Safe Drinking Water?
Effect of Wastewater Inputs and Source Water Impairment and Implications for Water Reuse

Susan D. Richardson

Safe Drinking Water: What are the Issues?

Chemical risk:

- Exposure to hazardous chemicals that enter drinking water supplies (e.g., perchlorate, MTBE, arsenic, etc.)

- Formation of DBPs from reaction of disinfectants with
  - natural organic matter
  - pollutants

Microbial risk:

- Pathogens (e.g., Cryptosporidium, Giardia, etc.)

Stresses on Water Supplies

- Increased N inputs to source waters
  - Can form more toxic N-DBPs
- Increased algal growth → Algal toxins
- Increased drought
  - Increased Br and I →
    - toxic Br- and I-DBPs
- Increased wastewater input into source waters
  - Pesticides, pharmaceuticals, estrogens, textile dyes, alkylphenol ethoxylate surfactants, bisphenol A, musks, etc.
- Energy extraction activities
  - Hydraulic fracturing →
    - Surfactants & other fracking chemicals can enter ground water or surface waters
    - Br and I released in produced waters (cause salinity change in ecosystem and can form more toxic DBPs in drinking water)

Emerging Contaminants Found in Drinking Water

- Antimony (bottled water)
- PFOS & PFOA (including new study from Australia; ~50% of samples)
- Pharmaceuticals: ibuprofen, triclosan, carbamazepine, phenazone, clofibric acid, acetaminophen have highest occurrence (<1 ug/L)
    - Most pharmaceuticals can be 'removed' in drinking water treatment
- Hormones
- Bisphenol A
- Benzotriazoles
- Dioxane
- Perchlorate (median exposure in U.S. 1.2 ug/L; Blount et al., ES&T 2010)
- Algal toxins

Exposure routes

Inhalation

(shower, swimming pool, etc.)

Volatile DBPs/Chemicals e.g., NCl_3, THMs

Ingestion

(water, coffee, tea, water-based food and beverages)

All DBPs/Water soluble contaminants

Dermal absorption

(swimming pool, bath, etc.)

Permeable DBPs/Chemicals

e.g., THMs, haloketones, …

TOTAL INTERNAL DOSE

Slide courtesy of Manolis Kogevinas, Centre for Research in Environmental Epidemiology/IMIM, Barcelona

Unlike other contaminants that may or may not be present in drinking water…

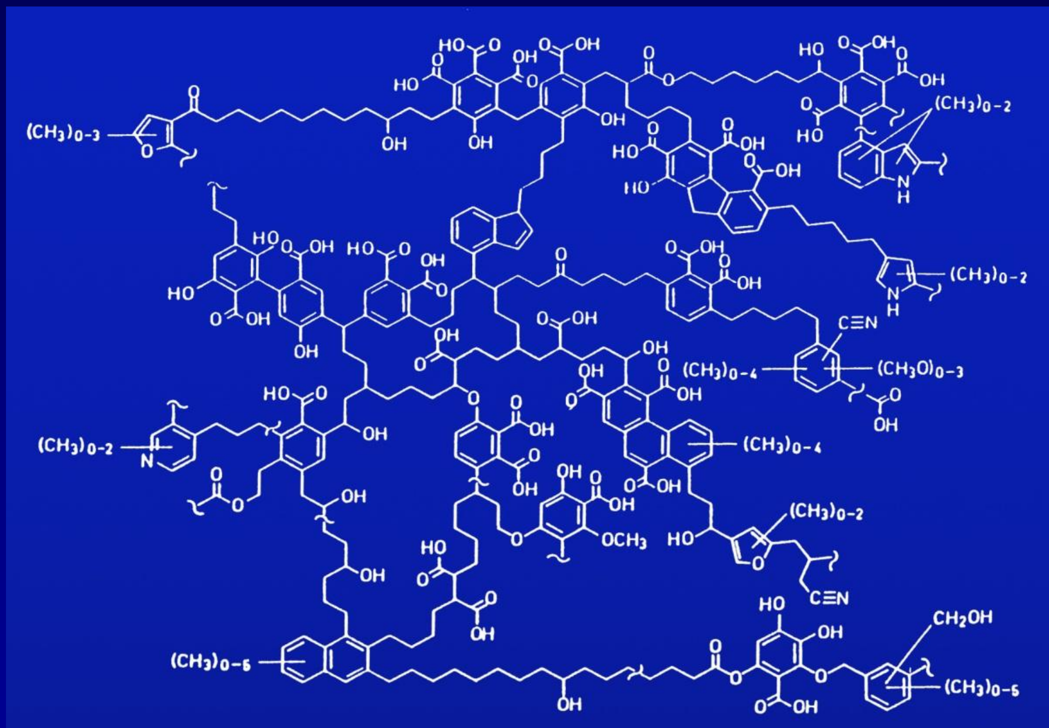
DBPs

are ubiquitous whenever chemical disinfectants used

DBPs:

Traditional vs. Pollutant DBPs

Traditional DBPs



NOM

+

Cl_2

O_3

NH_2Cl

ClO_2

⟶ DBPs

>600 DBPs Identified

Halogenated DBPs

- Halomethanes
- Haloacids
- Haloaldehydes
- Haloketones
- Halonitriles
- Haloamides
- Halonitromethanes
- Halofuranones (e.g., MX)
- Oxyhalides (e.g., bromate)
- Many others

Non-halogenated DBPs

- Nitrosamines
- Aldehydes
- Ketones
- Carboxylic acids
- Others

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Can have wastewater precursors

Only 11 DBPs Regulated in U.S.

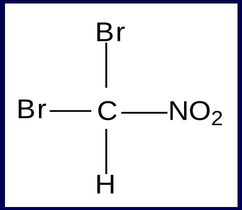
DBP	MCL (μg/L)
Total THMs	80
5 Haloacetic acids	60
Bromate	10
Chlorite	1000

Little known about occurrence, toxicity of unregulated DBPs

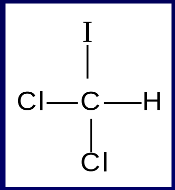
Regulated DBPs do not cause bladder cancer in animals!

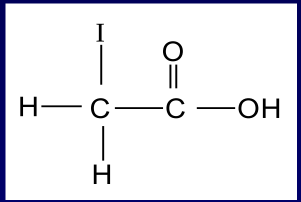
Emerging DBPs

- Halonitromethanes (up to 3 ppb; highly genotoxic); new *in vivo* effects; increased with preozonation
  Krasner, Weinberg, Richardson, et al., *ES&T* 2006, 40, 7175-7185.

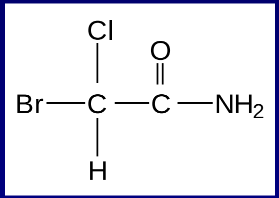


- Iodo-THMs and Iodo-Acids (iodo-THMs up to 15 ppb; iodo-acids up to 1.7 ppb; both classes highly cytotoxic or genotoxic); increased with chloramination
  Richardson et al., *ES&T* 2008, 42, 8330.

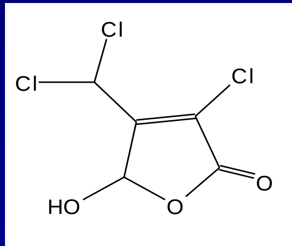




- Haloamides (up to 14 ppb; highly genotoxic) may be increased with chloramination

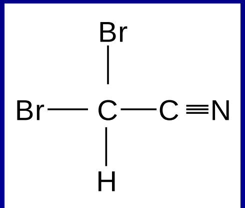


- Halofuranones (up to 2.4 ppb for total MX analogues; genotoxic, carcinogenic); chloramination can also form

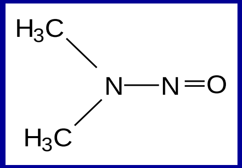


MX

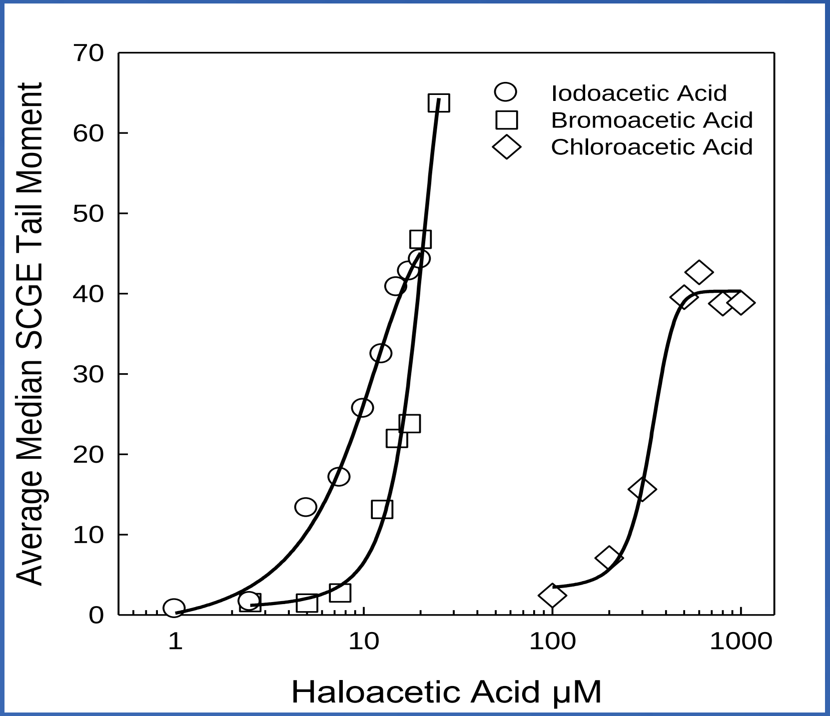
- Haloacetonitriles (up to 41 ppb; ~10% of THM4; genotoxic, cytotoxic); may be increased with chloramination



- Nitrosamines (up to 630 ppt; probable human carcinogens) increased with chloramination

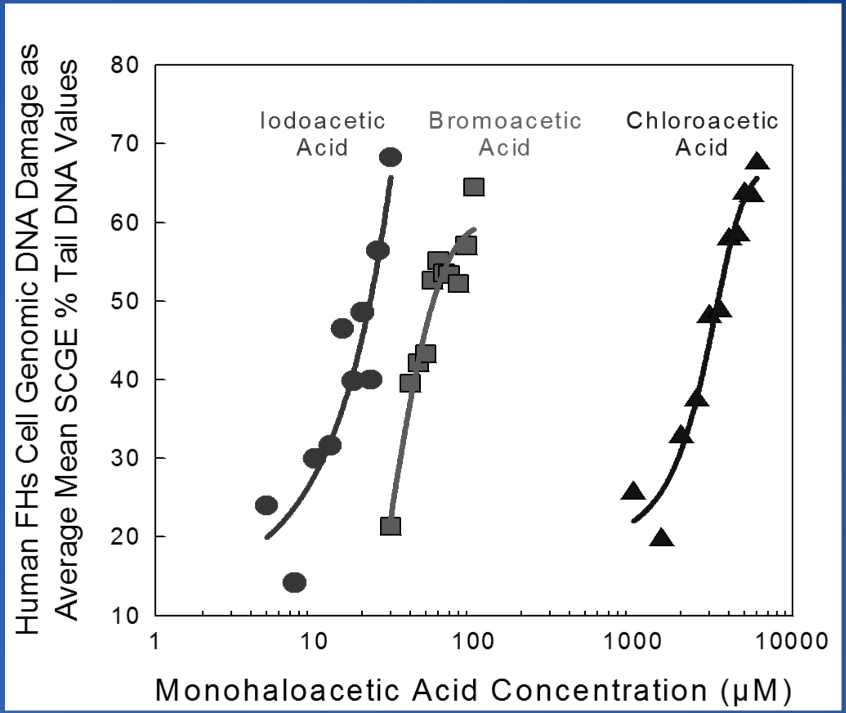


New Human Cell Results



CHO Cells

Plewa et al., ES&T. 2004, *38*, (18), 4713-4722.



Human Cells

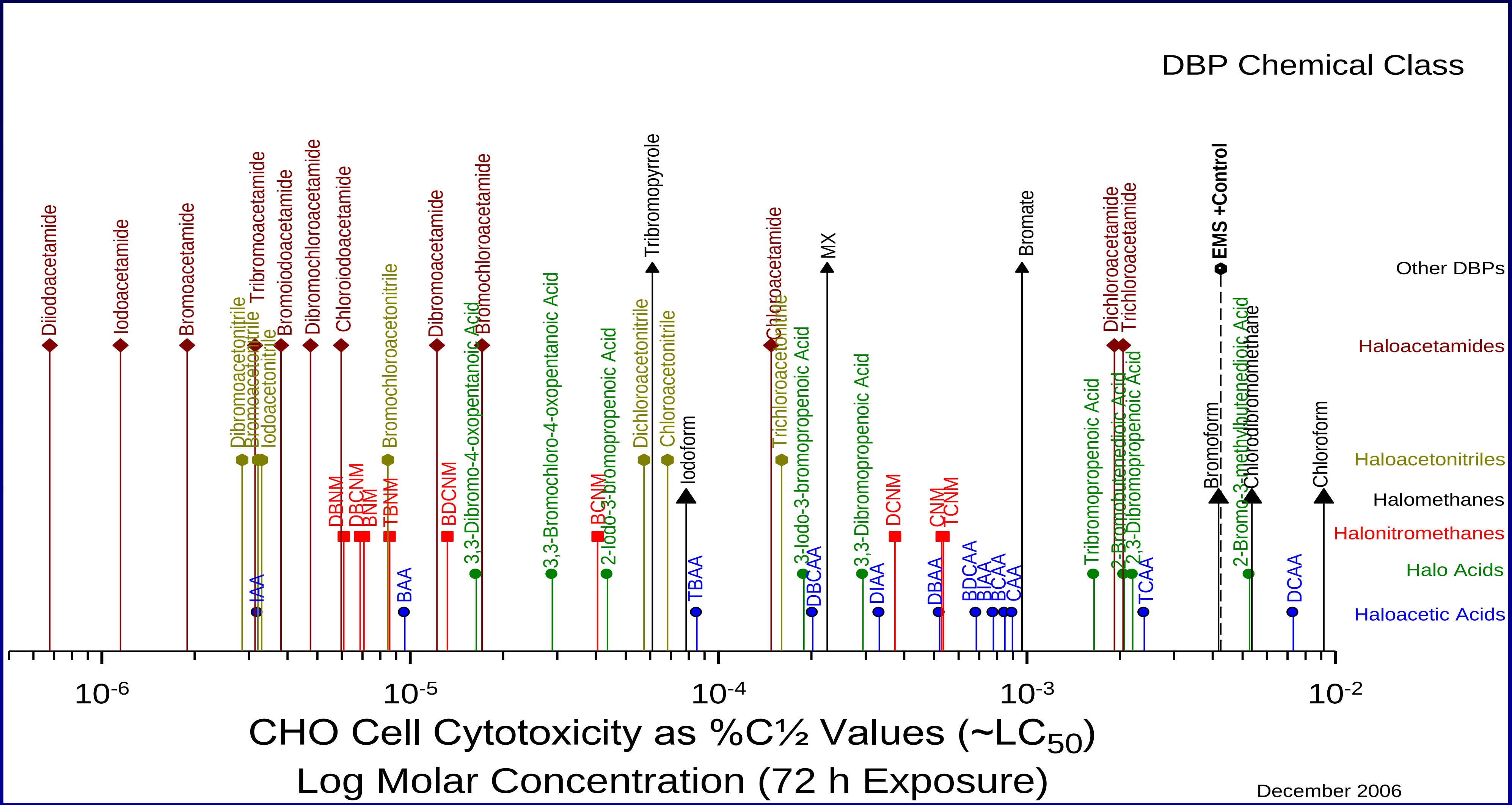
Attene-Ramos, Wagner, Plewa, *ES&T, 2010, 44 (19), 7206-7212*.

Nontransformed human small intestine epithelial cells

waterCAMPwS

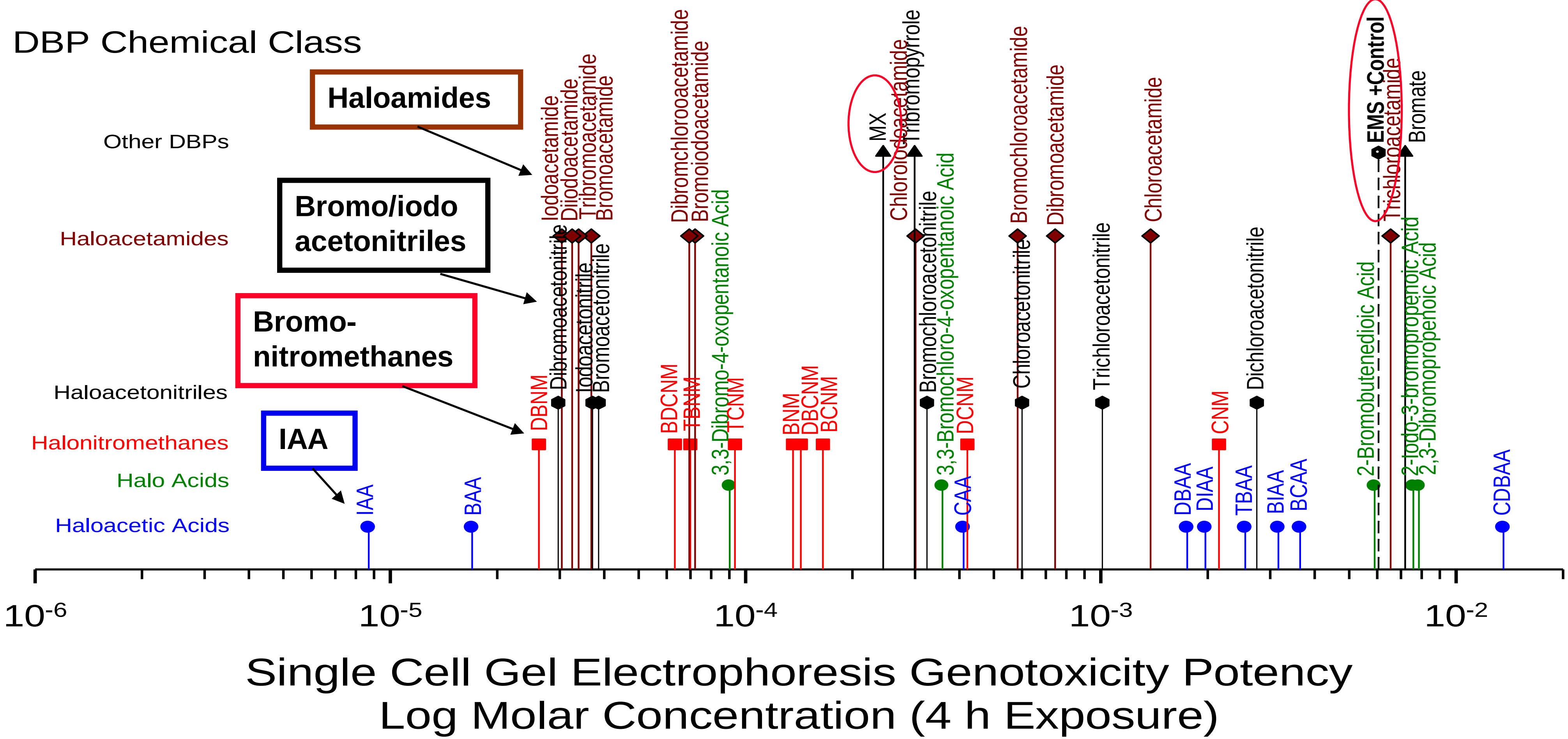
Slide courtesy of Michael Plewa, Univ. IL

Cytotoxicity of DBPs



Data courtesy of Michael Plewa, University of Illinois

Genotoxicity of DBPs



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

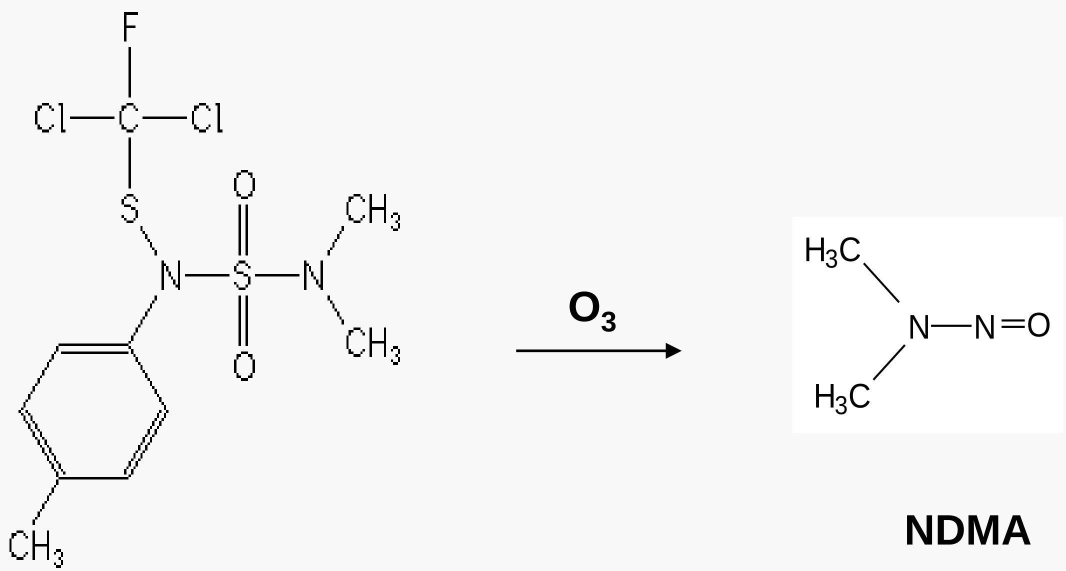
December 2006

Data courtesy of Michael Plewa, University of Illinois

‘Pollutant’ DBPs

- Pesticides
- Pharmaceuticals
- Antibacterial agents
- Estrogens
- Textile dyes
- Bisphenol A
- Parabens
- Alkylphenol ethoxylate surfactants
- Musks
- Algal toxins

Formation of NDMA from a fungicide



NDMA

Tolylfluanide fungicide

Schmidt and Brauch, *ES&T* 2008

Urs von Gunten also has recent results indicating the catalytic effect of bromide on this reaction

Antibiotic DBPs from Chlorine Dioxide

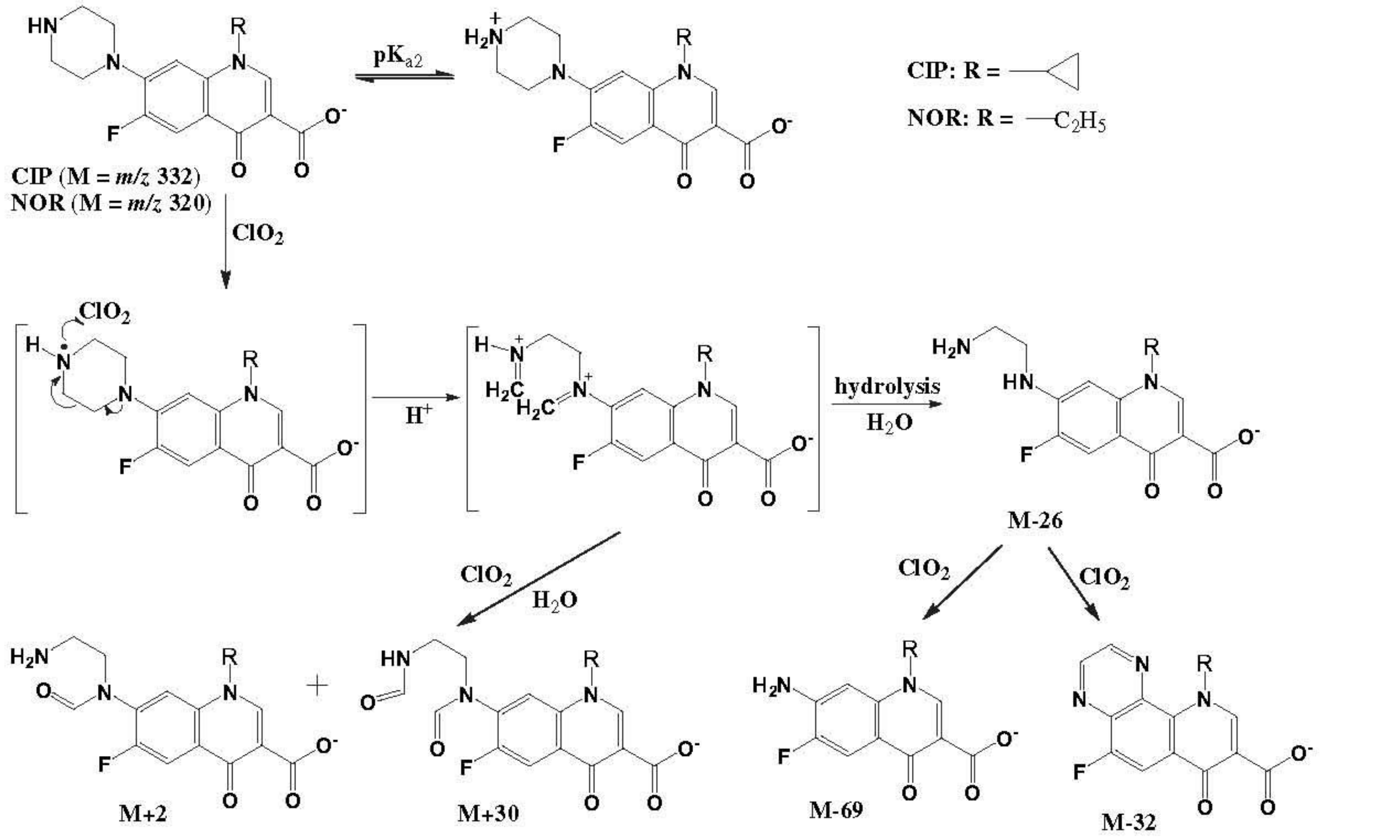


Fig. 3 – Proposed reaction pathways and products in the oxidation of CIP and NOR by chlorine dioxide. M − 26 was the main product under limited ClO_2 conditions, while excess ClO_2 yielded products of M − 69, M − 32, M + 2 and M + 30. Compounds in brackets are intermediates not actually detected by LC/(ESI+)MS.

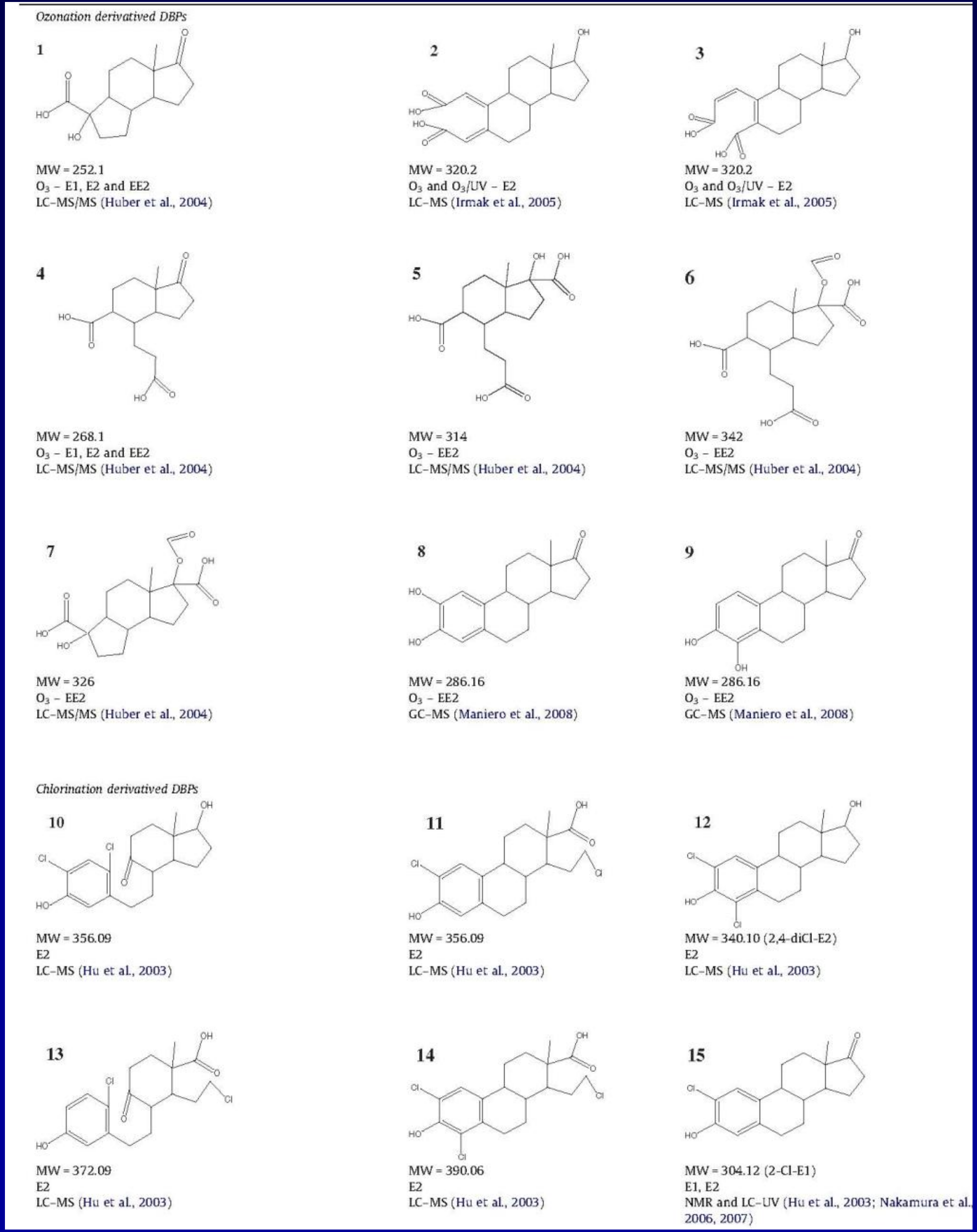
Reacts with N in piperazine ring

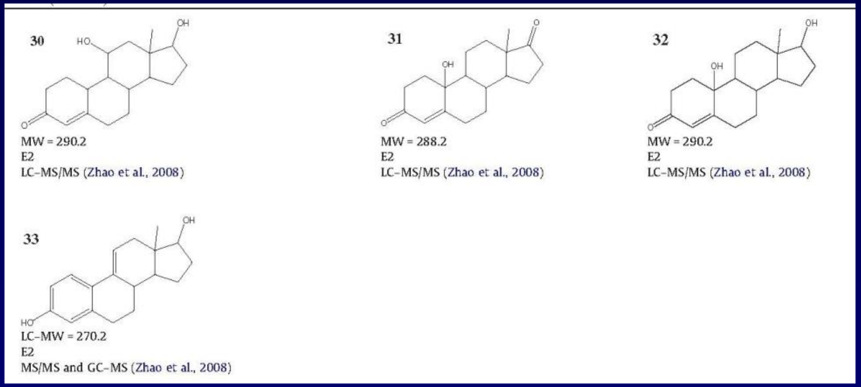
No Cl incorporation

Still likely active

Wang et al., *Water Research* 2010.

Estrogen DBPs from Ozone and Chlorine





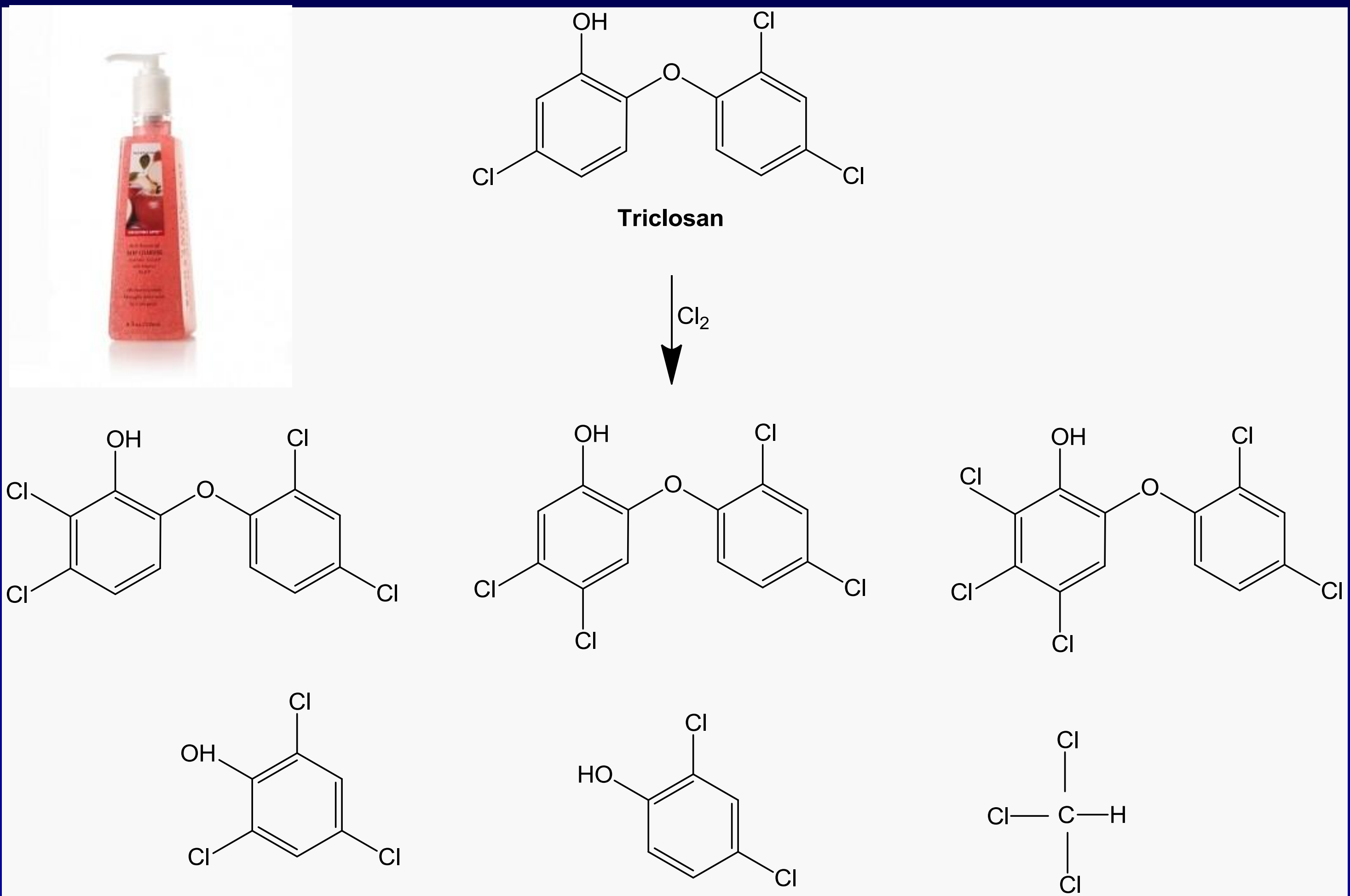
Pereira et al., *Chemosphere* 2011.

Reacts with phenol moiety

Estrogenicity significantly reduced with ozone (94-99%)

Estrogenicity generally reduced with chlorine, except one DBP from EE2

Triclosan DBPs from Chlorine

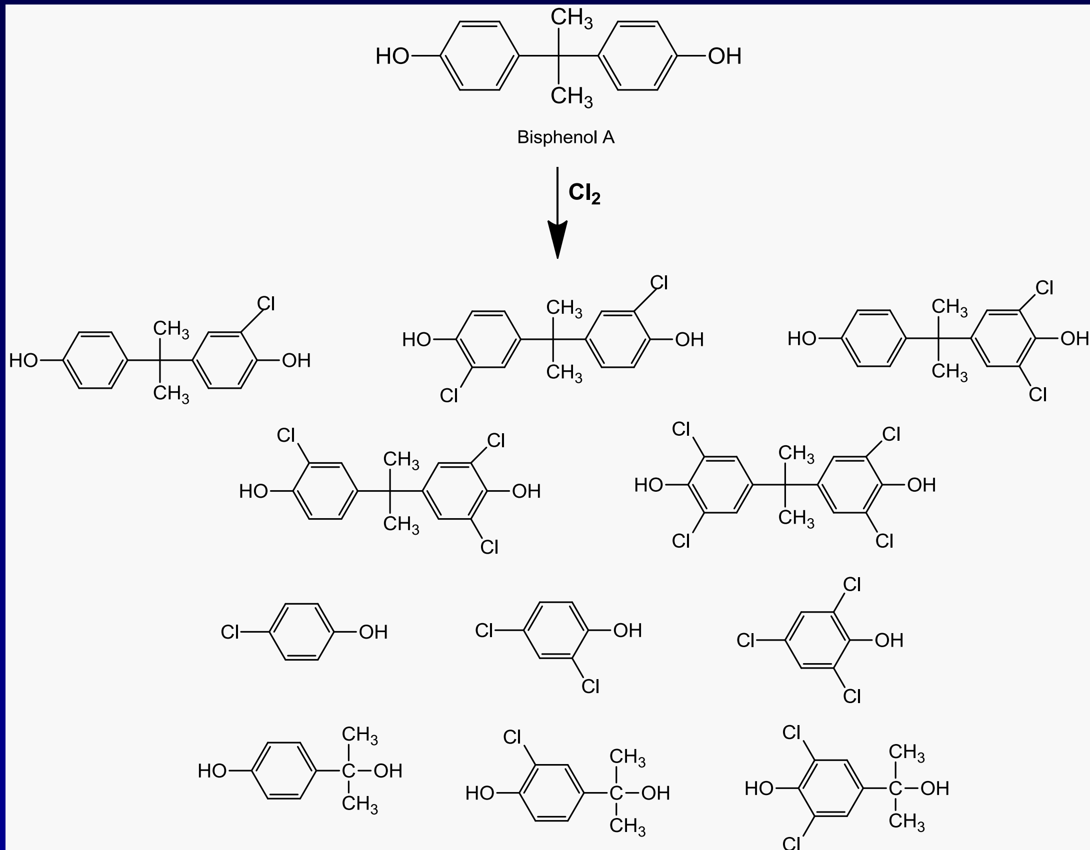


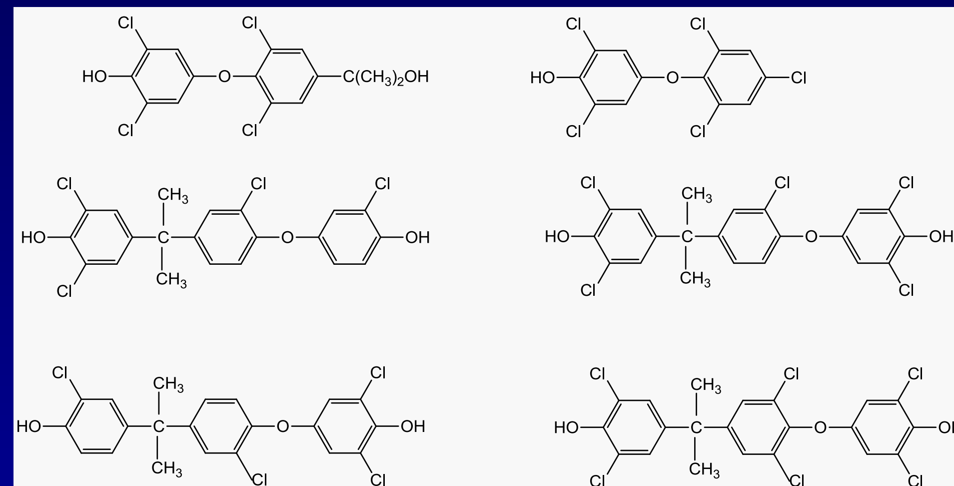
Reacts with phenol moiety

Fast reactions

Rule et al. *ES&T* 2005.

Bisphenol A DBPs from Chlorine





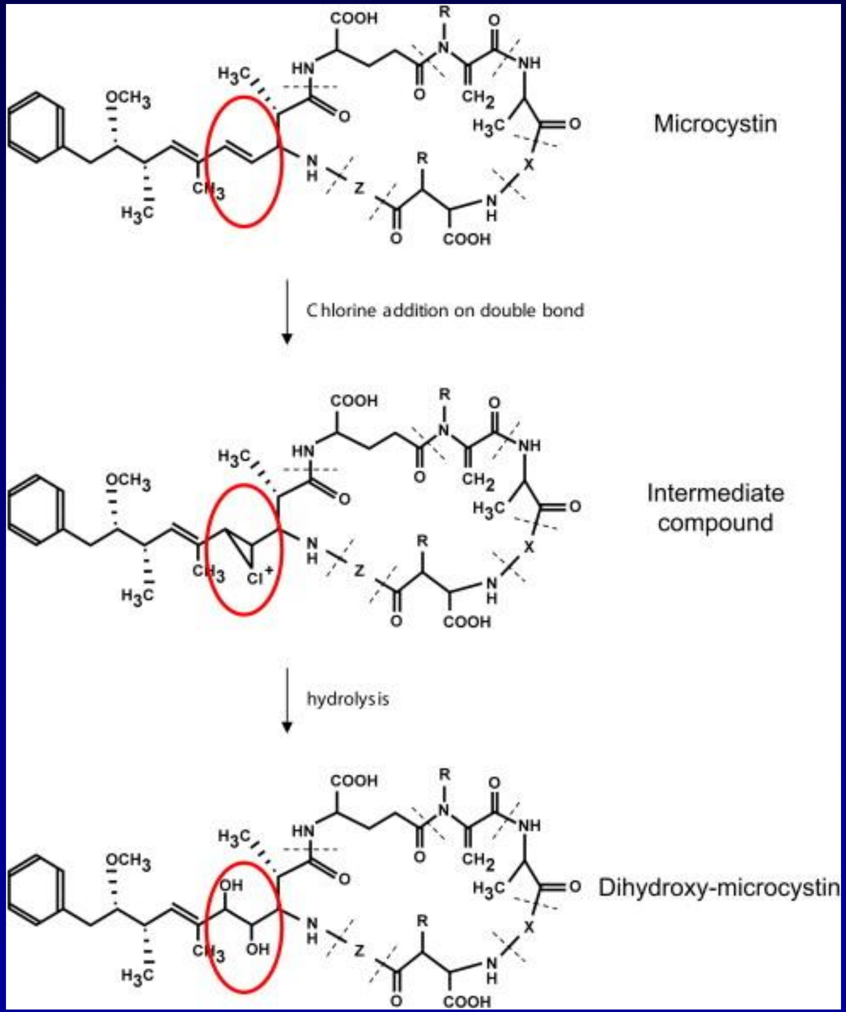
Reacts with phenol moiety

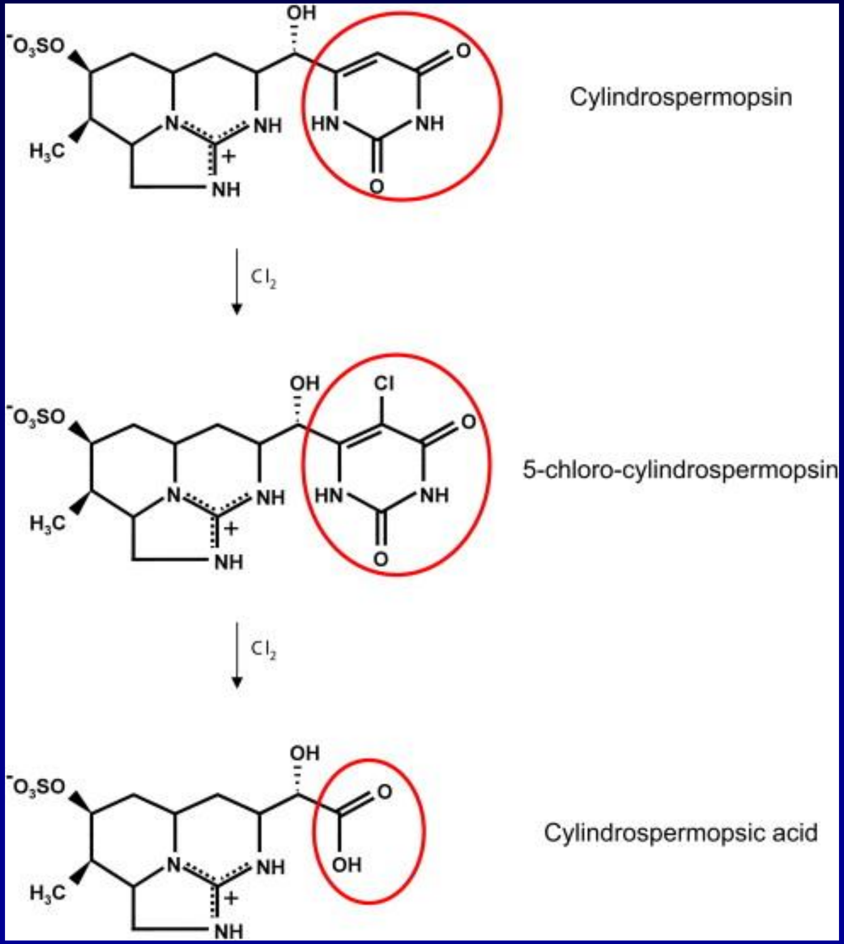
Fast reactions (80% gone in 10 min)

Some products estrogenic

Hu et al. *ES&T* 2002.

Algal Toxin DBPs from Chlorine



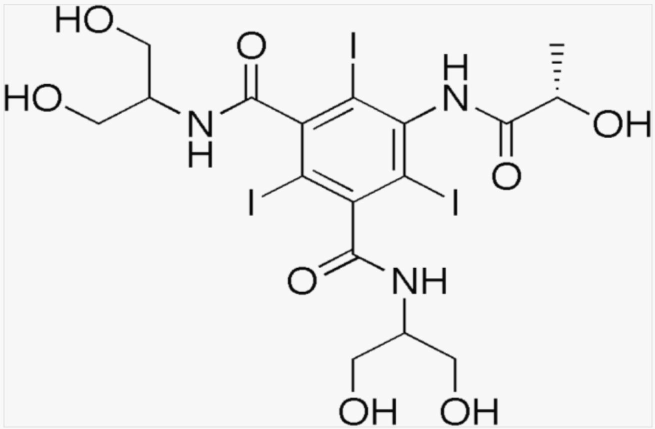


Merel, Clement, and Thomas, *Toxicon* 2010.

Reacts with C=C double bonds

Toxicity reduced

Formation of iodo-DBPs from X-ray contrast media

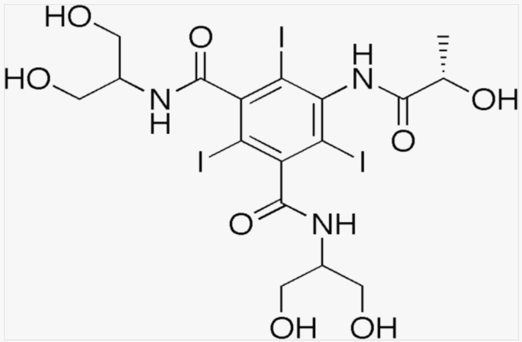


Iopamidol

+ NOM $\xrightarrow[NH_2Cl]{HOCl}$ Iodo-DBPs

Duirk, Lindell, Cornelison, Kormos, Ternes, Attene-Ramos, Osiol, Wagner, Plewa, and Richardson, *ES&T* 2011.

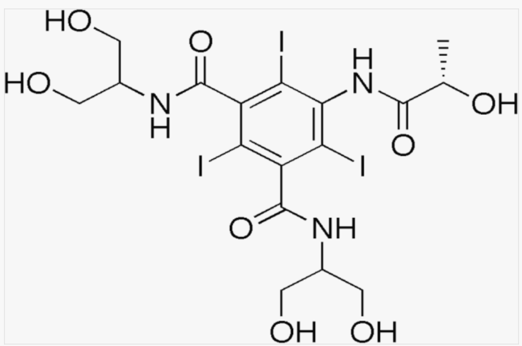
Results



Iopamidol

HOCl / NH_2Cl → Iodo-DBPs

trace



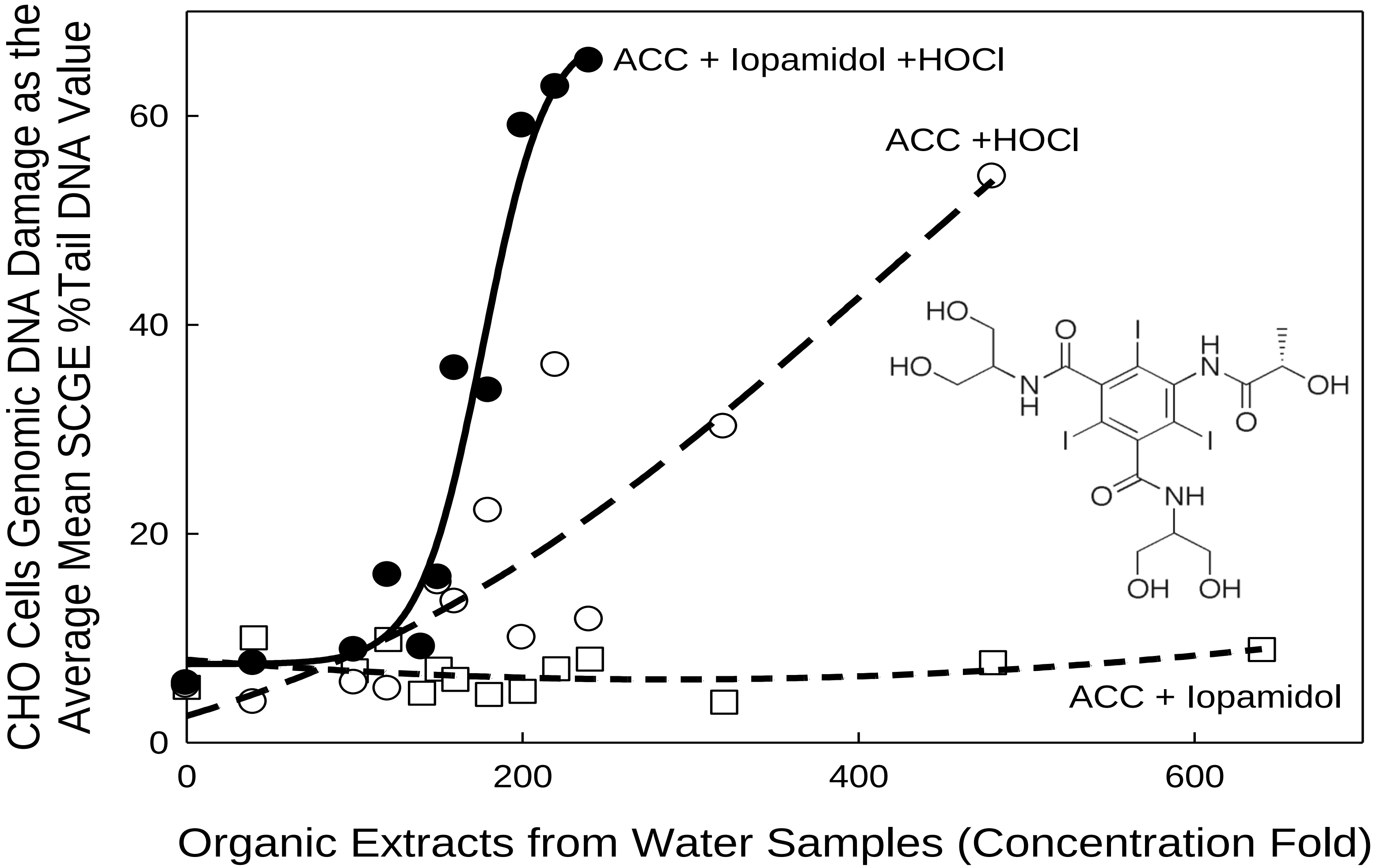
Iopamidol

\+ NOM

HOCl / NH_2Cl → Iodo-DBPs ✓

Iodo-THMs
&
Iodo-Acids

Genotoxicity of Chlorinated Waters Containing Iopamidol



Implications for Water Reuse

- Increased complexity of chemicals in total drinking water exposure
- Some chemicals will react with disinfectants to form 'pollutant' DBPs (e.g., NDMA from tolylfluanide; iodoacetic acid from iopamidol)
- Some chemicals very difficult to remove
    - RO doesn't remove some very low MW chemicals well (e.g., NDMA, MTBE, acetaminophen, gemfibrozil, mefenamic acid) (Mitch et al., 2003; Radjenovic et al. 2008)
    - UV won't remove some contaminants unless extremely high (unrealistic) doses used
    - Advanced oxidation doesn't always work
- There may be some surprises….there usually are
    - Wise to look beyond a few target regulated chemicals