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CEE 697z
Organic Compounds in Water and Wastewater

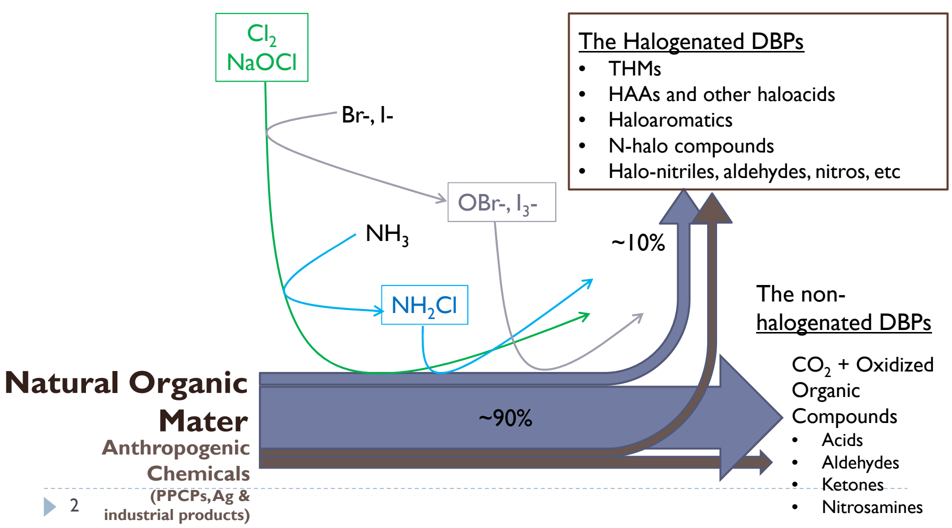
NOM and DBPs
Special Lecturer: Rassil El Sayess

Lecture #9

http://www.ecs.umass.edu/eve/research/nyc_chloramines/literature.html

Dave Reckhow - Organics In W & WW

Formation of Cl_2-driven DBPs



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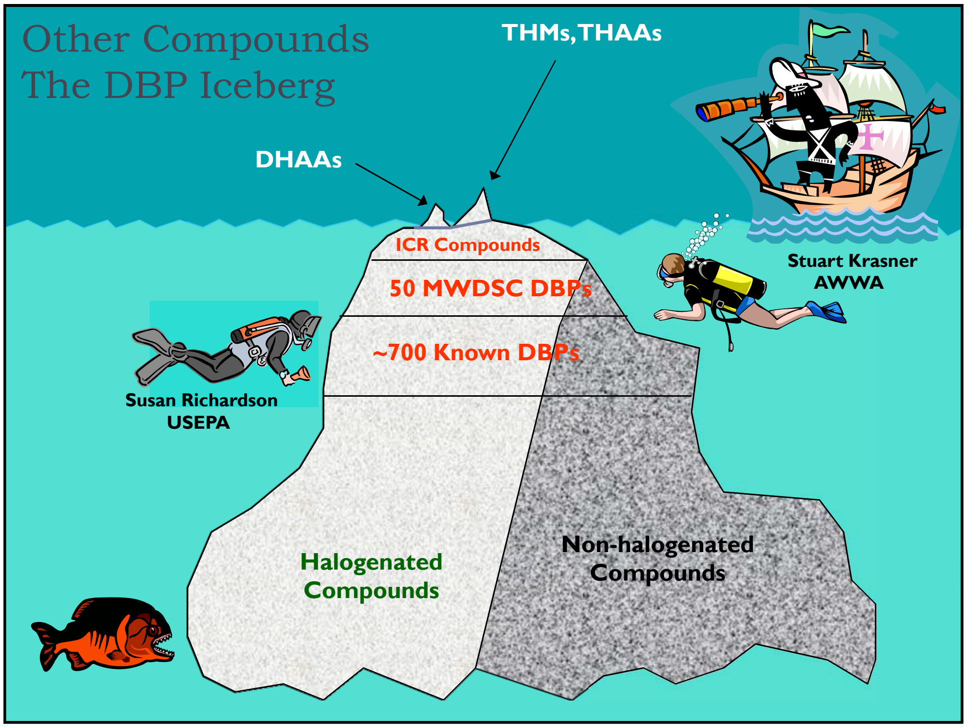
Other Compounds
The DBP Iceberg



The Trihalomethanes (THMs)

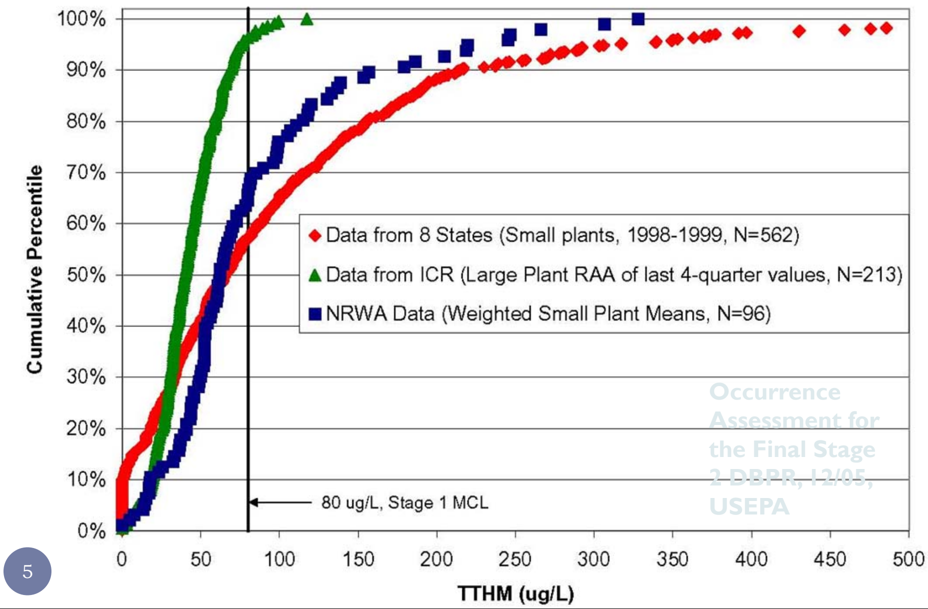
Chloroform | Bromodichloromethane | Chlorodibromomethane | Bromoform

- Published in Dutch journal H2O, Aug 19, 1972 issue
- Deduced that they were formed as byproducts of chlorination
- Proposed chemical pathways

1921-2010

4 Rook, 1974, Water Treat. & Exam., 23:234

Treated Waters: TTHMs from US Surveys



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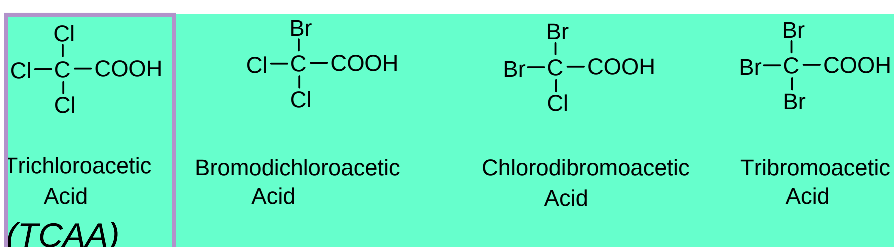
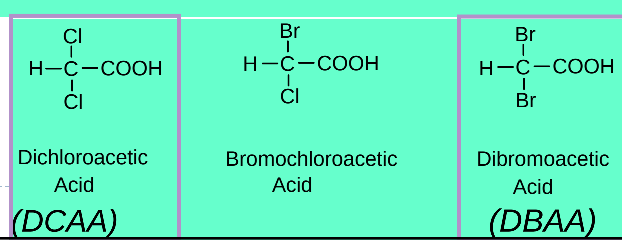
The Haloacetic Acids (HAAs)

- HAA5 include the two monohaloacetic acids (MCAA & MBAA) plus
  - One of the trihaloacetic acids:



  - And 2 of the dihaloacetic acids



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Regulated Compounds

- THMs
- HAA5
- Bromate
- Chlorite
- The regulated compounds are
  - Common "end products" produced by almost all precursors
  - Chemically very stable
    - This is not typical of other DBPs

DBP Precursor Materials

General Groups

- Bulk NOM
- Hydrophobic NOM
  - Acids (Fulvics & Humics)
  - Neutrals
  - Bases
- Hydrophilic NOM
  - Acids, Bases, Neutrals
- Mesophilic NOM
  - Acids, Bases, Neutrals
- Soluble Metabolics

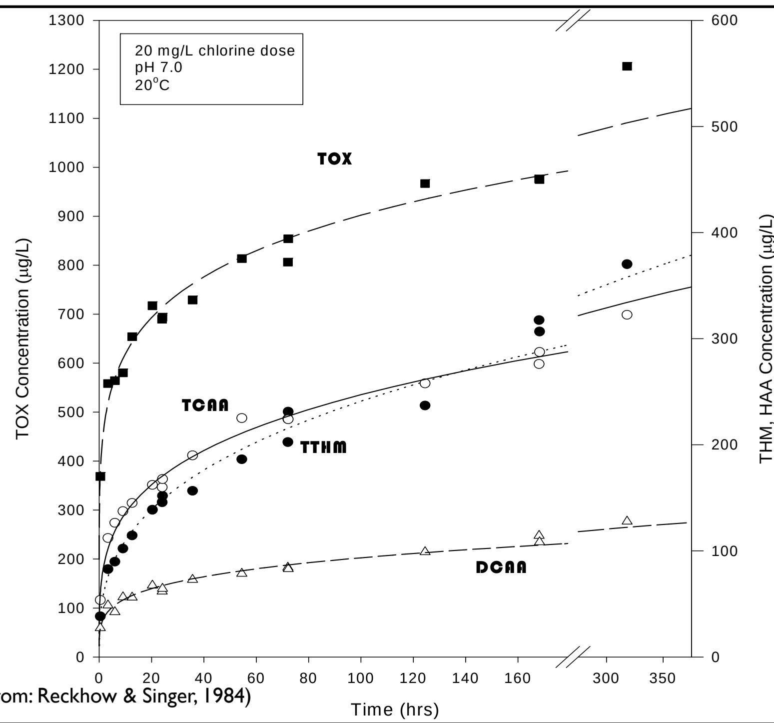
Specific Structures

- Lignin
- Carbohydrates
- Proteins & Amino Acids
- Terpenoids
- Fatty Acids
- Tannins
- Anthropogenics
  - Ranitidine

DBP Data - Availability

- Based on precursors
  - Bulk NOM: most data, from raw & treated waters
  - NOM Fractions: some data
  - Specific Structures: far less data
- Based on type of DBP
  - Regulated compounds (THMs & HAAs)
    - Extensive Data, especially for bulk NOM
  - Common unregulated compounds
    - Moderate level, especially from ICR and selected "studies"
  - Emerging unregulated compounds
    - Very little data

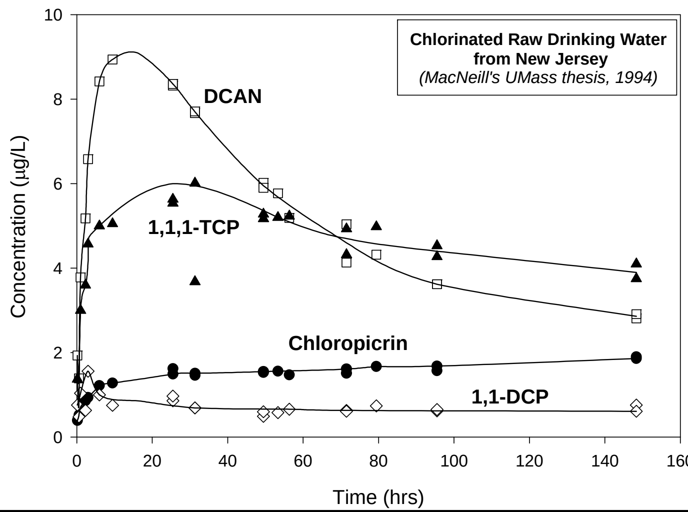
Fulvic Acid



10 (from: Reckhow & Singer, 1984)

Some Common Unregulated DBPs

- Many decrease wit time
- Degradation
  - Chemical
  - Biological
    - Not shown

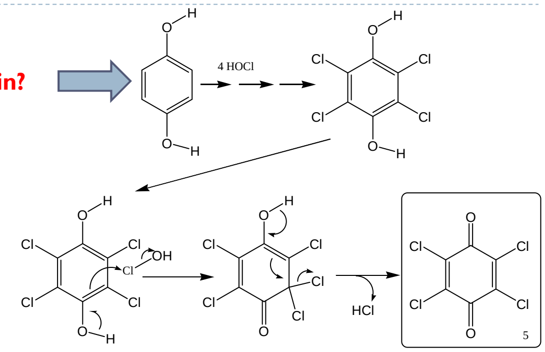


Model Compound Studies

- Model compounds
  - Synthetically prepared in the lab: water that has been spiked with certain compounds
- Most have been used to assess formation of regulated DBPs (THMs & HAAs)
- Some have been conducted to find new DBPs and especially intermediates formed along the way to the final byproducts

Lignin: Halobenzoquinones (HBQs)

Lignin?



- Many pathways
  - Plants to HQs
- Toxicity
  - HQs are known to be reactive and damaging to DNA
  - Postulated to be bladder carcinogen of high potency

Bull et al., 2006

Halobenzoquinones (cont.)

- Identified following QSAR deductive reasoning
  - SPE - LC/MS/MS method: Zhao et al., 2010
- Little occurrence data:
  - U Alberta: 7 samples in 2 publications
    - Dichloro (DCBQ): 14 ng/L median (165 ng/L max)
    - Others much lower
  - UMass: several dozen samples - unpublished
    - Dichloro: 306 ng/L high value

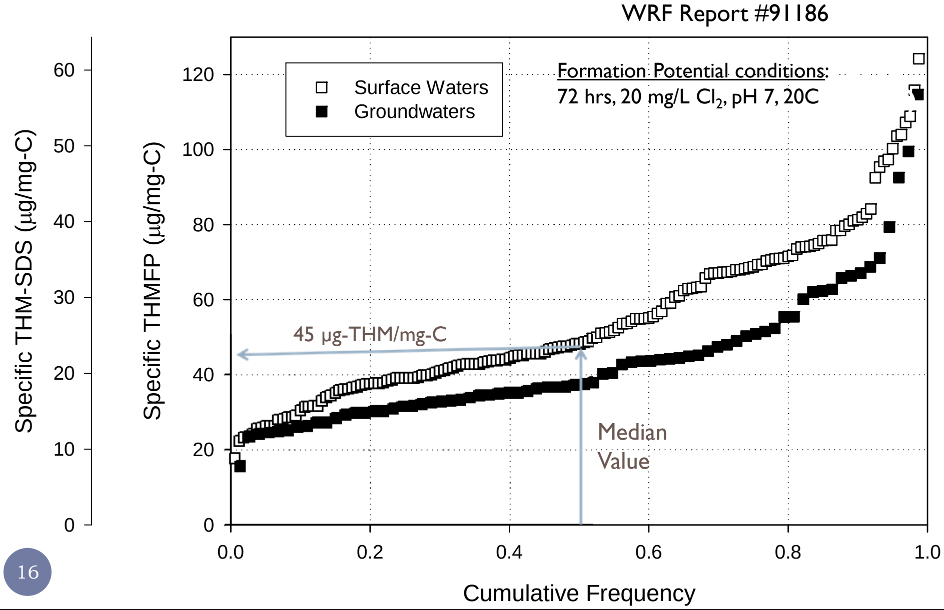
Formation Potential

- Experiments designed to maximize exposure of water to chlorine (in this case) under optimal conditions and measure the concentration of DBP for a specified duration

- Disinfection by-product formation potential (DBP-FM): 72 hr, 20 mg/L Cl2 dose, pH 7, 20C
- Simulated distribution system (SDS) test: 24 hr, 4 mg/L Cl2 dose, 20C and pH 7

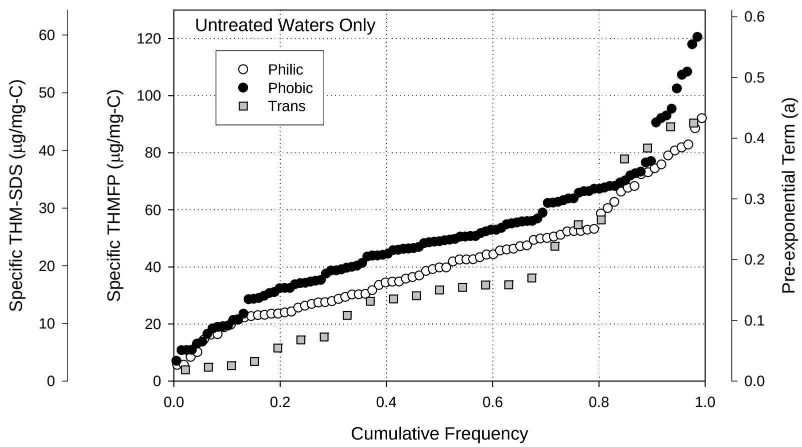
THM-FP

From: Reckhow et al., 2007
WRF Report #91186

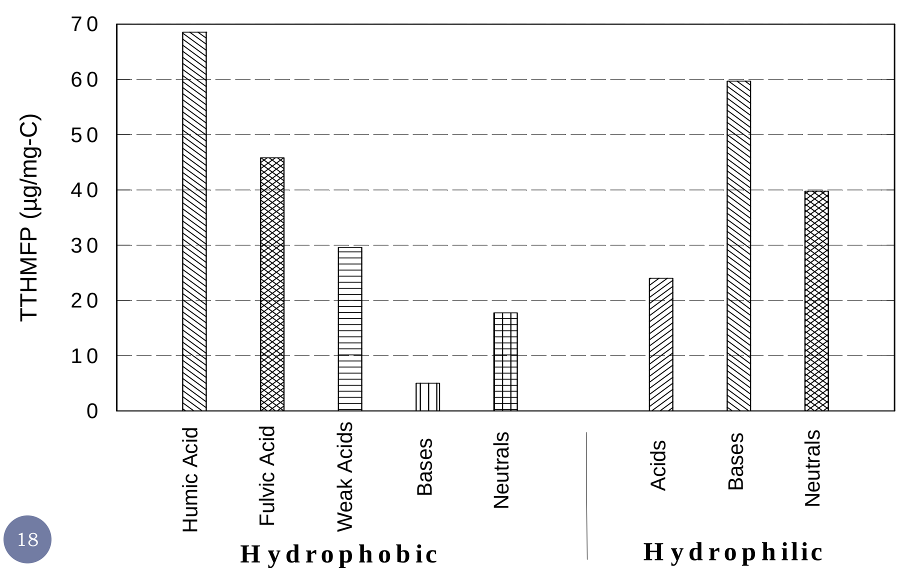


FP and SDS for NOM Fractions

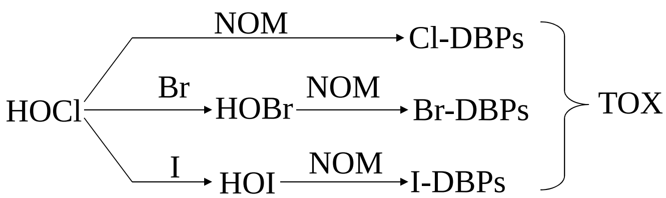
- Cumulative Frequency Plot for THM Precursor Content in Major RW Fractions



Formation Potentials of NOM Fractions



TOX Formation



TOX=TOCl + TOBr + TOI

Other disinfectants: NH_2Cl, O_3, ClO_2

From: Guanghui Hua; 2004 WQTC

David Reckhow

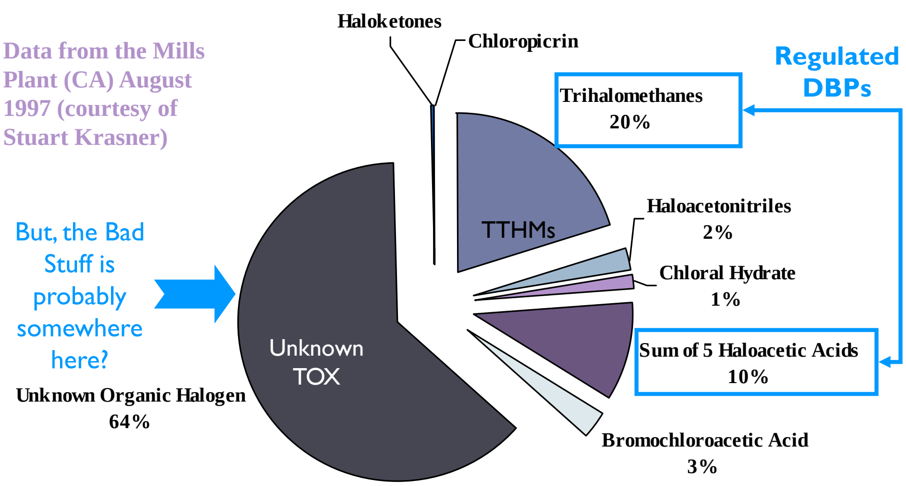
What do we know so far?

- Approximately 50% of the TOX formed by drinking water chlorination is not accounted for→ concern about the identity and concentrations of DBPs
- Not feasible to account for each and every compound that might be formed in disinfected water
- TOX: A surrogate measure for organically-bound halogenated DBPs in a disinfected water sample.
- Comparing the TOX vales with the halides attributed to the identified DBPs: allow for the estimation of the unidentified TOX
- TOX analyzers: used to quantify amounts of organically-bound chlorine, bromine and iodine in raw and disinfected water samples

TOX: Known & Unknown

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

But, the Bad Stuff is probably somewhere here?



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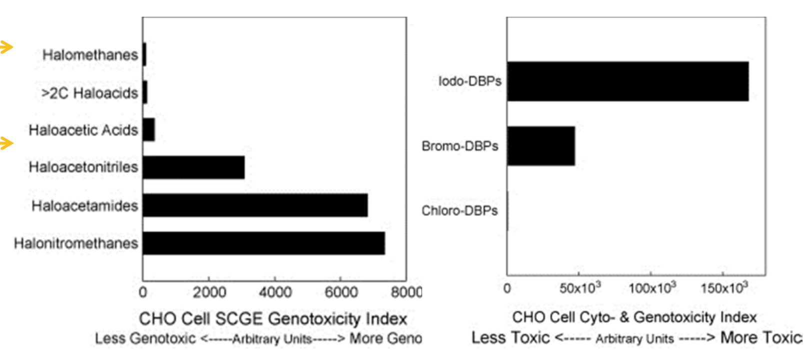
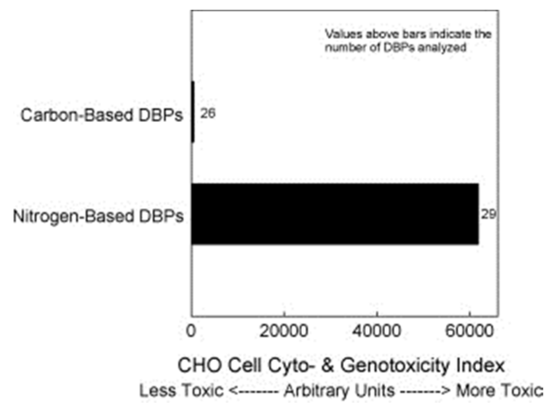
Cyto- and Geno-Toxicity of DBP classes



Occurrence, genotoxicity, and carcinogenicity of regulated and emerging disinfection by-products in drinking water: A review and roadmap for research
. (Richardson et al., 2007)

C- and N-based DBPs



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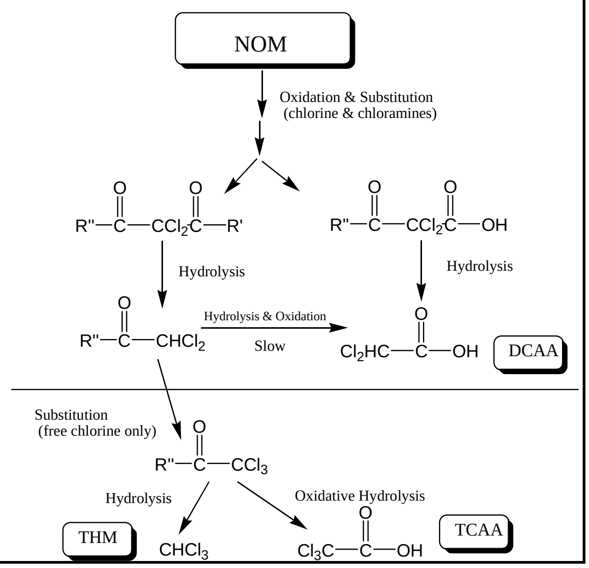
Final disinfectant

- Drinking water treatment plants usually employ a chemical as a final disinfectant
- Common oxidative chemicals
  - Free chlorine
  - Chloramines
  - Chlorine dioxide
  - Manganese oxide
  - Potassium permanganate

Use of chloramine vs chlorine as final disinfectant

- Less formation of regulated DBPs
  - THMs & HAAs
- Hydrolysis and oxidation is slow which minimizes further oxidation to TXAA
- Dihalo products, but little trihalo



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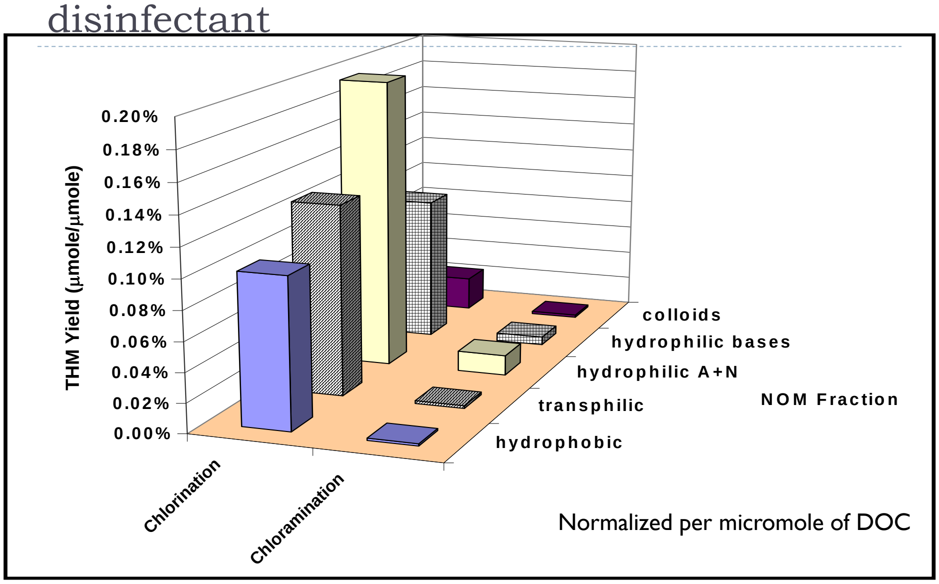
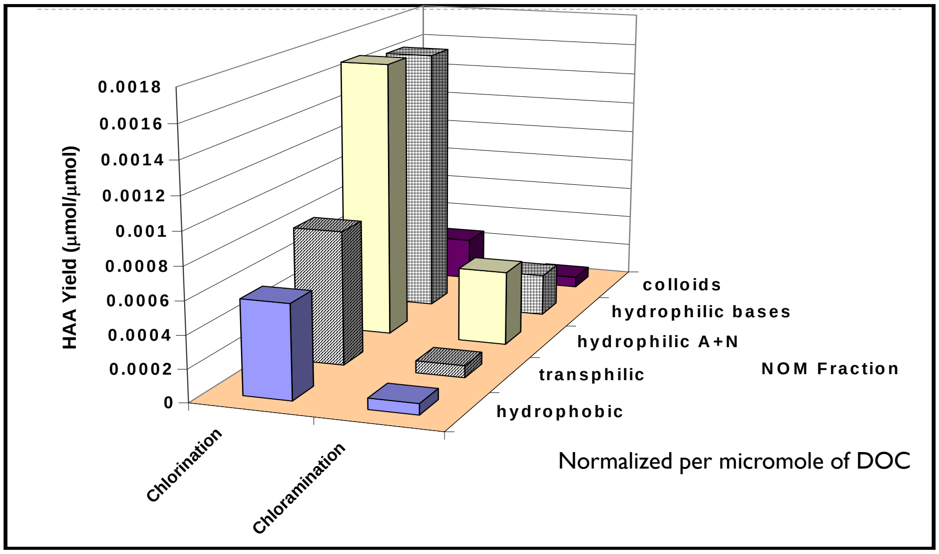


DBP Formation Reactivities of NOM Fractions of a Low-Humic Water" by Hwang, Sclimenti & Krasner

Use of chloramine vs chlorine as final disinfectant



"DBP Formation Reactivities of NOM Fractions of a Low-Humic Water" by Hwang, Sclimenti & Krasner

Final Thought

- US federal and state environmental agencies still only regulate four THMs and five HAAs (none of which include iodinated species) in addition to bromate and chlorite.
- How to change that?
- Literature is lacking in studies conducted on treated drinking waters that are not spiked with model compounds
  - ➔attention should be put in that direction.
- Focus on quantifying more harmful compounds or TOI/TOBr in drinking water
- With the recent advances in analytical techniques, it is possible to have data that will supplement existing and ongoing epidemiological/toxicological evidence.
- Once enough concrete evidence is generated, regulatory agencies will have no choice but to improve on current regulations.

- To next lecture