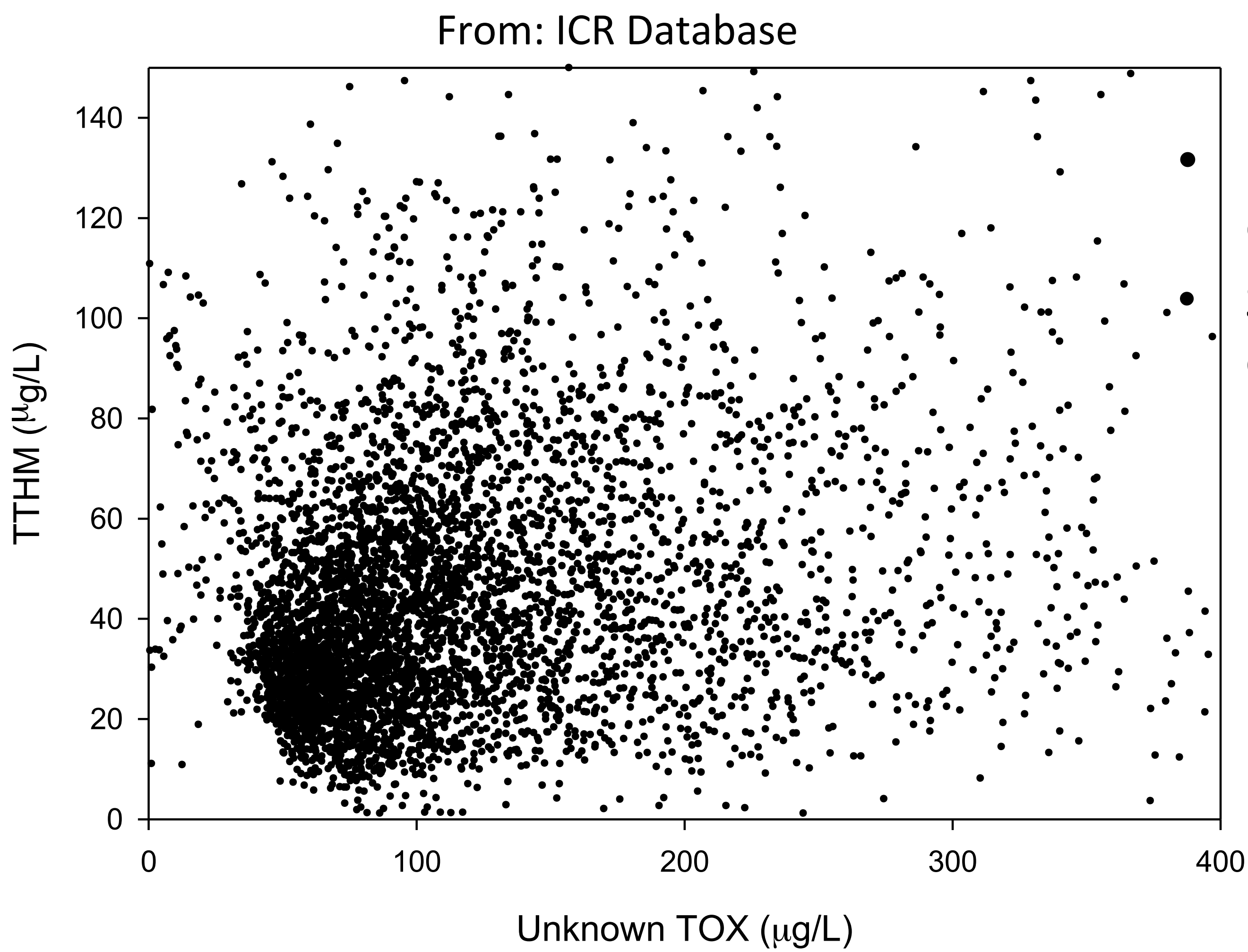
Control of Non-Regulated DBPs

- We need to know what these compounds are first



"I think you should be more explicit here in step two"

Regulated DBPs as surrogates or indicators

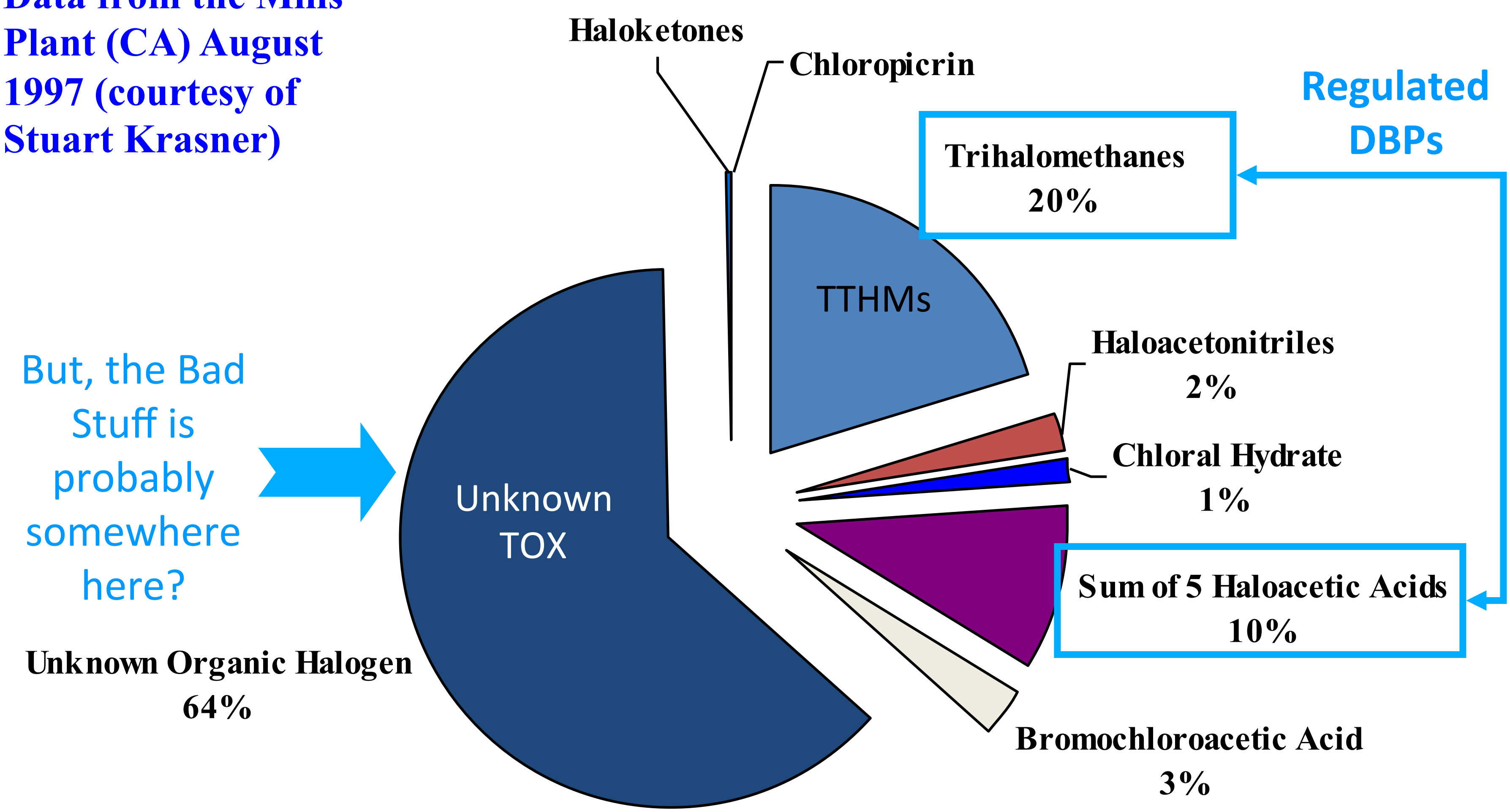


- Not a perfect correlation
- So what can we do?
  - Maybe we need a more diverse group of surrogates
  - Look at occurrence characteristics

TOX: Known & Unknown

Data from the Mills Plant (CA) August 1997 (courtesy of Stuart Krasner)

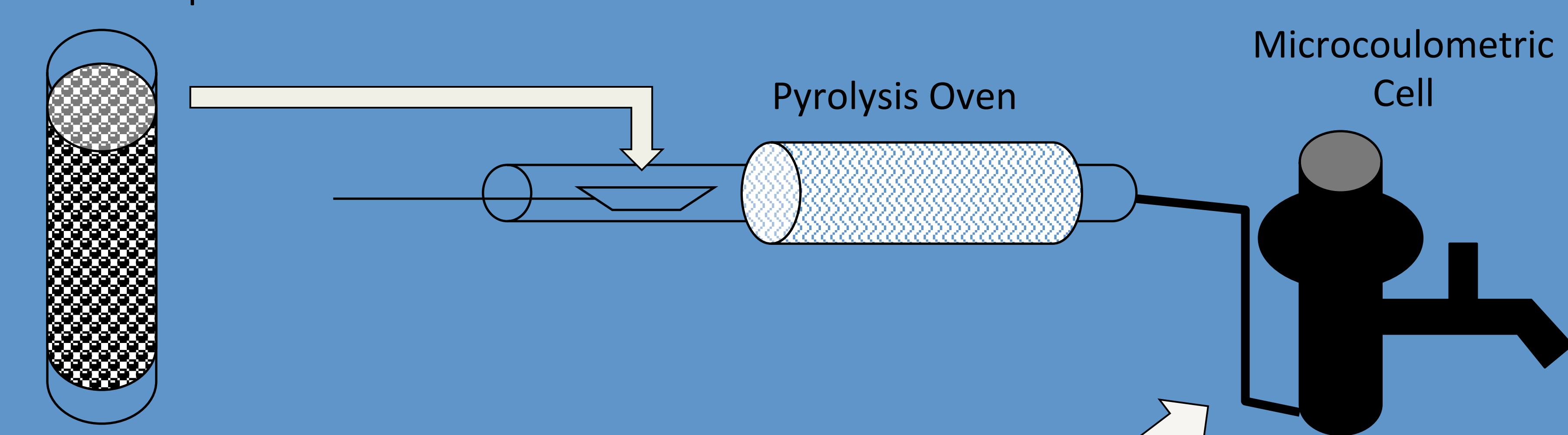
But, the Bad Stuff is probably somewhere here?



TOX as Measured Today

METHODS & ISSUES

Total Organic Halogen



- Standard Methods; USEPA Method #1650
  - Activated Carbon Adsorption & Pyrolysis & Microcoulometric Detection of halide
- Extended Method for TOCl, TOBr, TOI
  - Trap gases & ion chromatography
    - (e.g., Hua & Reckhow, 2008)

TOX in Drinking Water

- Originally proposed by researchers at the University of Karlsruhe in the 1970s
  - Led to development of commercial instrument: Dohrmann, Euroglass, Mitsubishi (current)
- Proposed regulatory action for TOX
  - As a surrogate for unknown DBPs
  - Eventually deemed too problematic by EPA and others to pursue
    - Although EU has a TOX guideline

Why is TOX not regulated?

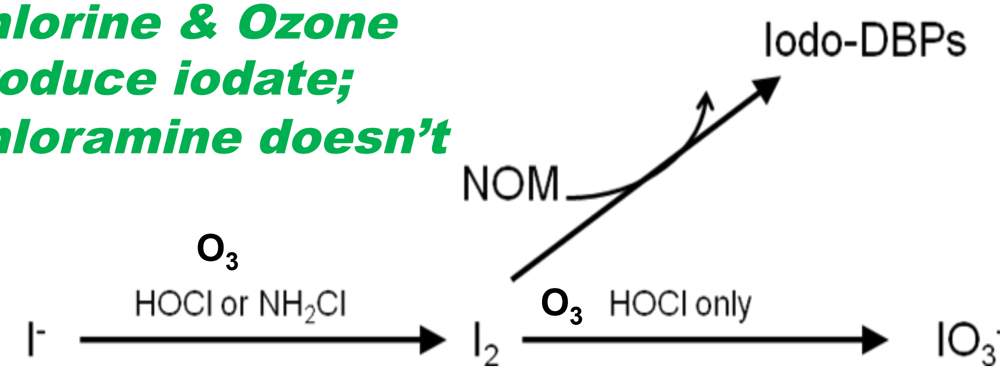
- Mostly problems with method
  - Costly instrumentation that is only used for TOX
  - Difficult to operate and not easily automated
  - High and variable GAC blanks limit precision and sensitivity
  - Recovery is not good for all compounds
  - Chemical information can be expanded to specific halogens, but this may require special accommodations for TOBr and TOI (e.g., ICP/MS)
  - The most important information is not accessible
    - number and type of halogens per molecule

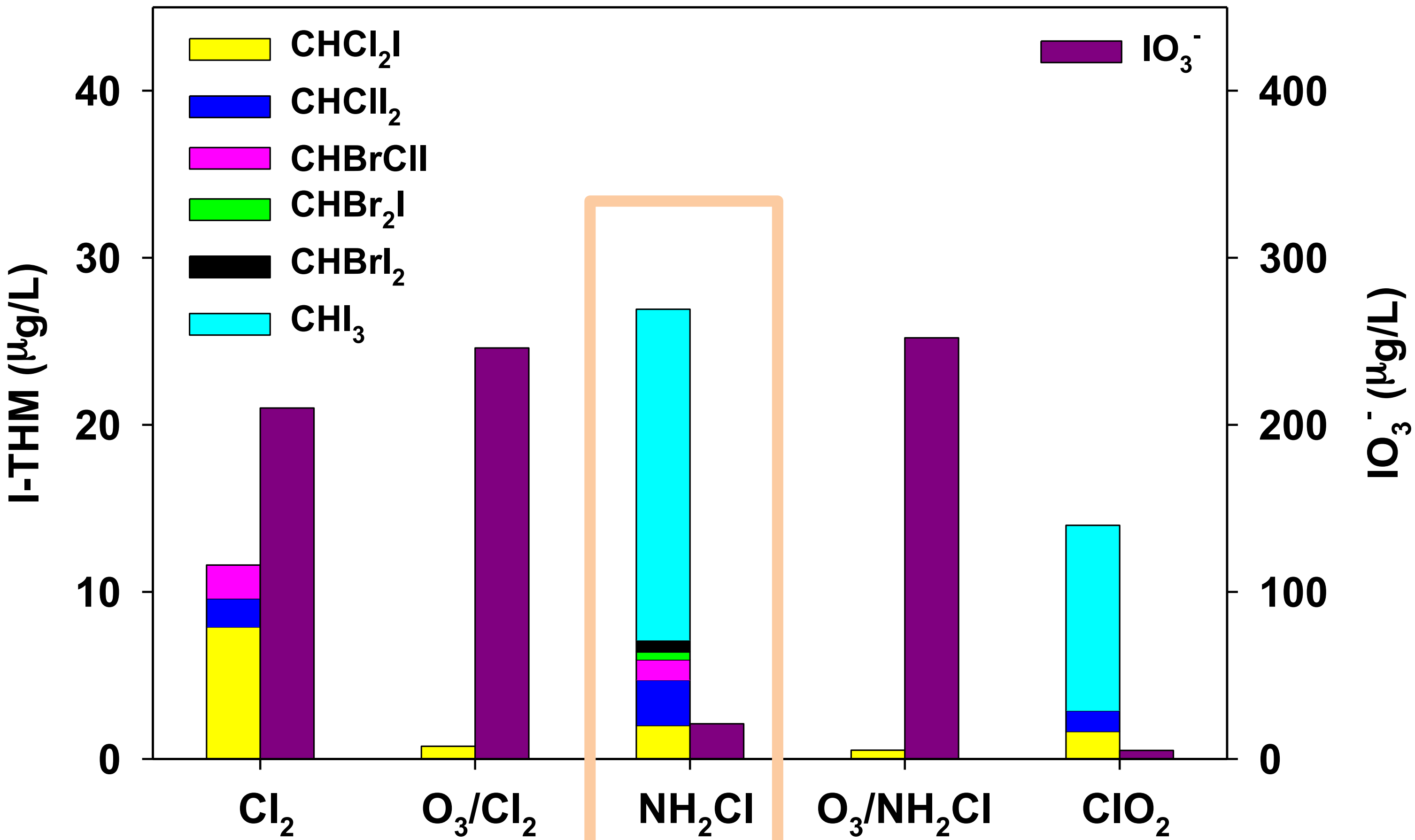
What do we know about TOI

DATA FROM WATERS HIGHLY FORTIFIED WITH IODIDE

Iodo-THMs

Chlorine & Ozone produce iodate; Chloramine doesn't



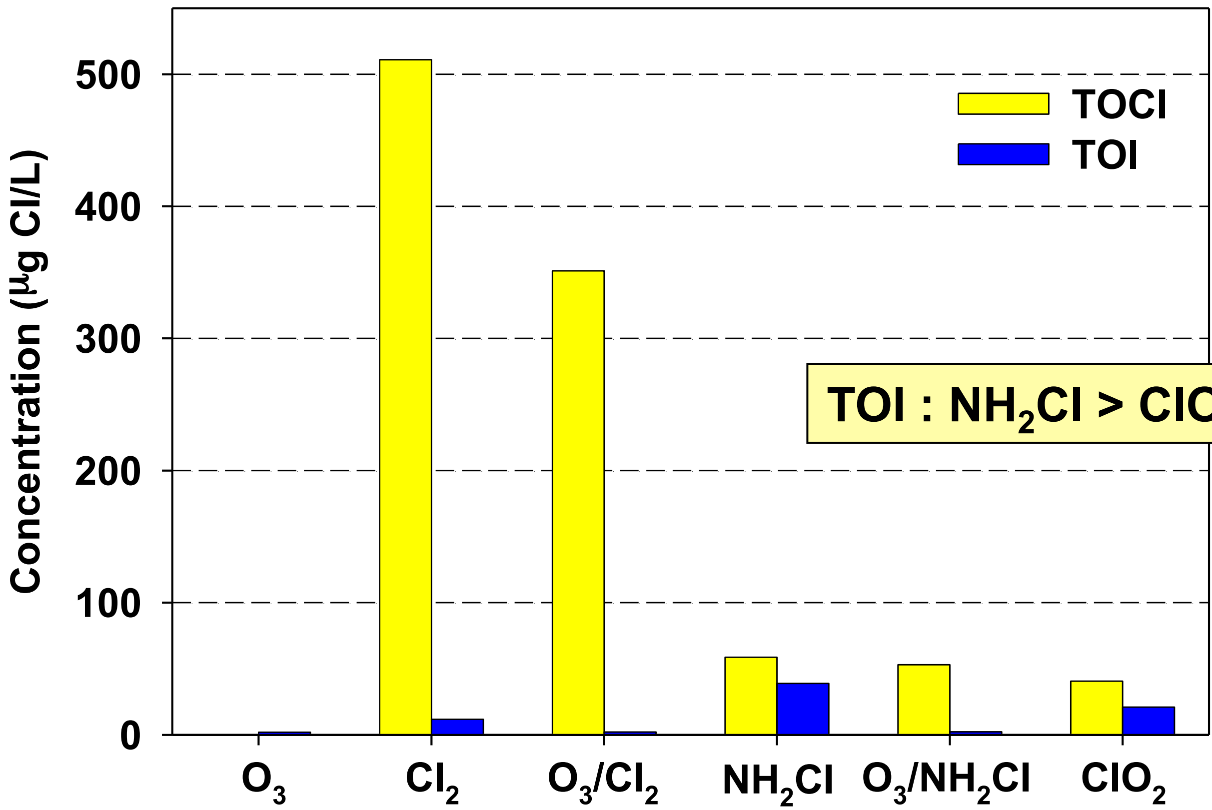


Cambridge MA Water, DOC: 4.2 mg/L, I: 200 μg/L

Hua & Reckhow, 2007

Iodinated TOX (TOI)

Cambridge MA Water, DOC=4.2 mg/L, I^-=200 μg/L (added)



TOI : $NH_2Cl > ClO_2 > Cl_2 > O_3$

Hua & Reckhow, 2007

What do we know about TOI

DATA FROM A FEW STUDIES MEASURING I-THMS

Iodo-DBP Occurrence

- Iodo-THM Occurrence
  - Concentrations
    - From 12 systems in NA

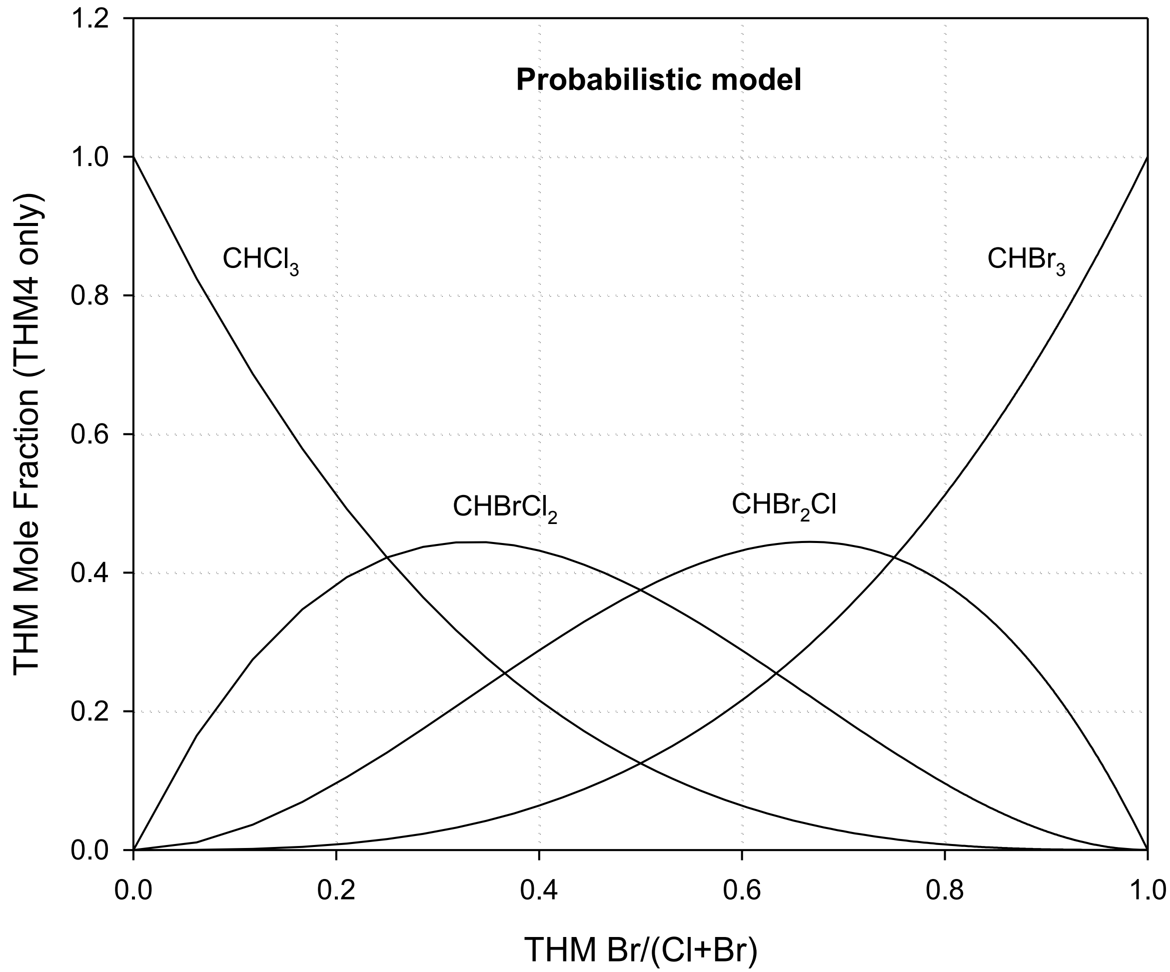
Percentile	Conc (µg/L)
50%	0.4
75%	2
90%	4

    - Up to 25 µg/L for direct chloramination
  - Relative Prevalence
    - 2% of THM4 at 50%ile; 7% at 75%ile?
    - Iodo-THMs ≈ 0.1* Bromo-THMs
- Iodo-HAA Occurrence
  - Little or no triHAAs containing iodine??

From: Weinberg, Krasner, et al., 2002

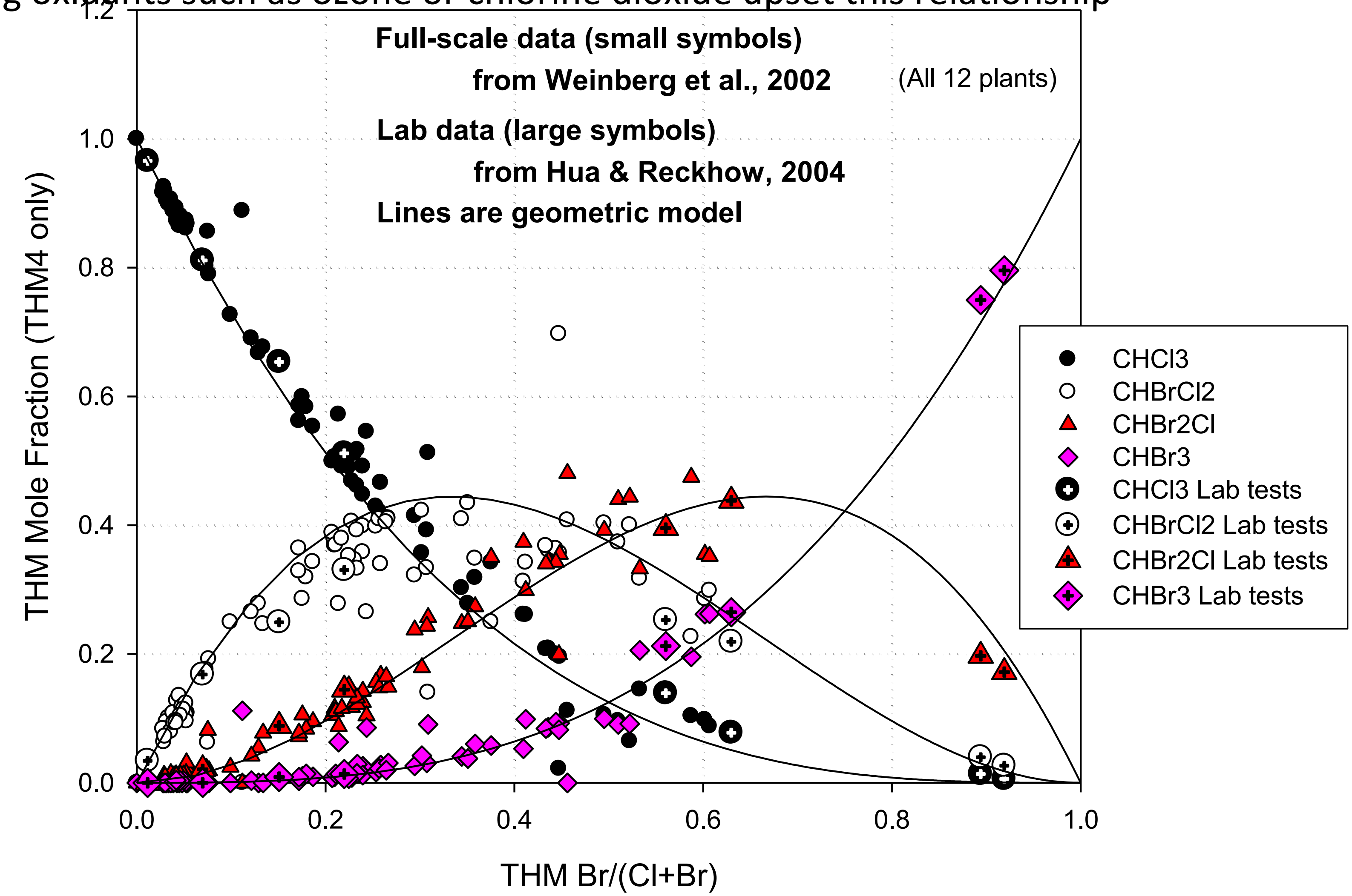
Cl vs Br: Species Model

- Simple competitive kinetic model: applicable to all DBPs?
  - From: MacNeill, 1993; Cowan & Singer, 1996



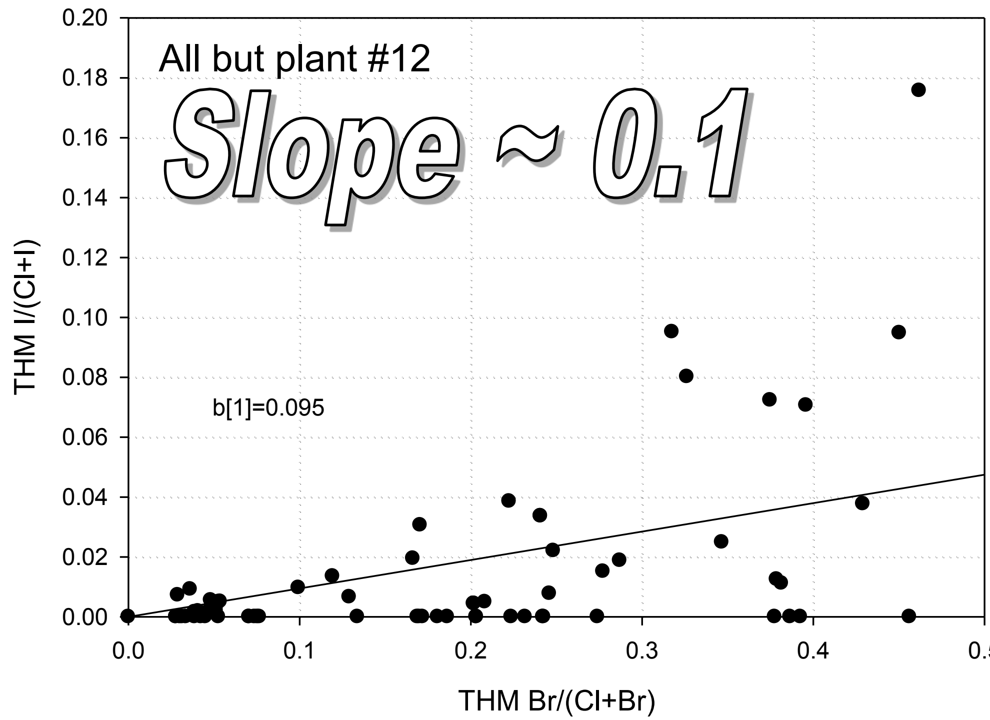
Bromo-chloro speciation for THMs

Strong oxidants such as ozone or chlorine dioxide upset this relationship



Estimating I-THM Occurrence

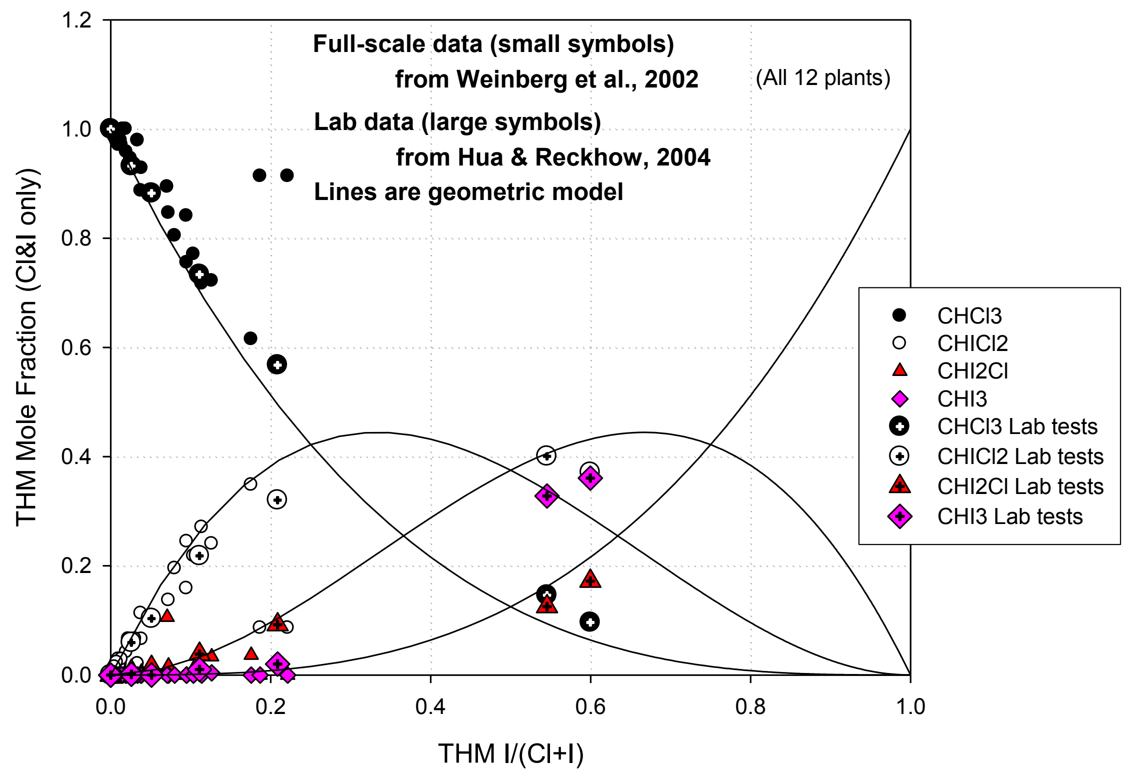
- I originates from sea water
  - More volatile than Cl or Br, so continental waters are relatively enriched in I
  - Still, I should be roughly correlated with Br
- I-THMs are related to iodide concentration
  - Just as Br-THMs are related to bromide level
- Therefore I-THM fraction should be positively correlated with Br-THM fraction



DS Data from Weinberg et al., 2002

Iodo speciation is similar

- Only low THM I data available from field sites
- Suggestions of departure from probabilistic model at high THM I
  - Higher iodoform than expected
  - Possible decomposition of larger TOI structures



What do we know about TOI

DATA FROM MODEL COMPOUND STUDIES

Many Iodo-acids decompose

- Decarboxylation rates of THAAs in water
  - From Zhang and Minear, 2002; expanded by UMass

	Half-life (hr)		% Remaining @ 24 hr		
HAA	20C	55C	20C	55C	degradation product (THM)
TCAA	99000	130	100.0%	88.0%	chloroform
BDCAA	21600	36	99.9%	63.0%	bromodichloromethane
DBCAA	4400	8	99.6%	12.5%	chlorodibromomethane
TBAA	620	3	97.4%	0.4%	bromoform
DCIAA	2414	3.2	99.3%	0.5%	dichloroiodomethane
BCIAA	479	0.63	96.6%	0.0%	bromochloroiodomethane
DBIAA	95	0.12	84.0%	0.0%	dibromoiodomethane
CDIAA	62	0.08	76.5%	0.0%	chlorodiiodomethane
BDIAA	12	0.02	26.0%	0.0%	bromodiiodomethane
TIAA	2	0.00	0.0%	0.0%	triiodomethane

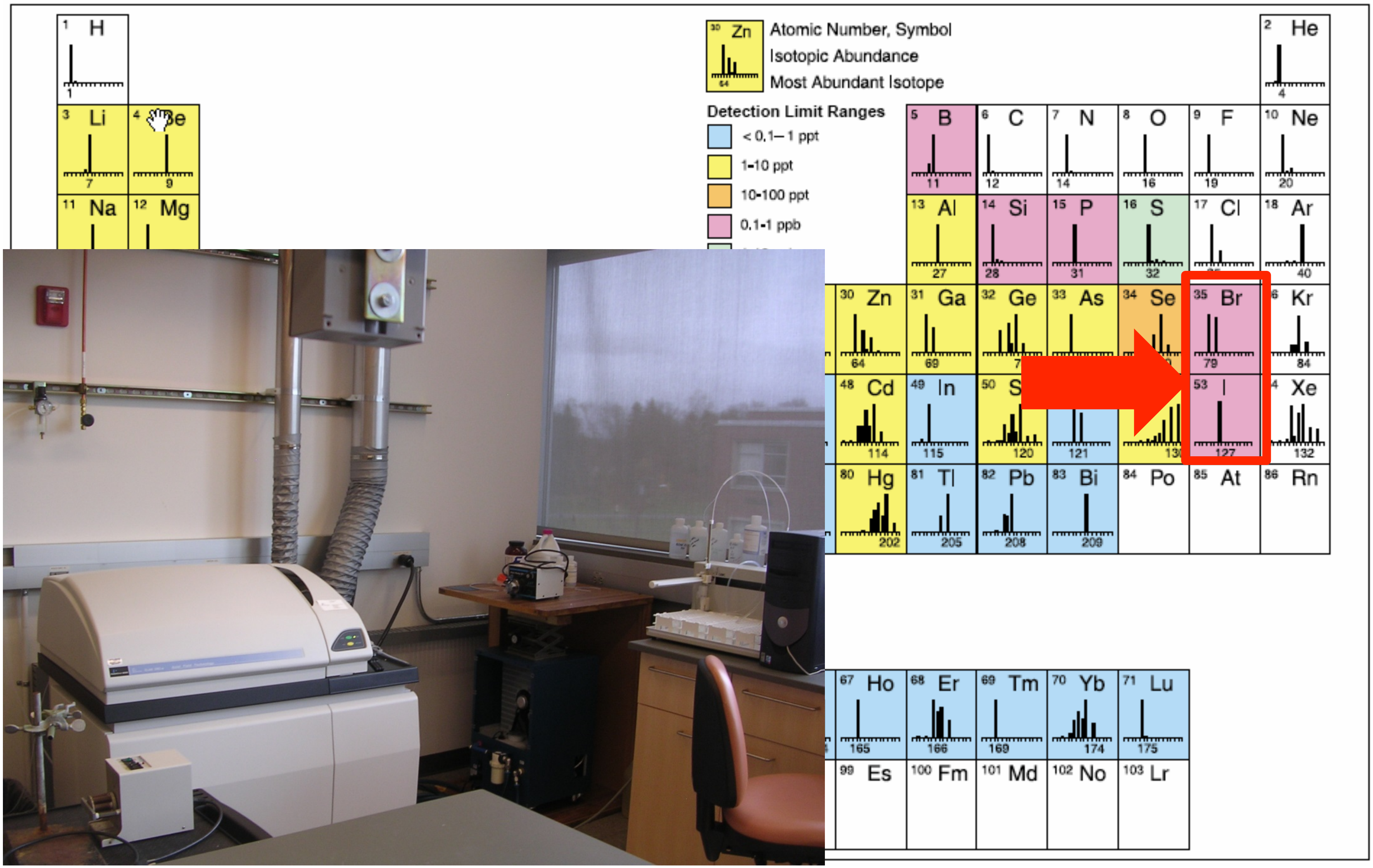
Distribution System → (20C column)

Water Heater → (55C column)

How can we actually measure ambient TOI?

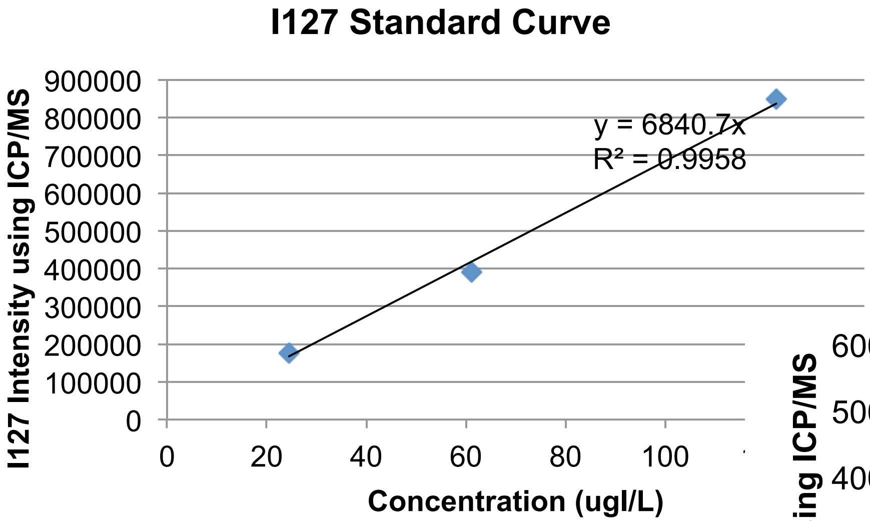
USE OF ICP/MS FOR QUANTIFICATION OF I IN TOX

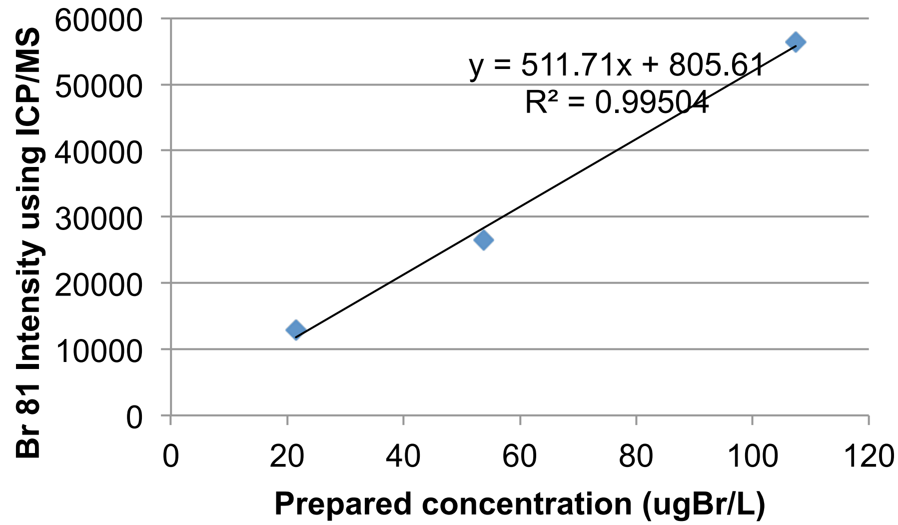
Improved MDL with ICP/MS



Standard Curves with ICP/MS

- Especially good for Iodine





Method Detection Limit

- ICP/MS detection of halides (µg/L)

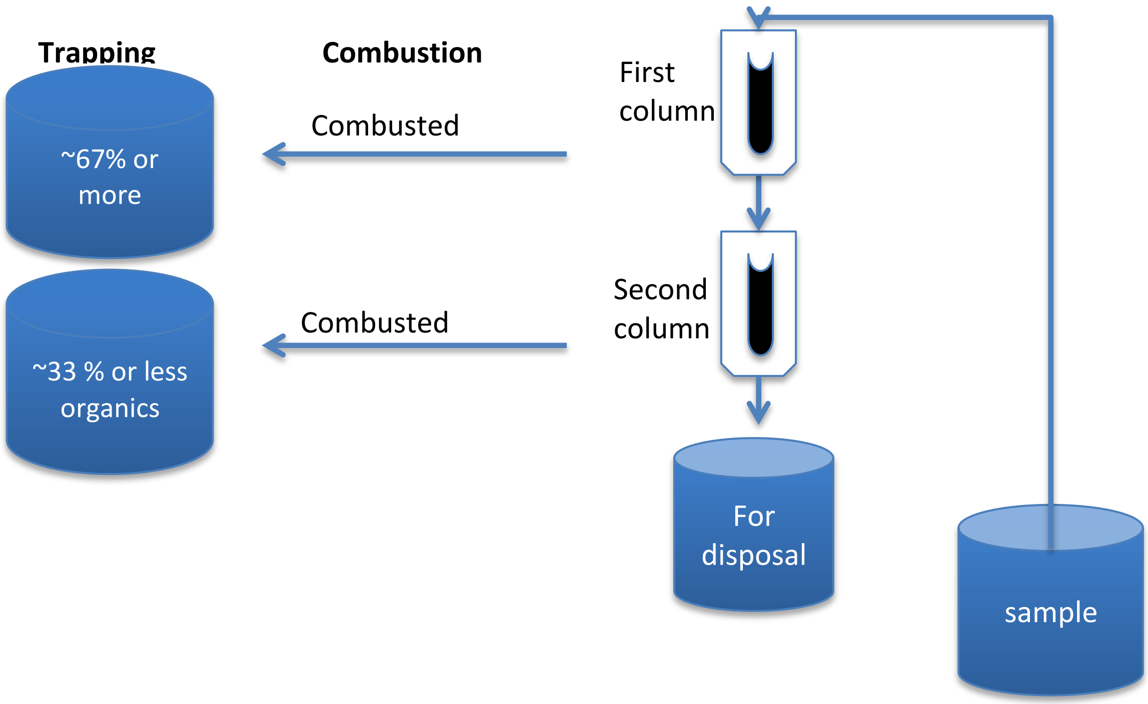
Set	Iodide			Bromide		
	Measured concentration (ugI/L)	**MDL**	LOQ	Measured concentration (ugBr/L)	**MDL**	LOQ
High Replicate	1.74	**0.49**	1.57	0.97	**0.58**	1.85
	2.10			0.81		
	2.16			1.04		
	1.80			1.28		
	1.91			1.24		
	1.82			1.32		
	1.87			1.08		
Low Replicates	1.28	**0.19**	0.61	0.89	**0.98**	3.13
	1.35			0.73		
	1.40			0.22		
	1.23			0.03		
	1.35			0.58		
	1.32			0.42		
	1.25			0.77		

Testing TOI recovery with ICPMS

- Recovery in TOI is often good but not always

	Analyte	Prepared concentration (ugI/L)	Concentration in original solution (ugI/L)	Iodine Recovery (%)	Total Iodine Recovery (%)
Iodo-acetic Acid	Raw	126.90	116.12	91.5%	
	1st collected effluent		21.19	16.7%	**91%**
	2nd collected effluent (nitrate solution)		10.51	8.3%	
	TOX		83.56	65.8%	
Iodoform	Raw	114.21	130.44	114.2%	
	1st collected effluent		34.78	30.5%	**78%**
	2nd collected effluent (nitrate solution)		22.07	19.3%	
	TOX		31.66	27.7%	
Iodo-toluene	Raw	152.28			
	1st collected effluent		46.19	30.3%	**72%**
	2nd collected effluent (nitrate solution)		10.44	6.9%	
	TOX		53.00	34.8%	
Tri-iodoacetic Acid	Raw	152.28			
	1st collected effluent		14.24	9.4%	**47%**
	2nd collected effluent (nitrate solution)		1.53	1.0%	
	TOX		55.96	36.7%	

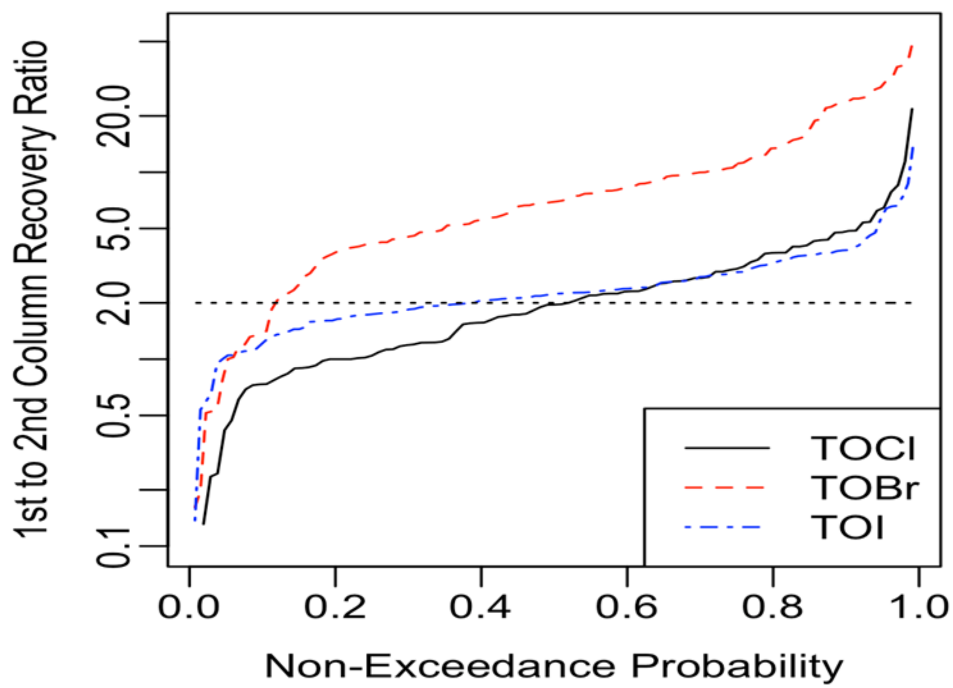
Where does the missing X go?



- Not adsorbed?
- Washed out?

GAC breakthrough characteristics

- The non-exceedance probability diagram of the 1st: 2nd column recovery ratio of TOCl, TOBr, and TOI.



Field Studies using actual treated drinking waters

TARGETING HAAS AND ICMS

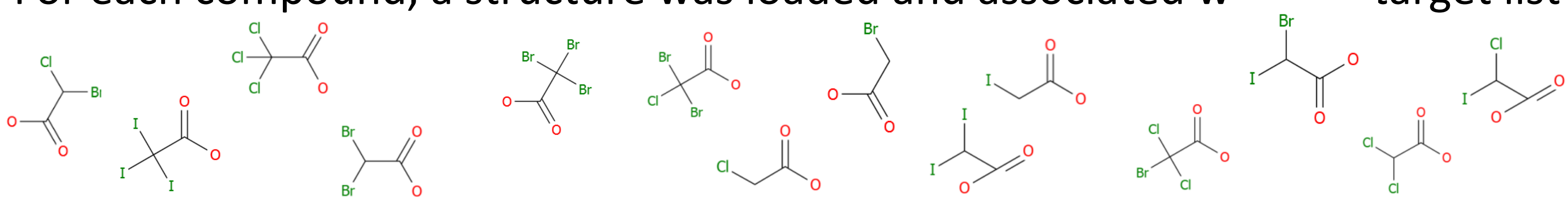
Target List: Searched Following Full Spectral QTof Acquisition

Manage Components

Create Import Paste Results Delete Edit Fragments... Edit Adducts... Add To Common Fragments Add To Neutral Losses

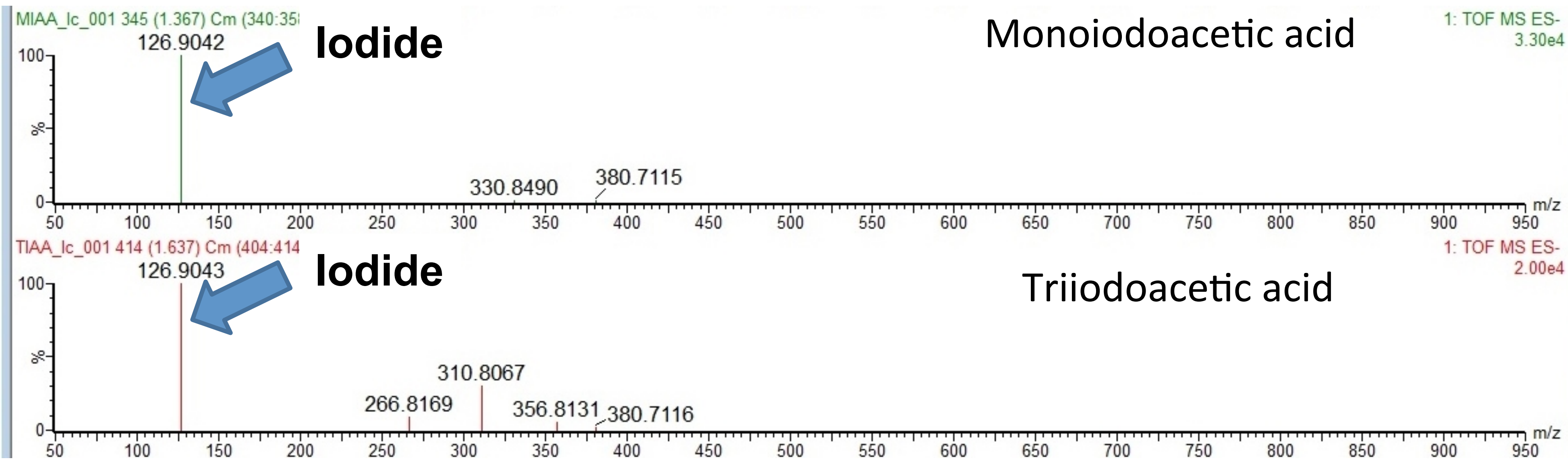
	Component name	Label	Item tags	Expected RT (min)	Expected neutral mass (Da)	Expected fragment (m/z)	Adducts	Excluded	Formula
1	BCAA				171.8927	126.8956, 78.9189			C2H2BrClO2
2	BIAA				263.8283				C2H2BrIO2
3	CIAA				219.8788				C2H2ClIO2
4	DBAA				215.8422	170.8451			C2H2Br2O2
5	DBCAA				249.8032				C2HBr2ClO2
6	DCAA				127.9432	82.9461			C2H2Cl2O2
7	DCBAA				205.8537				C2HBrCl2O2
8	DIAA				311.8144				C2H2I2O2
9	IAA				185.9178				C2H3IO2
10	MBAA				137.9316	77.9105			C2H3BrO2
11	MCAA				93.9822	33.9610			C2H3ClO2
12	TBAA				293.7527				C2HBr3O2
13	TCAA				161.9042	116.9071			C2HCl3O2
14	TIAA				437.7111				C2HI3O2

- For each compound, a structure was loaded and associated with the target list

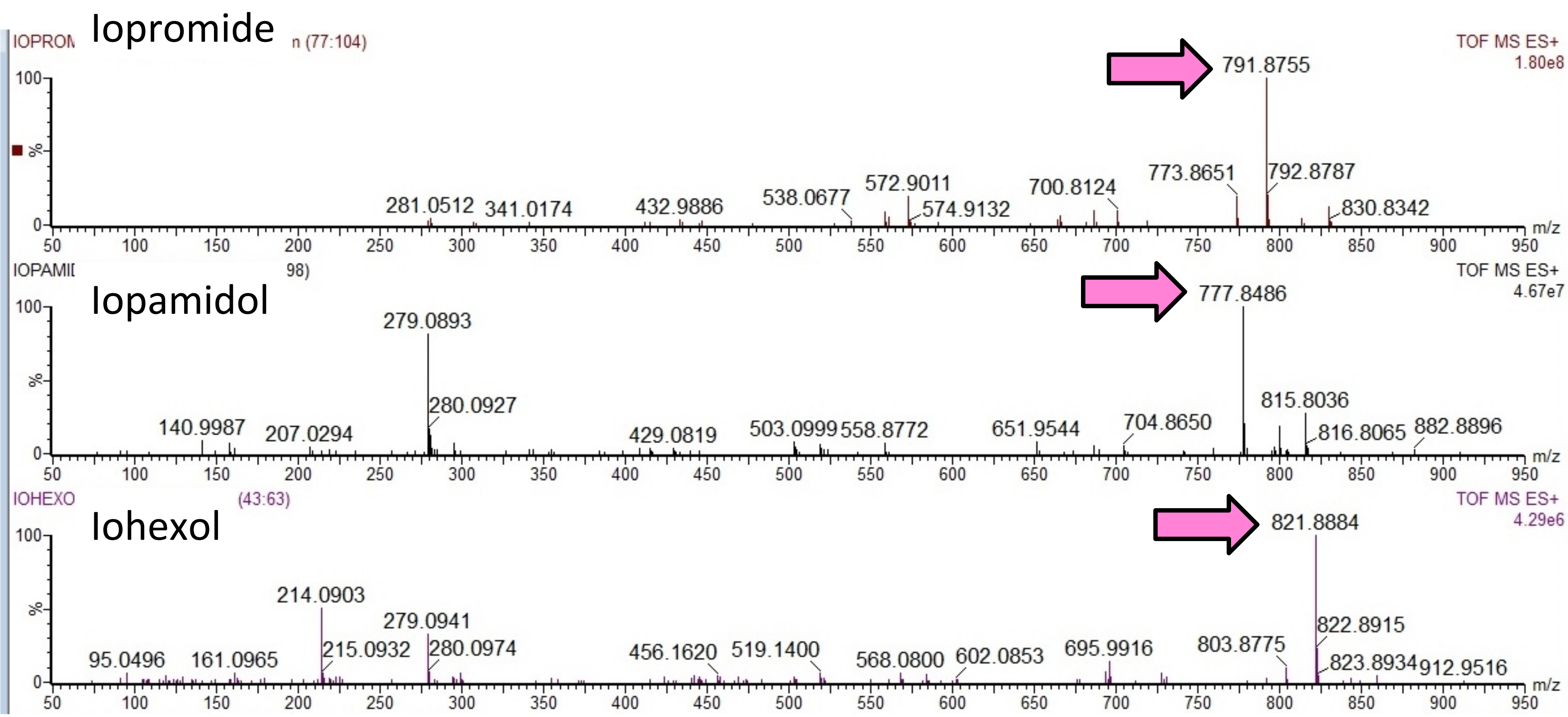


- Fragment masses were obtained from a literature source which utilized MRMs; exact masses were calculated from these known fragments and entered in the component search

ESI negative mode



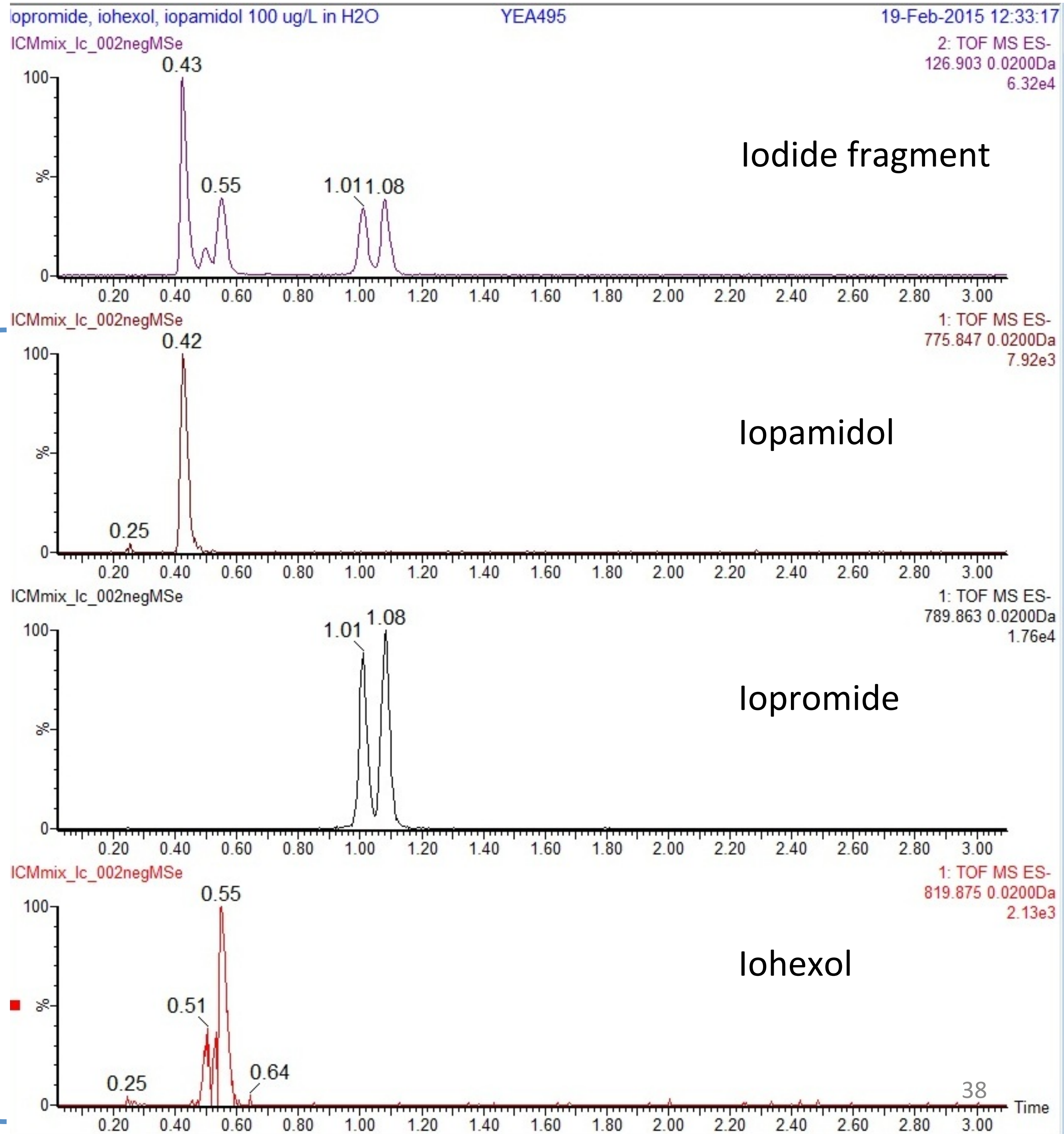
ESI positive mode



High fragmentation energy channel

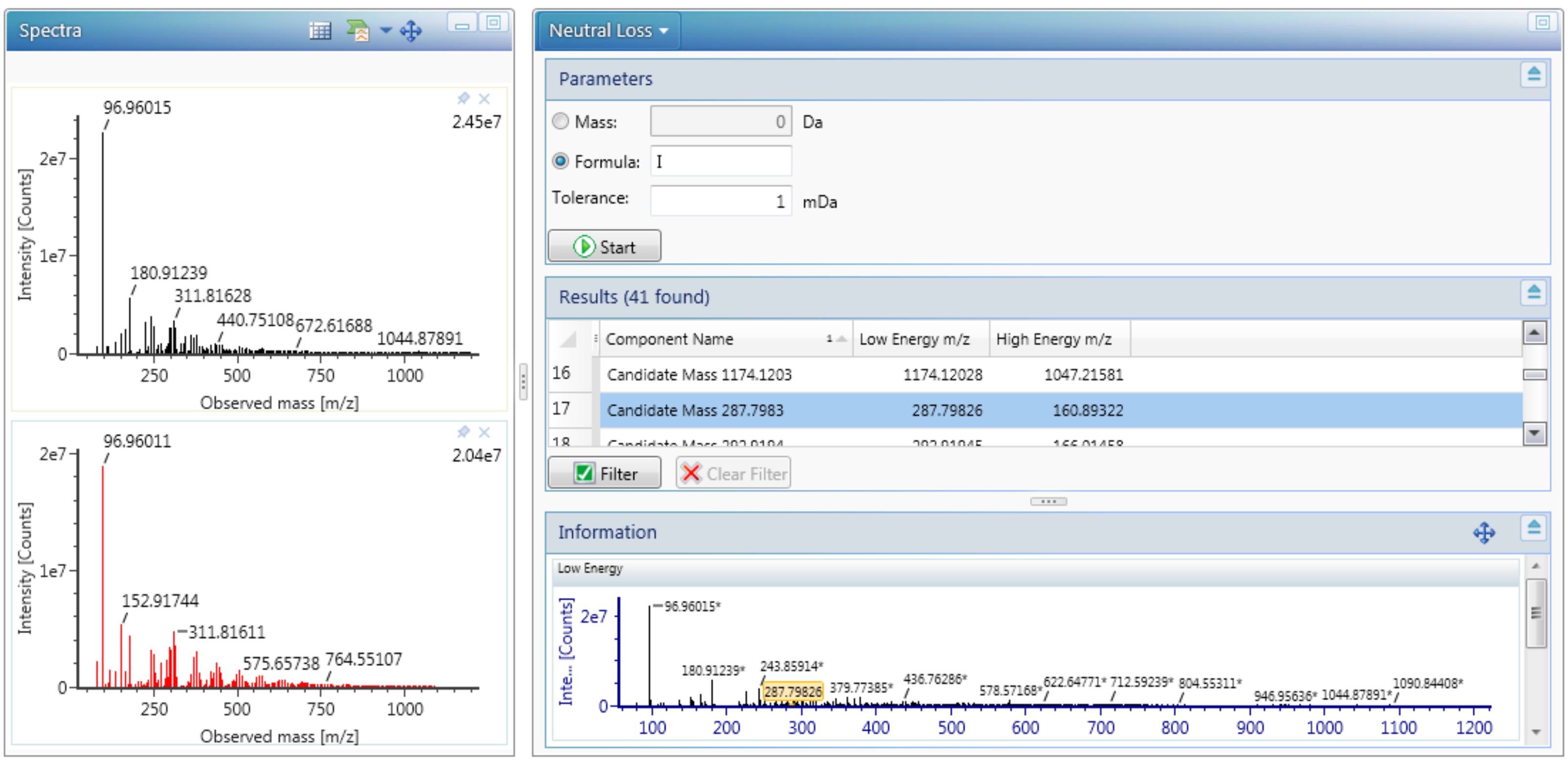
ESI negative mode (MS^e)

Low fragmentation energy channel



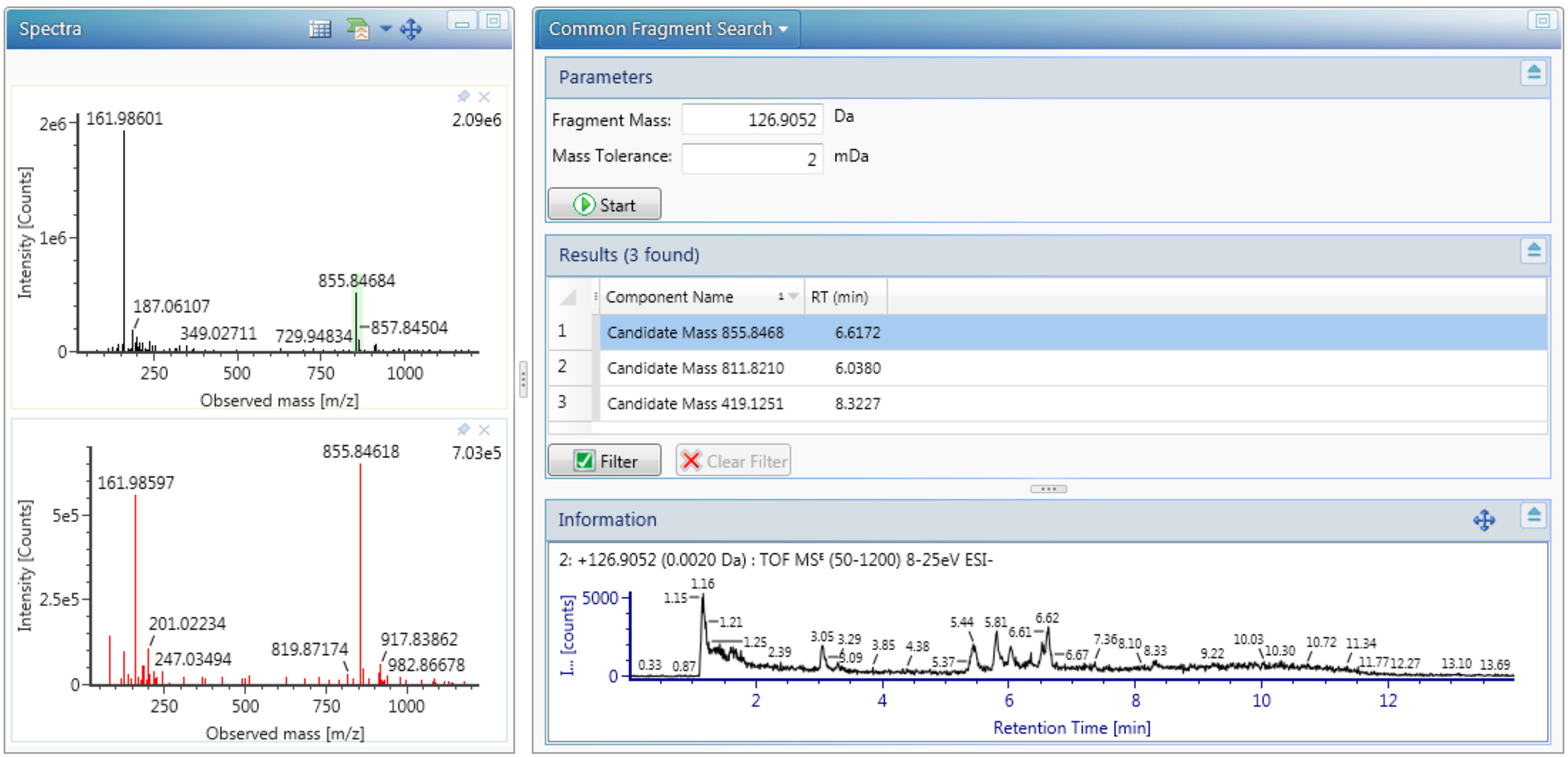
Searching for Unknown Iodinated Compounds

- Neutral Loss Search: from list of unassigned masses, the neutral loss of –I was performed by searching for the difference of 126.9045 between the low energy spectrum and high energy spectrum

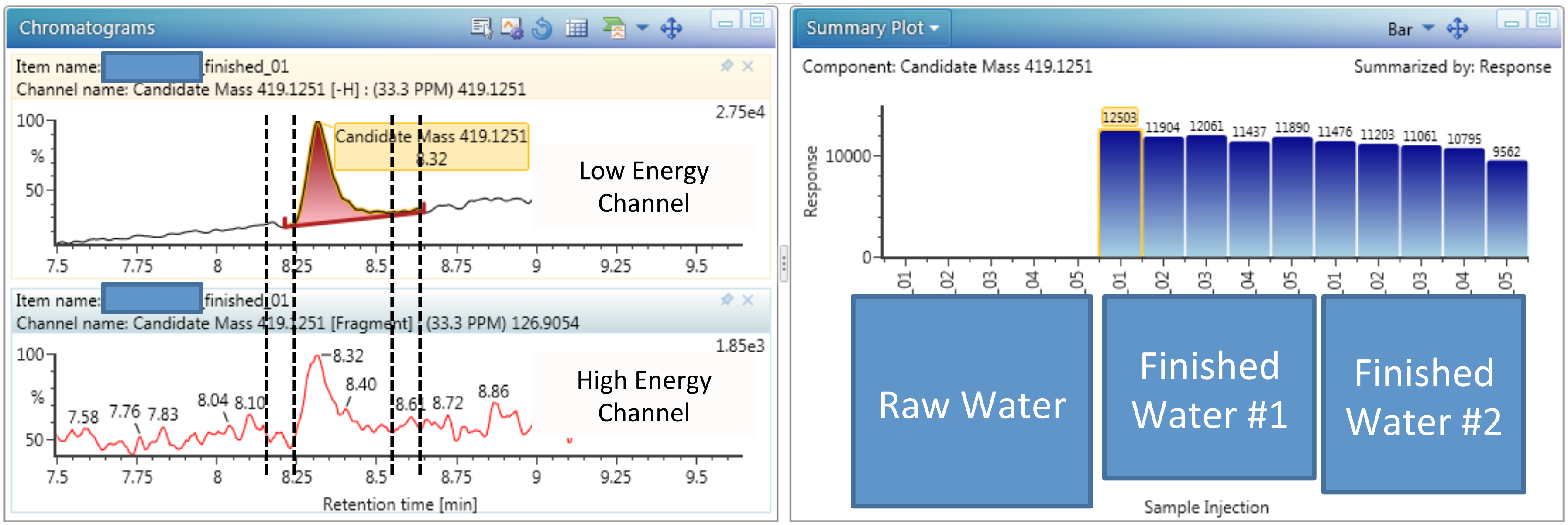


Searching for Unknown Iodinated Compounds

- Common Fragment Search: from list of unassigned masses, the common fragment of –I (m/z 126.9052) was performed by searching for said fragment in high energy spectrum

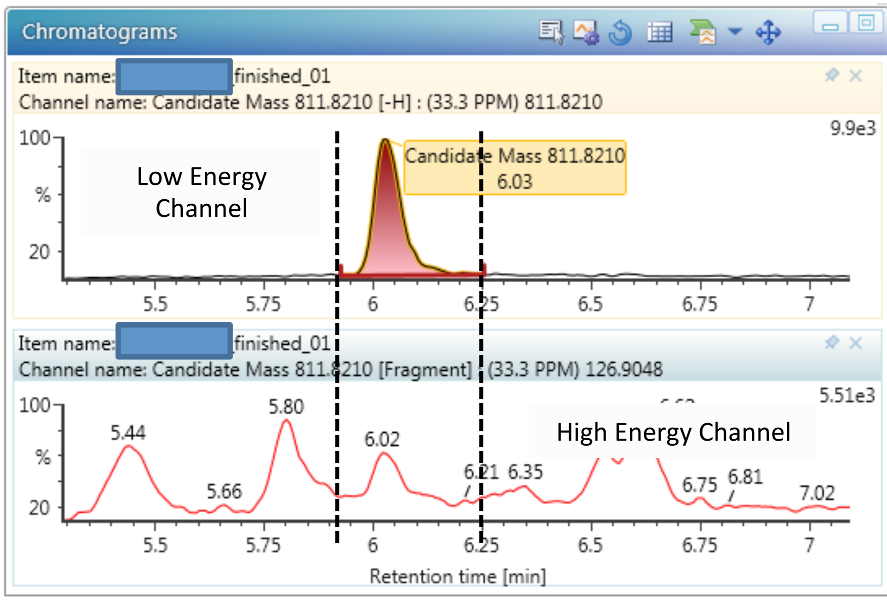


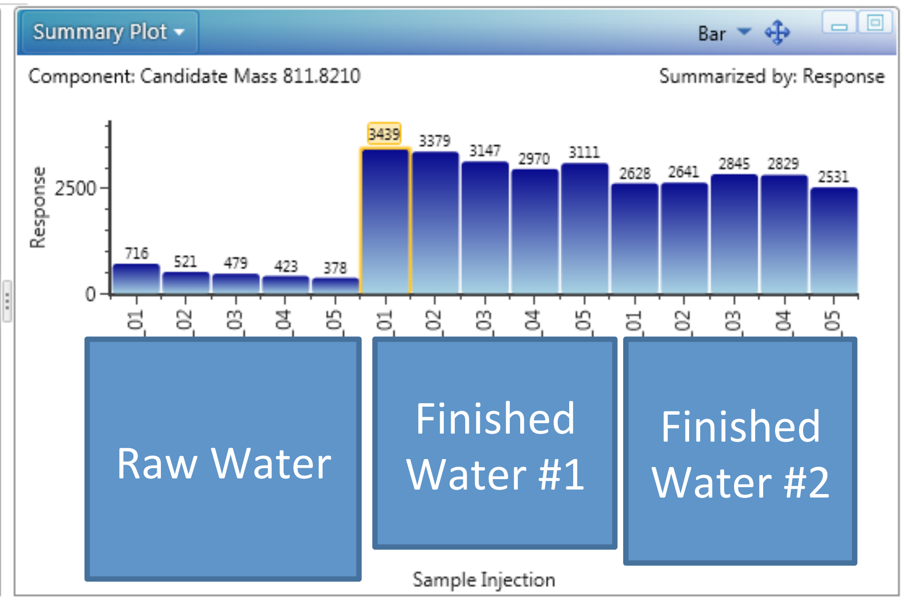
Proposed Identification 1



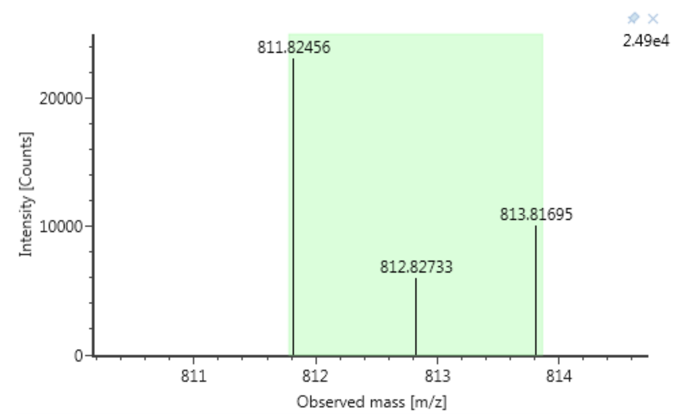
- Elemental Composition computation is based on isotope distribution pattern in observed spectrum and selected elements for search
- Result for 419.1251 = $C_{22}H_{29}I$
- Mass Error for proposed ID = 2.2 ppm

Proposed Identification 2





- Result for 811.8210 = $C_{19}H_{5}\mathbf{Cl}IN_{7}O_{20}$
- Mass Error for proposed ID = -4.9 ppm



Conclusions

- TOX is still quite relevant to assessing adverse health effects in drinking water, however:
  - Halogen specific detection is needed
  - More structural information would improve its usefulness
- Standard methods cannot be used to measure TOI
  - Solution: incorporate ICP/MS
- Conventional TOX loses key structural information
  - Solution: use LC/QTOF with modern methods of data analysis as an alternative

Acknowledgments

- Waters Corporation
  - Especially: Lauren Mullin
- National Science Foundation
  - Major Research Instrumentation program
- Mitsubishi - Cosa