Overview of Emerging Contaminants of Concern in Drinking Water

Susan D. Richardson

U.S. Environmental Protection Agency,
National Exposure Research Laboratory, Athens, GA

Emerging Contaminants

- DBPs (including NDMA and nitrosamines)
- PFOA
- Pharmaceuticals
- Algal toxins
- Perchlorate
- Pesticide degradation products
- Organotins
- *Cryptosporidium* & *Giardia* (and other pathogens)

Drinking Water DBPs

Formed by the reaction of isinfectants with natural organic natter

oncern over possible human ealth risk:

Epi studies: risk of bladder cancer; some cause cancer in laboratory animals

Recent concerns about possible reproductive & developmental effects (from epi studies)

DBPs Regulated by the U.S. EPA

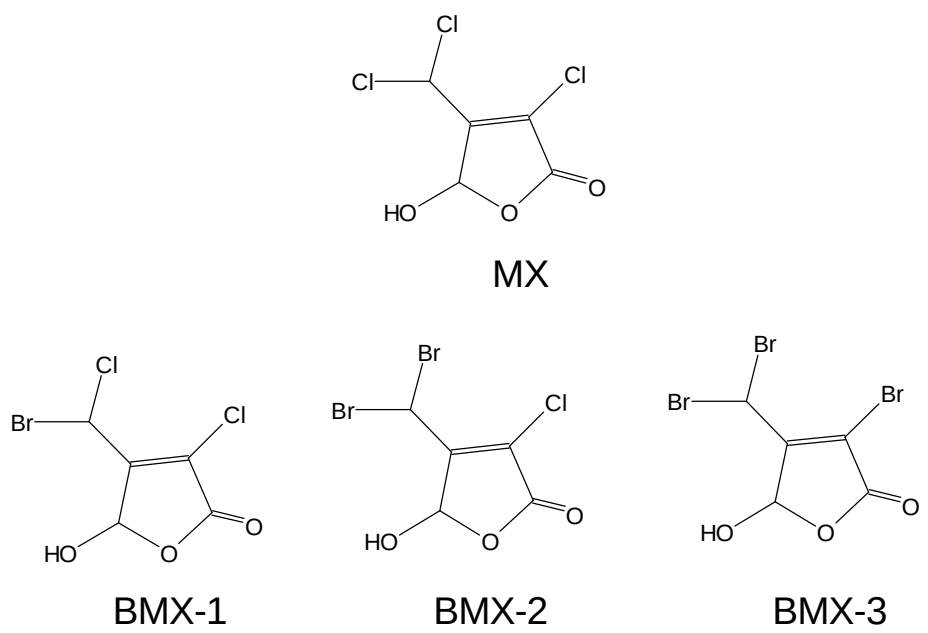
DBP	MCL (µg/L)
Total THMs	80
5 Haloacetic acids	60
Bromate	10
Chlorite	1000

But more than 600 DBPs have been identified

Little known about occurrence, toxicity of unregulated DBPs

Nationwide DBP Occurrence Study

X and BMX analogs
3-Dichloropropenoic acid
do-THMs
alonitromethanes
aloacetonitriles
aloketones
aloaldehydes
aloacetates
aloamides



C & GC/MS methods used

ww.epa.gov/athens/publications/DBP.html

Important Findings

- Many of the high priority DBPs found in drinking waters across the United States (including iodo-THMs, MX & BMXs, halonitromethanes)
- MX levels exceeded previous levels in limited surve (300-400 ng/L found); BMXs reached 100-200 ng/L
- Although the use of alternative disinfectants minimized the formation of THM4, certain other DBP formed at significant concentrations

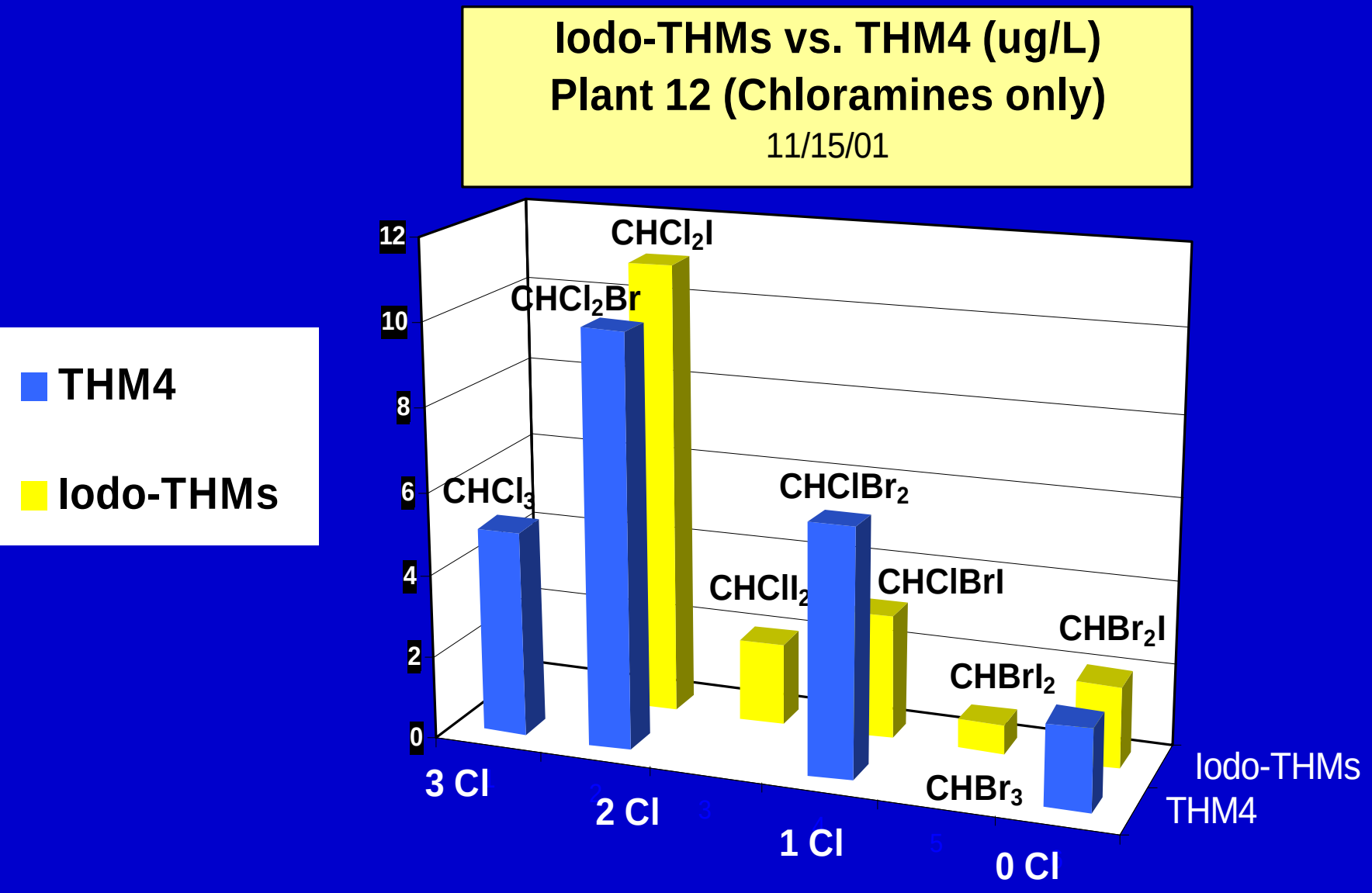
Important Findings

- Use of alternative disinfectants did not control many DBPs:
  - Bromo-trihalonitromethanes highest at a plant using pre-ozonation (ranged from 0.1 to 3 ppb)

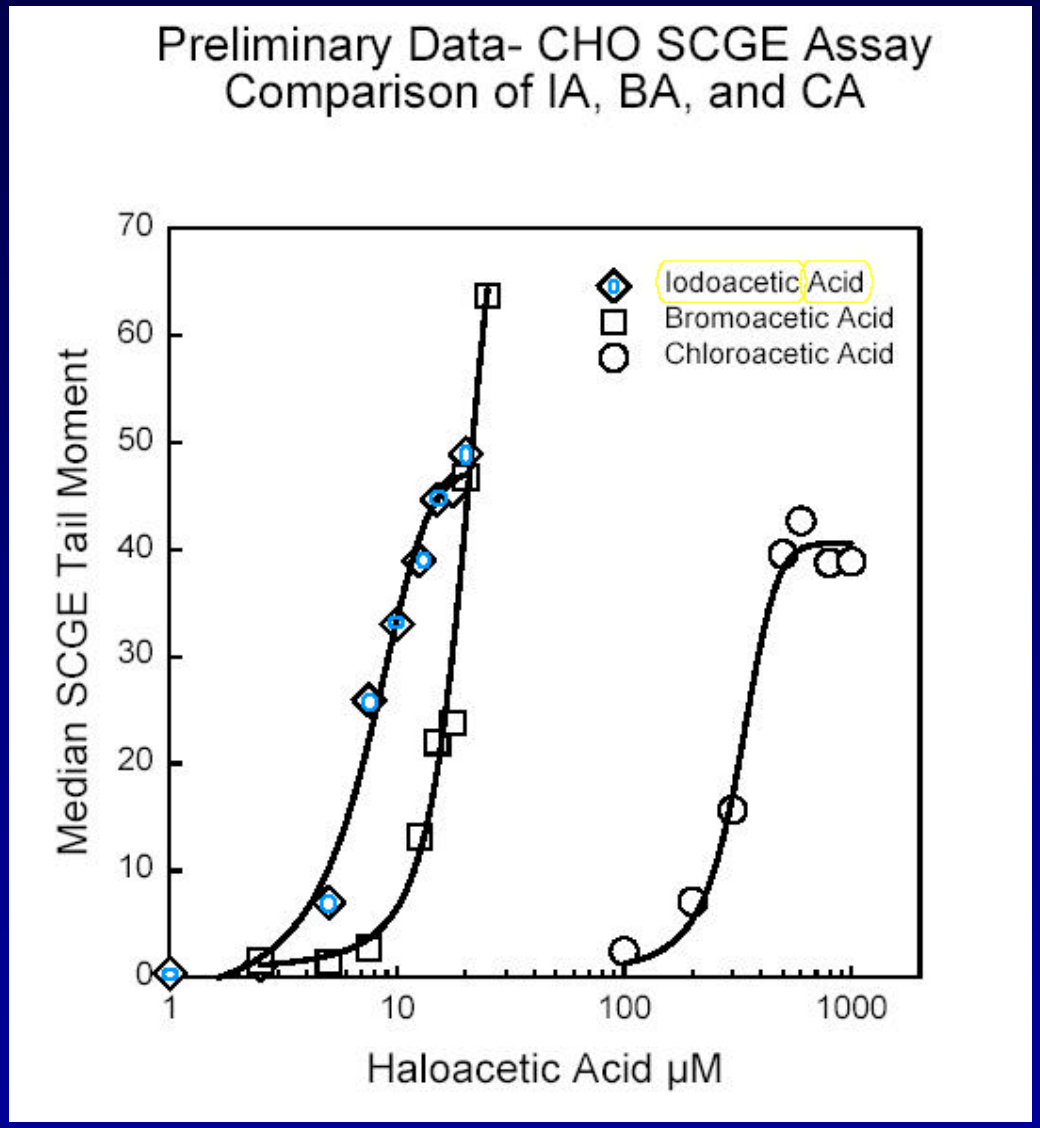
    *New laboratory studies: mono- and di-halonitromethanes also increase with pre-ozonation (prior to post-Cl2)

    *Nitrite and pre-ozone: greatly increase their formation
  - Dihaloaldehydes highest at plant using chloramines & ozone (3rd largest fraction by wt; dichloroacetaldehyde ranged from low ppb to 16 ppb)
  - MX & BMXs high at a plant using chlorine dioxide (followed by chlorine-chloramines) that treated waters high in NOM and bromide
  - Iodo-THMs highest at plant using chloramines alone (up to 15 ppb, 81% of THM4)
- Iodo-acids identified for the first time (also new bromo-acids)

Iodo-THMs


Iodo-THMs vs. THM4 (ug/L)
Plant 12 (Chloramines only)
11/15/01
THM4
Iodo-THMs
12
10
8
6
4
2
0
$CHCl_3$
$CHCl_2Br$
$CHCl_2I$
$CHClI_2$
$CHClBr_2$
$CHClBrI$
$CHBrI_2$
$CHBr_3$
$CHBr_2I$
3 Cl
2 Cl
1 Cl
0 Cl
Iodo-THMs
THM4

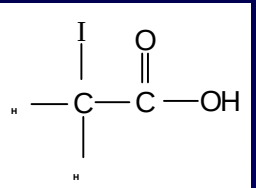
Iodoacetic acid identified as DBP for first time



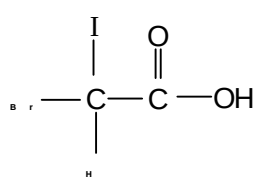
Data courtesy of Michael Plewa, University of Illinois

IA also caused developmental effects in mouse embryos (Hunter et al., 1995)

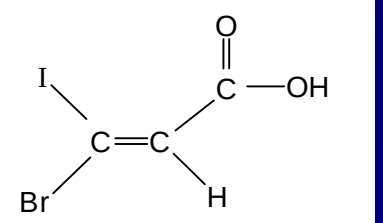
New Iodo-Acids



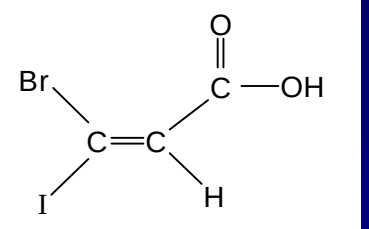
Iodoacetic acid



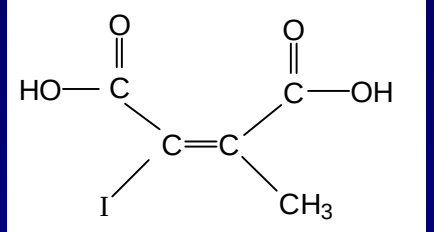
Bromoiodoacetic acid



(Z)-3-Bromo-3-iodopropenoic acid



(E)-3-Bromo-3-iodopropenoic acid



(E)-2-Iodo-3-methylbutenedioic acid

Found in drinking water treated with NH_2Cl (2 separate samplings, 2001 and 2003)

Standards synthesized and confirmed identifications

Iodo-Acid Occurrence Study

- Focus on Chloramination plants
- May 2005: 5 Plants
- August/September: 21 Plants
- Using liquid-liquid extraction, derivatization, and GC/NCI-MS
- CDC measured iodo-THMs in August/September sampling

odo-Acid Concentrations in Finished Drinking Water, ppb
August-September 2005

DBP	Plant 1	Plant 2	Plant 11	Plant 13	Plant 15	Plant 17	Plant 19
lodoacetic acid	0.018	0.020	0.015	0.012	0.026	0.021	0.062
Bromoiodoacetic acid	0.069	0.27	0.16	0.42	0.15	0.49	1.4
(*Z*)-3-Bromo-3-iodopropenoic acid	0.043	ND	0.021	0.085	ND	0.50	ND
(*E*)-3-Bromo-3-iodopropenoic acid	0.030	ND	0.010	ND	ND	0.086	ND
(*E*)-2-Iodo-3-methylbutenedioic acid	0.050	0.050	0.032	0.055	0.046	0.31	0.58

* Based on extraction from a 1-L drinking water sample; values represent mean of 2 samples
Detection limits: 0.25-1.0 ppt (ng/L) detection in drinking water

odo-THM Concentrations in Finished Drinking Water, ppb
August-September 2005

DBP	Plant 1	Plant 2	Plant 11	Plant 13	Plant 15	Plant 17	Plant 1
Bromochloroiodomethane	6.6	1.6	2.1	1.9	0.31	10.2	0.16
Dichloroiodomethane	2.1	3.5	2.2	3.4	2.5	2.1	0.61

* Values represent the mean of two samples

Haloamides

New class not previously measured

Chloroacetamide
Dichloroacetamide
Dibromoacetamide
Trichloroacetamide

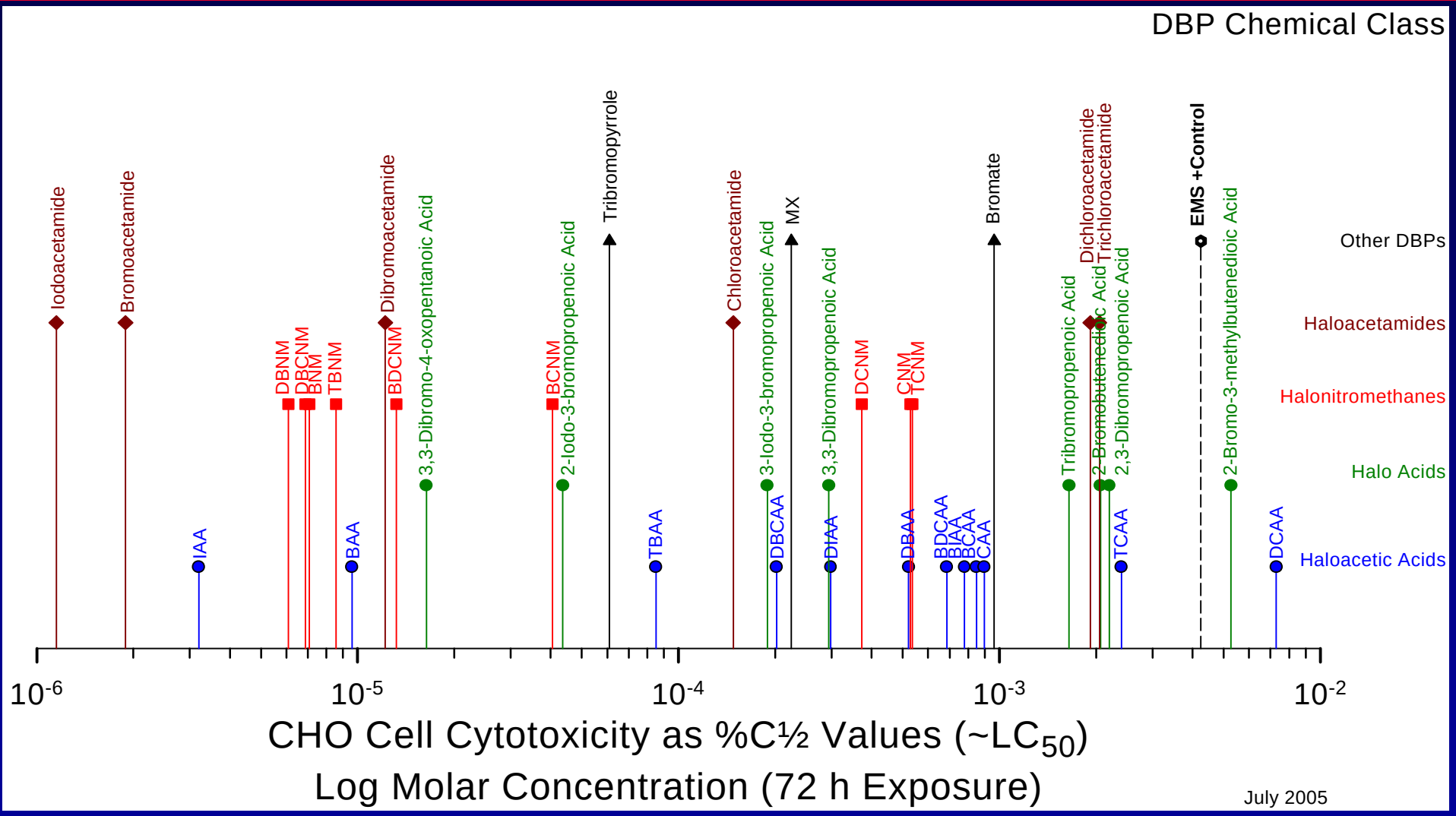
Found in most plants sampled

Individual haloamides ranged from 0.1 to 9.4 ppb

Levels similar to other commonly measured DBPs

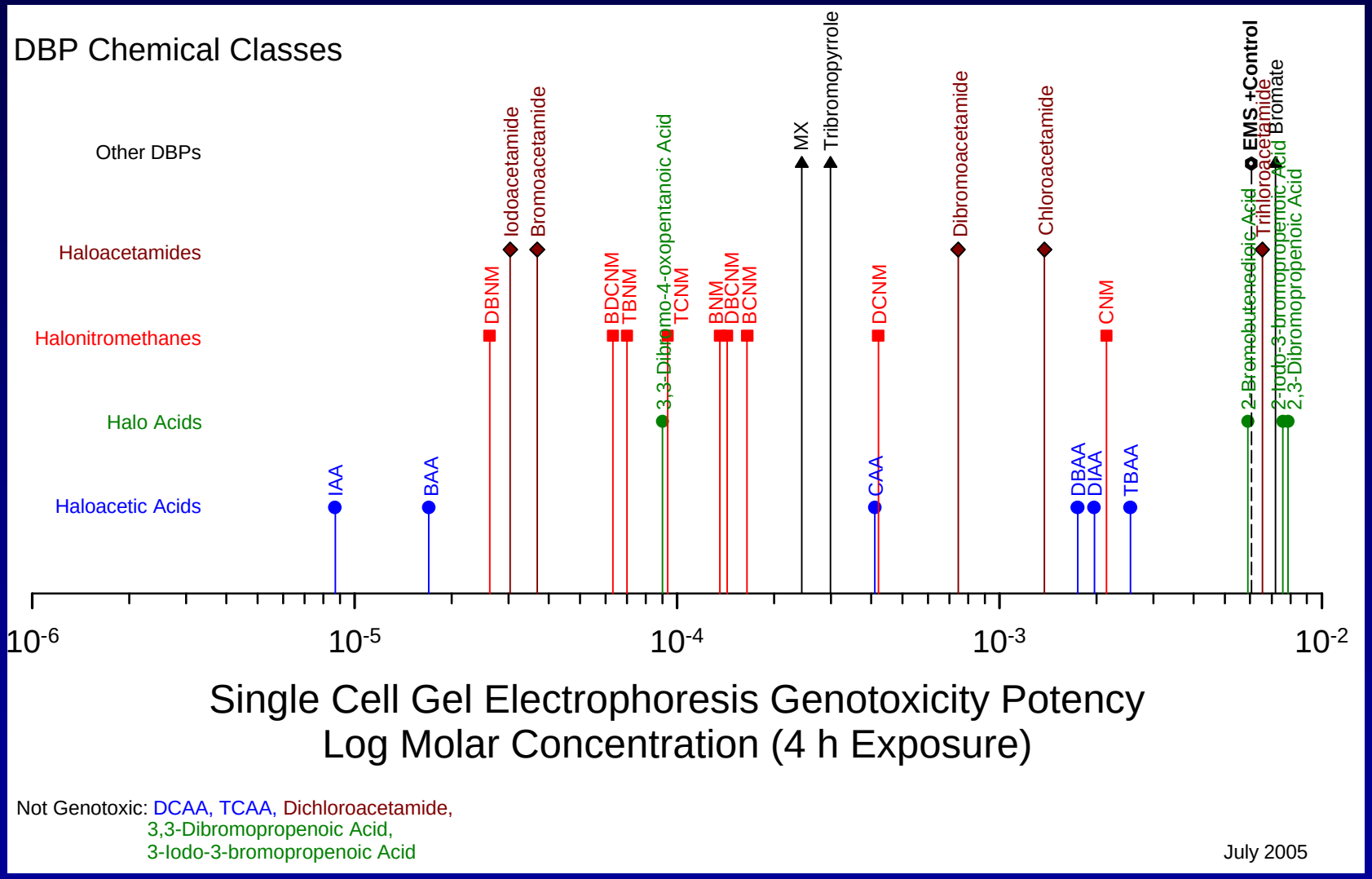
Indication that they may be increased with chloramines

Haloamides--Cytotoxicity



Data courtesy of Michael Plewa, University of Illinois

Haloamides--Genotoxicity

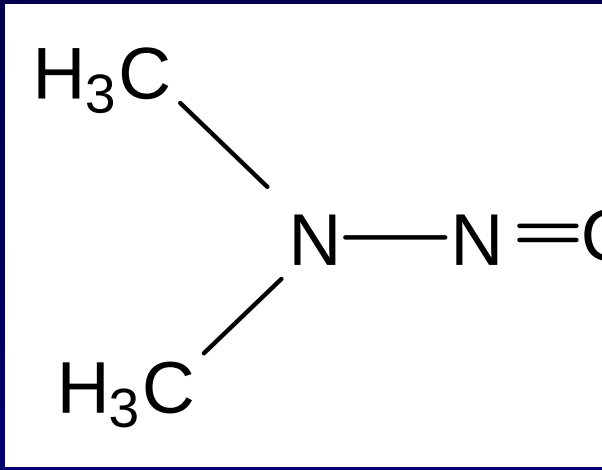


Not Genotoxic: DCAA, TCAA, Dichloroacetamide,
3,3-Dibromopropenoic Acid,
3-Iodo-3-bromopropenoic Acid

July 2005

Data courtesy of Michael Plewa, University of Illinois

Nitrosodimethylamine (NDMA)



- On the UCMR-2
- Formed as a DBP from chloramine and chlorine (DADMAC coagulants)
- Probable human carcinogen
- NDMA is also a contaminant from rocket fuel, plasticizers, polymers, batteries, etc.
- 2004: Found up to 180 ng/L in finished water from Canada
- *N*-nitrosopyrrolidine and *N*-nitrosomorpholine also now found as DB
- Initially detected in Calif. groundwater wells in 1998 at 0.15 ppb
- Action level is 10 ppt (ng/L) (in Calif.)
- Ontario has MCL of 9 ng/L in drinking water

New EPA Method for NDMA and 6 other Nitrosamines (GC/CI-MS/MS)
www.epa.gov/nerl/research/2004/g2-6.html

PFOS/PFOA

PFOS: $CF_3—(CF_2)_7—SO_3^-$

Perfluorooctane sulfonate

- Used to make soil-, stain-, grease-, and water-resistant coatings (e.g., Teflon) that are widely applied to fabrics, carpets, cookware, paper, and automobiles

- 1999: EPA began investigation of PFOS
  Unexpectedly toxic, persistent, bioaccumulative, found in bloo
  of general population & wildlife
- 2000: 3M discontinued manufacture of PFOS (but PFOA and other fluorinated surfactants still manufactured by several companies)
- 2000: EPA expanded investigation to include other fluorochemicals, including PFOA to determined whether there is concern (3M ha
  found PFOA in human blood during studies of PFOS)

PFOA

PFOA: $CF_3—(CF_2)_6—COOH$

- Persistent – not known to hydrolyze, photolyze, biodegrade
- Used as a processing aid in many products
- Concern about biodegradation of polymers to PFOA
- Hazard: bioaccumulative, liver toxicity, developmental toxicity mmunotoxicity, tumors in rodents, monkeys
- Effects magnified in successive generations (from rat studies)

PFOA

Ever wonder why grease doesn’t come through paper wrapper?

PFOA

Questions and Concerns

- Why is it in the bloodstream of almost everyone measured?
- Where is it coming from? How is it transported?
- Why is it biota in the Arctic?

(Up to 3112 ng/g in polar bears from Arctic—can be at greater levels than PCBs)

Hypothesis: telomer alcohols volatile, transported, oxidized to acid in atmosphere and in the body

- PFOA also found in well water (up to 10 ppb) in areas near a manufacturing plant and in stream water (up to 5 ppb) near a carpet manufacturing plant

Pharmaceuticals

onsidered as possible future CCL Drinking Water ontaminants:

Diclofenac (antirheumatic)
Carbamazepine (antiepileptic)
Chloramphenicol (antibiotic)

Concern about introduction of these compounds into drinking water

Possible estrogenic effects, could lead to antibiotic resistance

LC/ESI-MS is enabling their measurement in nvironmental waters (~150 out of 3000 possible being easured)

Pesticide Degradation Products

- May be more environmentally relevant than parent species
- Often found as groundwater contaminants in agricultural areas
- Previously overlooked
- Most highly polar; require LC/MS or LC/MS/MS
- Some on the CCL:
  - DCPA monoacid & diacid degradate
  - Alachlor ESA and other acetanilide pest. degradation products
  - Triazines and their degradation products (including cyanazine & atrazine-desethyl)

Organotins

Included on CCL

Used in anti-fouling paints for ships, but recently reported leaching from PVC pipe at continuous levels of 1 ppb (into drinking water)

Also dietary sources of organotins

Toxicity: trialkyl > di > mono

Neurotoxicity: Dibutyltin >> triethyl, trimethyl
Effect in brain cells as low as 30 ppb

ew EPA Method 8323 (µ-LC-ESI-MS) by Tammy Jones-Lepp, PA-Las Vegas (www.epa.gov/epaoswer/hazwaste/test/new-meth.htm)

Algal Toxins

ncluded on the CCL

Responsible for large fish kills, oisoning of shellfish, illness in eople

amples:

Microcystins, nodularins
blue-green algae; cyclic peptides)
–hepatotoxic

Saxitoxins, Anatoxins (blue-green algae; heterocyclic uanidine structures)—neurotoxic

Red Tide" toxins (polyethers)—neurotoxic

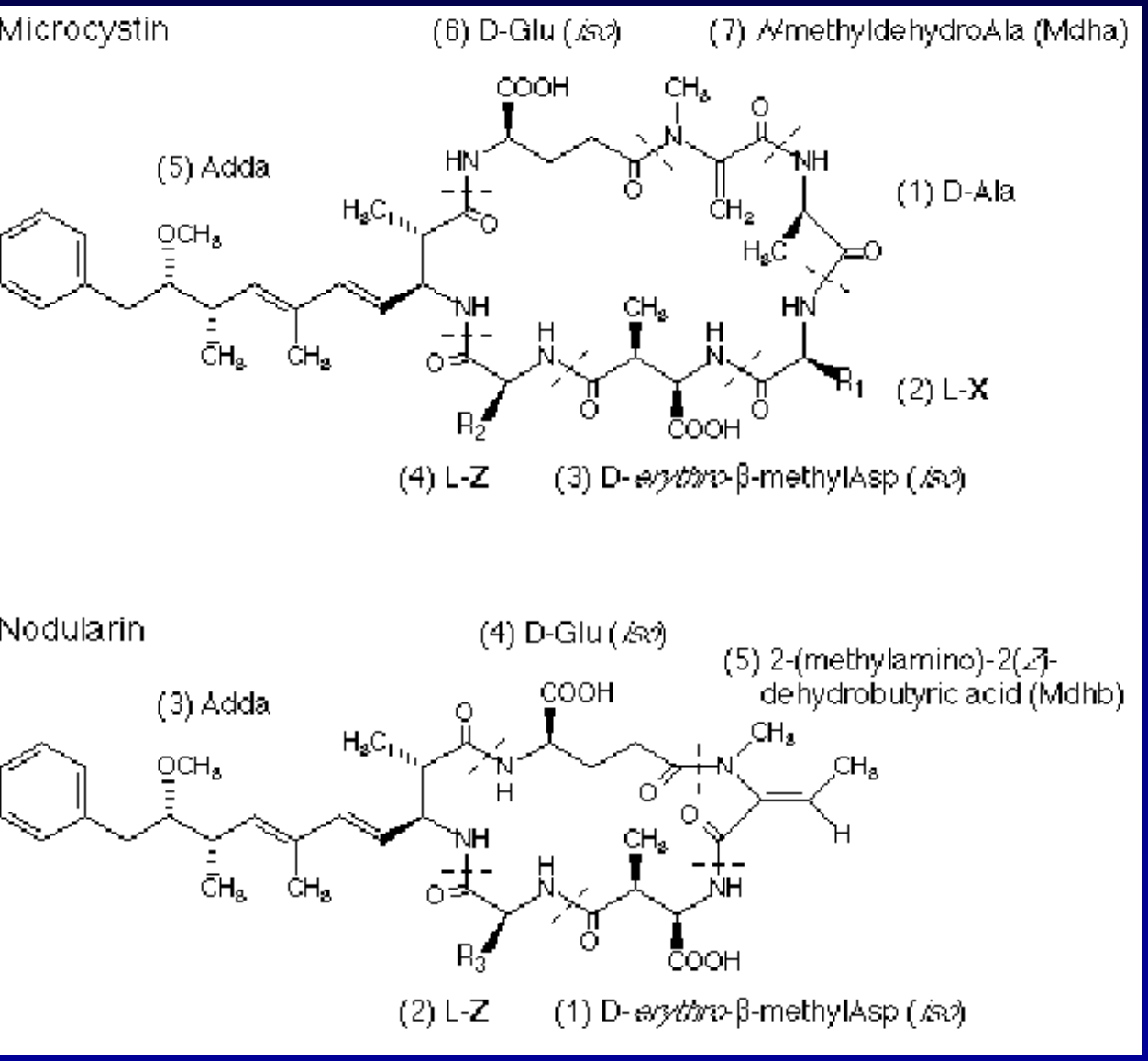
Algal Toxins

- Algal toxins found in finished drinking water in Florida:

Burns, J. *Cyanobacteria and Their Toxins in Florida Surface Waters and Drinking Water Supplies*. Report to the Florida Department of Health, Tallahassee, FL, 2003.

- Microcystins most common
- Anatoxin-a in 3 finished drinking waters up to 8.46 ug/L
- Cylindrospermopsin in 9 finished waters, 8.07-97.12 ug/L
- Cylindrospermopsin previously found in a DW reservoir in Australia, following a poisoning episode of 138 children and 10 adults

Algal Toxin Structures



Algal Toxin	L-X	L
Microcystin-LR	Leu	A
Microcystin-RR	Arg	A
Microcystin-YR	Tyr	A
Microcystin-LA	Leu	A
Microcystin-LW	Leu	T
Microcystin-LF	Leu	P
Nodularin	-	A

Slide courtesy of V. Taguchi, S. Jenkins, P. Crozier, J. Newman, Ontario Ministry of the Environment, Ontario, Canada

Perchlorate (ClO_4^-)

Included on the CCL

- Contaminant in groundwater, surface water—very soluble
- Ammonium perchlorate used as an oxygenate in solid propellants used for rockets, missiles, fireworks
- High quantities disposed of since 1950s in Nevada, Calif., Utah; now found in water supplies across U.S. at ppb levels (not limited to Western states)
- Accumulates in plants; possible introduction through use of fertilizers (with Chilean nitrate source)
- Perchlorate affects thyroid function—which affects normal metabolism, growth, development

New EPA Methods for Perchlorate

Developed to overcome problems when measuring perchlorate in hig ionic strength waters

- **EPA Method 330.0** (IC/ESI-MS; uses O-18 labeled internal standard; MDLs 0.02 ppb)
  www.epa.gov/nerlcwww/ordmeth.htm

- **EPA Method 331.0** (LC/ESI-MS/MS; uses O-18 labeled internal standard, MRM; MDLs 0.02 ppb)
  www.epa.gov/safewater/methods/sourcalt.html

- **EPA Method 314.1** (IC; uses a concentrator column to retain perchlorate while interfering anions are washed to waste; MDL 0.2 ppb)
  www.epa.gov/safewater/methods/sourcalt.hrml

Former EPA Method: Method 314.0, MDL 4 ppb, problems in high ionic strength wat

Other Upcoming EPA Work

- 1,4-Dioxane and other solvent stabilizers
- Triazine degradation products
- An overhaul of Method 524.2 for VOCs (including the investigatio of iodo-THMs by this method)
- HAAs by LC/MS/MS

Disclaimer: Although this work was reviewed by EPA and approved for presentation, it may not necessarily reflect official Agency policy. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Acknowledgments

Michael Plewa (Univ. Illinois)

Tom Jenkins (U.S. EPA, Athens)

Jane Ellen Simmons (U.S. EPA, RTP, NC)

Eric Weber (U.S. EPA, Athens)

Bill Budde (U.S. EPA, Cincinnati)

Jean Munch (U.S. EPA, Cincinnati)

Elizabeth Hedrick (U.S. EPA, Cincinnati)

Dave Munch (U.S. EPA, Cincinnati)

Disclaimer: Although this work was reviewed by EPA and approved for presentation, it may not necessarily reflect official Agency policy. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.