Occurrence of Iodo-Acid and Iodo-THM Disinfection By-Products in Chloraminated Drinking Water

Susan D. Richardson[1], F. Gene Crumley[1], J. Jackson Ellington[1], John J. Evans[1], Benjamin C. Blount[2], Lalith K. Silva[2], Frederick L. Cardinali[2], Michael J. Plewa[3] and Elizabeth D. Wagner[3]

[1]US EPA ORD/NERL/ERD, Athens, GA; [2]CDC, Atlanta, GA; [3]University of Illinois, Urbana, IL

Introduction

Why are DBPs Important?

Concern over possible human health risk:

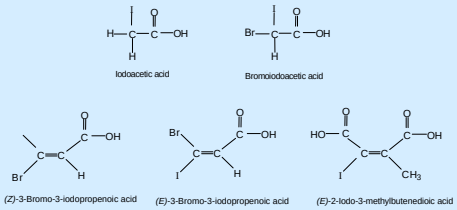
- Some cause cancer in laboratory animals
- Epi studies show increased risk of cancer (primarily bladder cancer)
- Recent concerns about possible reproductive & developmental effects (from epi and lab studies)

DBPs Regulated by the U.S. EPA

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

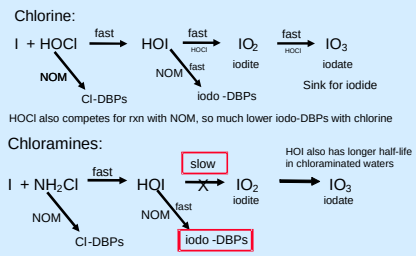
But more than 600 DBPs have been identified. Are the unregulated DBPs responsible for human health effects?

New Iodo-Acid DBPs

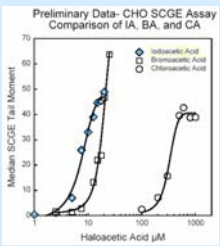


- Initially found in drinking water treated with chloramines (2001 and 2003)
- Standards synthesized and confirmed identifications

Iodo-DBPs Maximized with Chloramines



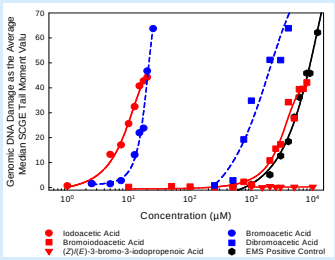
Genomic DNA Damage - Comparison of IAA, BAA, and CAA



Plewa et al., *Environ. Sci. Technol.* 2004, *38*, 4713.

IAA also causes developmental effects in mouse embryos (Hunter et al., 1995)

Mammalian Cell Genotoxicity of Iodo-Acids



Experimental Design

Iodo-Acid Occurrence Study

- Focus on Chloramination plants
- May 2005: 5 Plants
- Fall-Winter 2005: 21 Plants
- Hope to gain information on occurrence, concentrations, and how the length of free Cl_2 contact time (prior to NH_3 addition) affects their formation
- CDC measured iodo-THMs in Fall-Winter 2005 sampling

Methods

Iodo-Acid Method (May 2005)

- Initial method (similar to EPA method 552.3, May 2005): 1 L water, acidify, LLE with TAME, H_2SO_4/MeOH derivatization; GC/NCI-MS (SIM m/z 127)
- Revised method – Fall/Winter 2005 samplings

Revised Iodo-Acid Method (Fall/Winter 2005)

- Salting out with $NaSO_4$, Ethyl Acetate extraction
- Using diazomethane instead of H_2SO_4/MeOH (less time consuming for di-acid)
- Still using GC/NCI-MS
- **Recoveries greatly improved**

Iodo-THM Method (CDC)

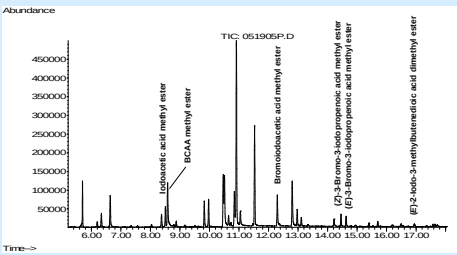
- Solid phase microextraction
- GC/HR-EI-MS with stable isotope dilution (deuterated forms of each analyte)

Results

Iodo-Acid Concentrations in Finished Drinking Water, ppb, May 2005

DBP	Plant 1	Plant 2	Plant 3	Plant 4	Plant 5
Iodoacetic acid	1.7	1.7	0.42	0.24	0.37
Bromoiodoacetic acid	0.52	0.083	0.063	ND	0.066
(Z)-3-Bromo-3-iodopropenoic acid	0.077	ND	ND	ND	ND
(E)-3-Bromo-3-iodopropenoic acid	0.061	ND	ND	ND	ND
(E)-2-Iodo-3-methylbutenedioic acid	0.36	ND	ND	ND	ND

Example of One Plant Sampled (Selected Ion Monitoring of m/z 127)



Iodo-Acid Concentrations in Finished Drinking Water, ppb, Fall-Winter 2005

DBP	Plant 1	Plant 2	Plant 11	Plant 13	Plant 15	Plant 17	Plant 19
Iodoacetic 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

Iodo-THM Concentrations in Finished Drinking Water, ppb, Fall-Winter 2005

DBP	Plant 1	Plant 2	Plant 11	Plant 13	Plant 15	Plant 17	Plant 19
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

Conclusions

- IAA, BrIAA, iodomethylbutenedioic acid found at all 21 plants; highest concentration 1.7 ppb; most concentrations sub-ppb
- Z/E Bromoiodopropenoic acids found at 4 plants
- Iodo-THMs found at all 21 plants; highest individual level (bromochloroiodomethane) 10.2 ppb
- Most iodo-acids genotoxic or cytotoxic to mammalian cells; IAA more cytotoxic & genotoxic than other iodo-acids (and regulated HAAs)
- Iodo-THMs will be tested for toxicity soon

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