Formation and Occurrence of Disinfection By-Products

Susan D. Richardson

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

U.S. Environmental Protection Agency

Office of Research & Development

Drinking Water DBPs

- **Formed by the reaction of disinfectants with natural organic matter**

Concern over possible human health risk:

- **Epidemiologic studies: risk of bladder cancer; some cause cancer in laboratory animals**

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

Will Cover

- How DBPs are formed
- Occurrence of regulated and emerging DBPs
- Issues with alternative disinfectants
- Ways to minimize DBPs
- Next steps for future research

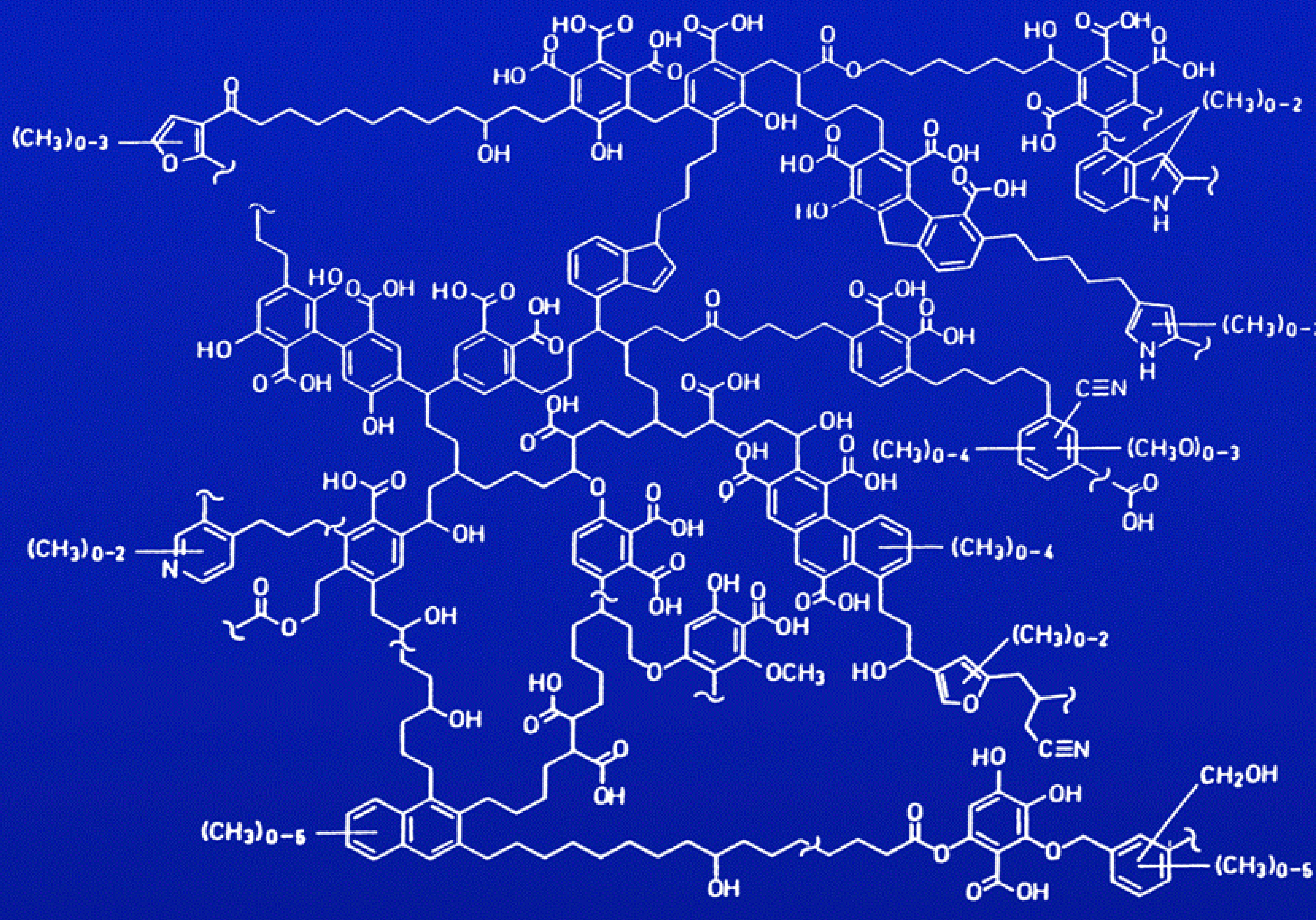


Fig. 12.7 Chemical network structure of humic acids according to Schulten and Schnitzer.[7] Reproduced by permission of Springer-Verlag.

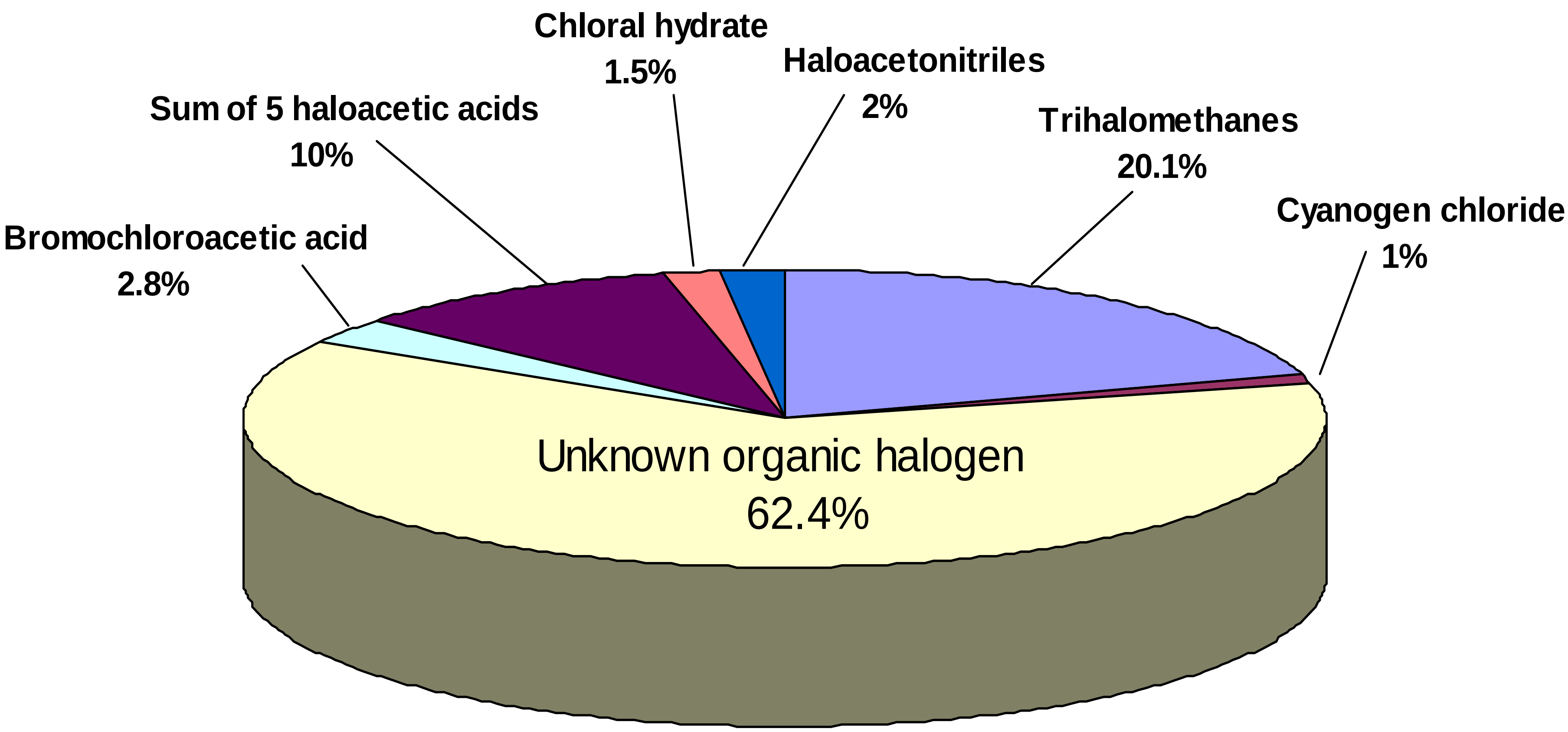
DBPs Regulated by the U.S. EPA

DBP	MCL (μg/L)
Total THMs (Chloroform, bromoform, bromodichloromethane, Chlorodibromomethane)	80
5 Haloacetic acids (Chloro-, dichloro-, trichloro-, bromo-, dibromo-acetic acid)	60
Bromate	10
Chlorite	1000

But more than 600 DBPs have been identified

Little known about occurrence, toxicity of unregulated DBPs

What we know about Total Organic Halide (TOX)



Data courtesy of Stuart Krasner, Metropolitan Water District of Southern California

~50% of TOX >1000 Da: Khiari, et al., Proc. 1996 AWWA Water Quality Technology Conference

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

DBPs
are ubiquitous

DBPs from Different Disinfectants

Chlorine
Halogenated organic DBPs
Chlorate (contaminant from hypochlorite bleach)
Non-halogenated aldehydes, ketones, carboxylic acids Nitrosamines (with nitrogen-containing coagulants)
Chloramine
Halogenated organic DBPs (but generally lower levels than chlorine)
Iodo-THMs and iodo-acids
Nitrosamines (higher levels than chlorine)
Inorganic chloramines (di-, tri-chloramine)
Haloamides, haloacetonitriles may be increased

DBPs from Different Disinfectants

Ozone
Non-halogenated aldehydes, ketones, carboxylic acids (e.g., formaldehyde)
Halonitromethanes (with post-chlorine/chloramine)
Bromate and other brominated DBPs (when bromide is present)
Chlorine dioxide
Chlorite, chlorate
A few brominated DBPs when bromide is present (but generally lower levels than chlorine or chloramine)
Non-halogenated aldehydes, ketones, carboxylic acids

Concentrations

THMs	Low to mid-ppb
HAAs	Low to mid-ppb
Oxyhalides	
Bromate	Sub to low-ppb
Chlorite	High ppb
Chlorate	High ppb
Haloacetonitriles	Sub to low-ppb
Haloaldehydes	Sub to low-ppb
Haloketones	Sub to low-ppb
Haloamides	Sub to low-ppb
Halonitromethanes	Sub to low-ppb
Iodo-THMs	Sub to low-ppb
Iodo- and other halo-acids	Sub to low-ppb
Halofuranones (MX analogues)	Low to mid-ppt

Non-halogenated DBPs

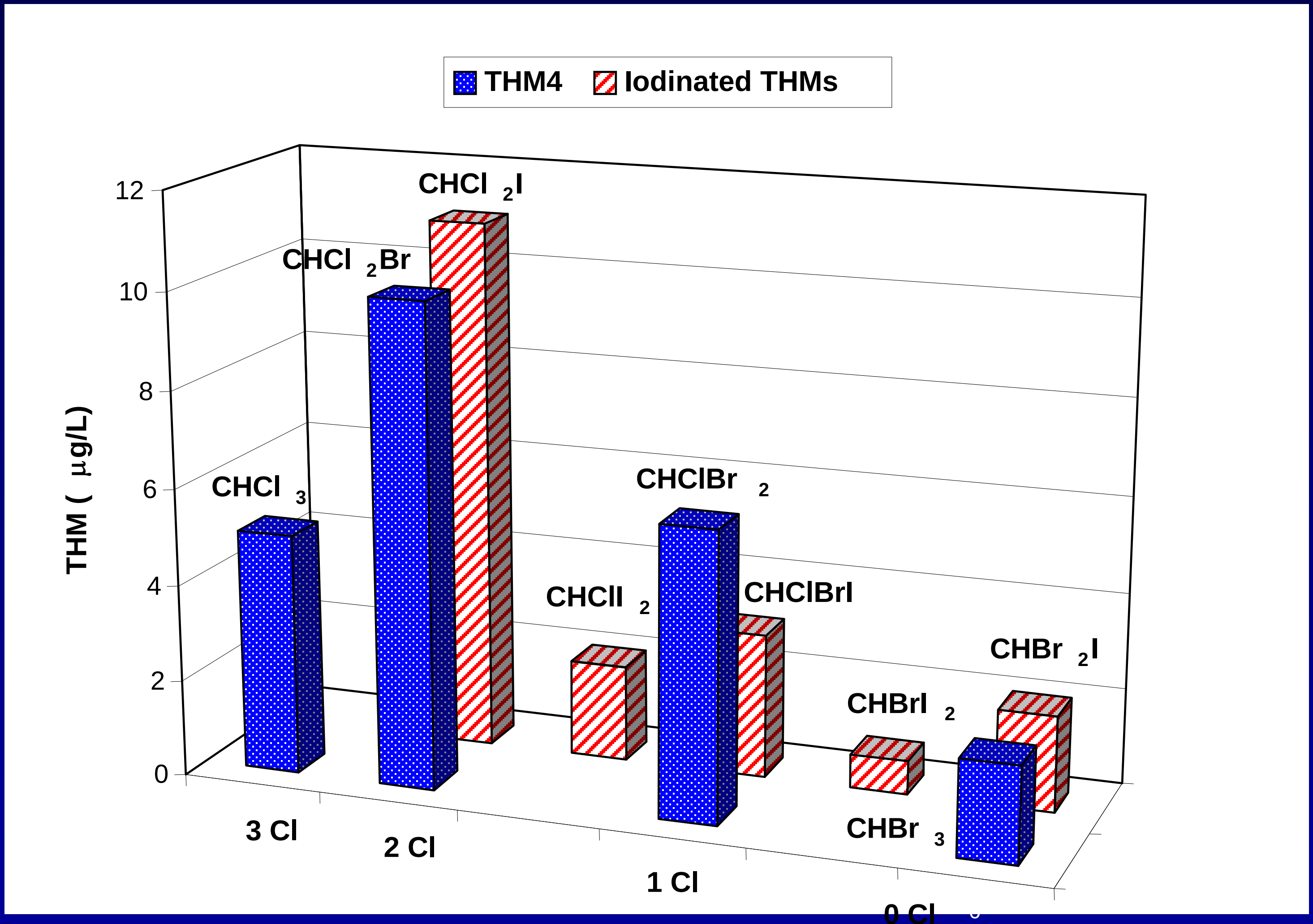
Aldehydes and ketones	Sub to low-ppb
Carboxylic acids	Sub to low-ppb
Nitrosamines	Low to mid-ppt

Nationwide DBP Occurrence Study

- Prioritized >500 unregulated DBPs reported in literature (likely to cause cancer)
- Measured these in waters across U.S.
- Important findings:
  - New emerging DBPs identified (e.g., iodo-acids)
  - Alternative disinfectants increased formation of many priority DBPs
  - Many priority, unregulated DBPs found at significant levels

Krasner, Weinberg, Richardson, et al., *Environ. Sci. Technol*. 2006, 40, 7175-7185.

Iodo-THMs



Highest levels found at a chloramination plant

Krasner, Weinberg, Richardson, et al., *Environ. Sci. Technol*. 2006, 40, 7175-7185.

Iodo-DBPs Maximized with Chloramines

Chlorine:

$$I^- + HOCl \xrightarrow{\text{fast}} HOI \xrightarrow[\text{HOCl}]{\text{fast}} IO_2^- \xrightarrow[\text{HOCl}]{\text{fast}} IO_3^-$$

iodite

iodate

$$I^- + HOCl \xrightarrow{\text{NOM}} \text{Cl-DBPs}$$

$$HOI \xrightarrow[\text{fast}]{\text{NOM}} \text{iodo-DBPs}$$

Sink for iodide

HOCl also competes for rxn with NOM, so much lower iodo-DBPs with chlorine

Chloramines:

HOI also has longer half-life in chloraminated waters

$$I^- + NH_2Cl \xrightarrow{\text{fast}} HOI \xrightarrow{\boxed{\text{slow}}} IO_2^- \longrightarrow IO_3^-$$

iodite

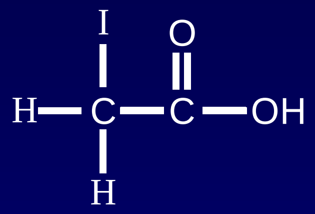
iodate

$$I^- + NH_2Cl \xrightarrow{\text{NOM}} \text{Cl-DBPs}$$

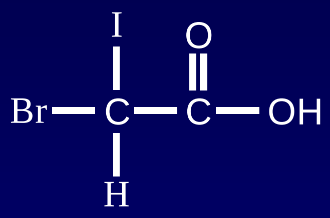
$$HOI \xrightarrow[\text{fast}]{\text{NOM}} \text{iodo-DBPs}$$

Adapted from Bichsel and von Gunten 1999 and 2000

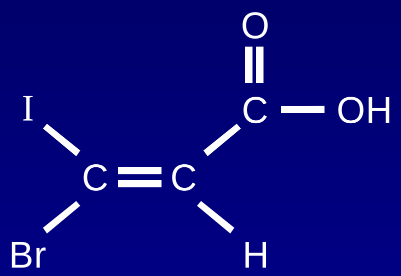
New Iodo-Acids



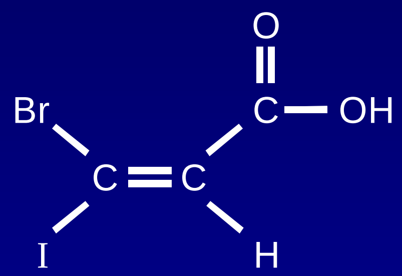
Iodoacetic acid



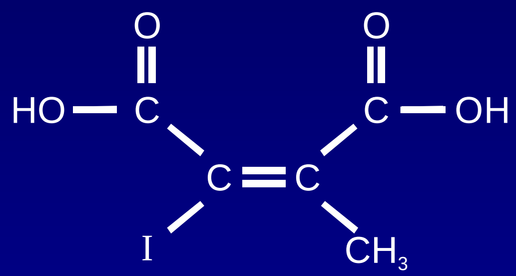
Bromoiodoacetic acid



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



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



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

Initially discovered using GC/MS

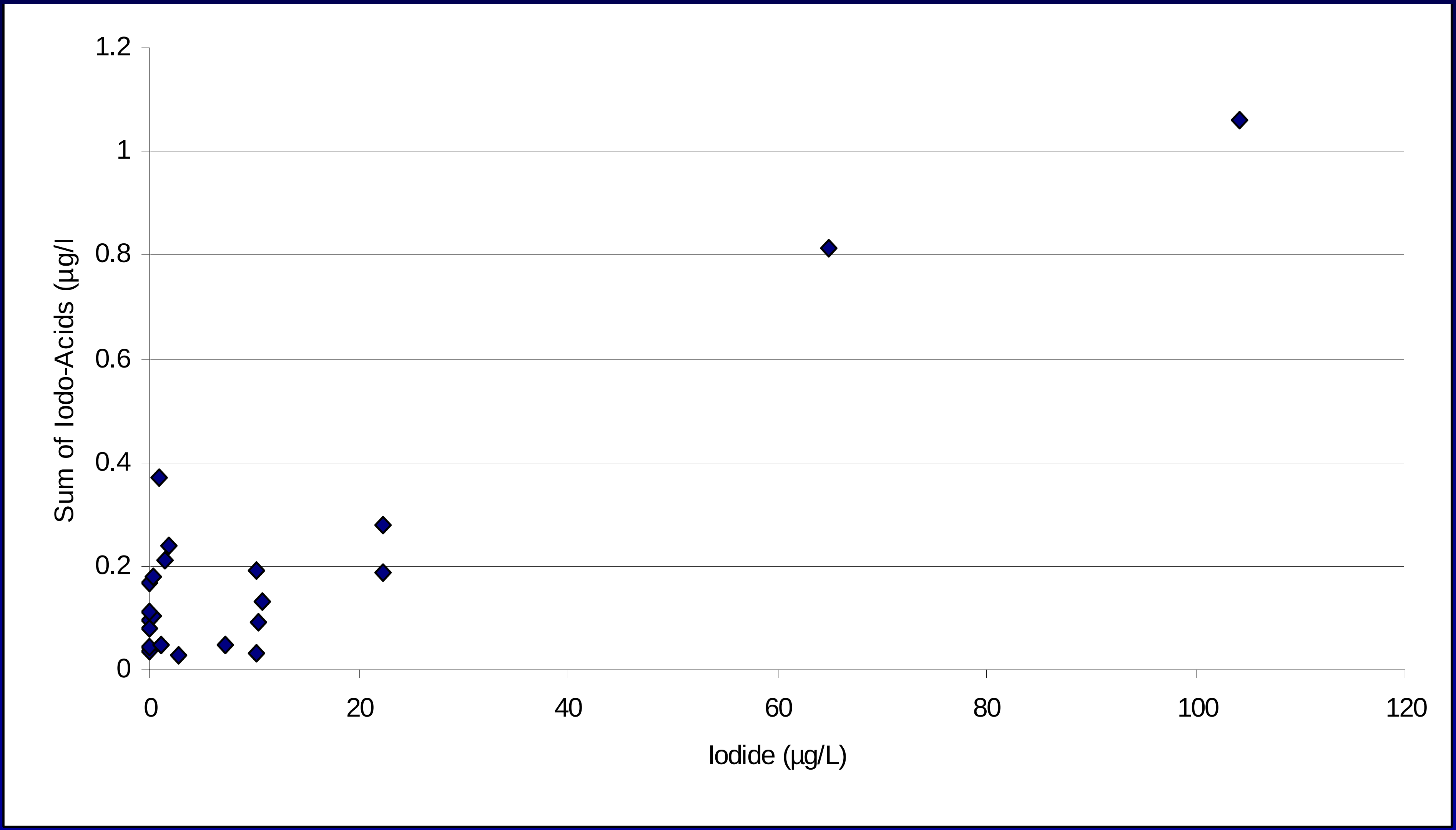
Highly genotoxic

Increase in formation with NH_2Cl vs. Cl_2 (up to 1.7 ppb)

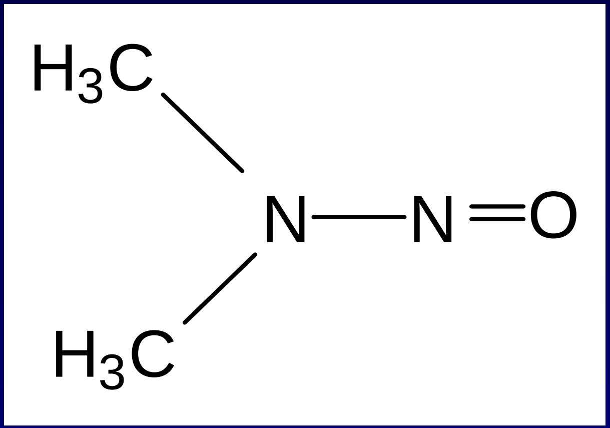
Occurrence Study now completed (23 cities in U.S. & Canada)

Richardson et al., *Environ. Sci. Technol*. 2008, ASAP.

Iodide vs. Iodo-Acid Concentrations



Nitrosodimethylamine (NDMA)



- **On the UCMR-2**
- **Formed as a DBP from chloramine and chlorine (DADMAC coagulants)**
- **Probable human carcinogen**
- **2004: Found up to 180 ng/L in finished water from Canada**
- ***N*-nitrosopyrrolidine, *N*-nitrosomorpholine, N-nitrosopiperidine, N-nitrosodiphenylamine also now found as DBPs**
- **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**

EPA Method 521: www.epa.gov/nerlcwww/m_521.pdf

How can we minimize DBPs?

Before

- Remove NOM (or Br/I) before treatment (e.g., enhanced coagulation, membranes)

During

- Change disinfectant or treatment conditions (e.g., pH)

After

- Remove DBPs after they are formed (e.g., biological filtration, GAC)

What's Next?

- Human health effects not solved yet—need more toxicity studies
- Studies on route of exposure
- DBPs are present as complex mixtures—need toxicity studies addressing this   Four Lab Study
- What is in the unidentified fraction—anything of concern?
  High Molecular Weight DBP Study
- What about DBPs from alternative disinfectants—do we know everything we need to know before plants switch?
- UV disinfection? Membrane disinfection?
- What about 'pollutant' DBPs?

‘Pollutant’ DBPs…

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

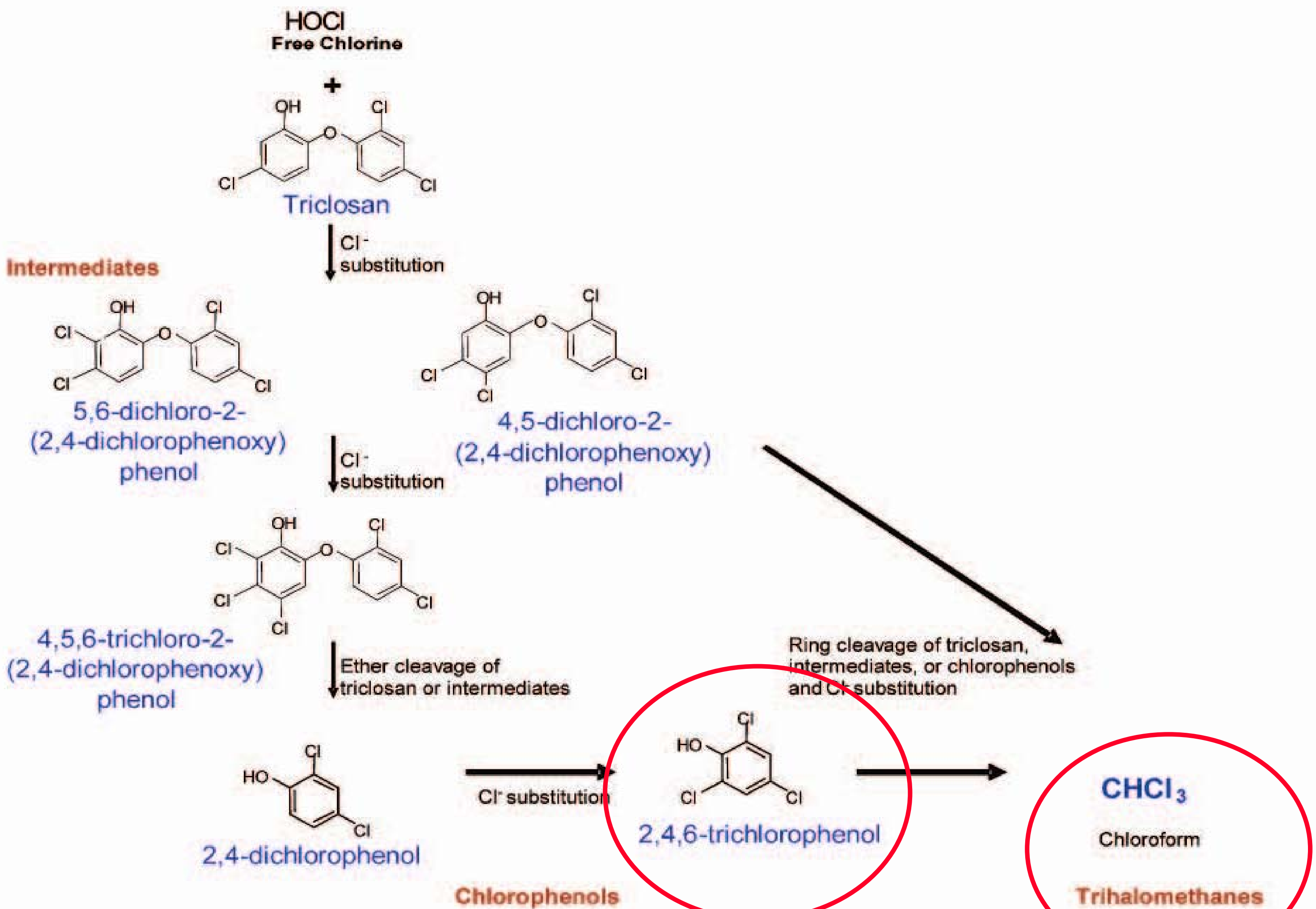


FIGURE 1. Reaction scheme showing reaction mechanisms and chemical structures for triclosan and its decay products. As detailed in ref *14*, all species were identified either by mass spectral analysis ((chlorophenoxy)phenols and chlorophenols) or comparison of retention times of the analyte to known standards (chloroform).

Fiss, Rule, and Vikesland, Environ. Sci. Technol. 2007, 41, 2387-2394.

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