Disinfection By-Products: Research Plans of the United States Geological Survey

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Outline

- DBP background and regulation
- Importance of unregulated DBPs
- Prioritization of compounds for targeted research assessments
- Analytical methods

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DBP Formation

- Drinking water is disinfected for waterborne diseases
  - Chlorine is traditional disinfectant
  - Newer technology includes chemical (ozone, chloramination, UV) and physical (ultrafiltration, reverse osmosis, activated carbon) treatment
- Disinfectant can react with other water components
  - Natural organic matter
  - Bromide or iodide
  - Anthropogenic components

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DBP Regulation

- Toxicity
  - Chlorinated water linked to cancer
- 11 are currently regulated in the U.S.
  - Trihalomethanes (4)
  - Haloacetic Acids (5)
  - Oxyhalides (2)
- Occurrence
  - National scale data - compliance monitoring
  - Only for MCL purposes – µg/L concentrations

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Why DBPs need further study

- Not all toxicity can be linked to regulated DBPs
  - Bladder cancer
  - Endpoints other than carcinogenicity
- Other pathways of DBPs exposure
  - Human health - drinking water, dermal and inhalation exposure
  - Ecological exposures - treated released to the environment
- Unknown fate and transport in the environment
- Determining how precursors affect DBP formation
- Changing disinfection technology
  - More ozone, chloramination → "emerging" DBPs formed
  - Toxicity of DBPs formed shifts

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Other DBP Sources

- Wastewater discharges
- Water re-use
- Irrigation with treated water
- Swimming pools

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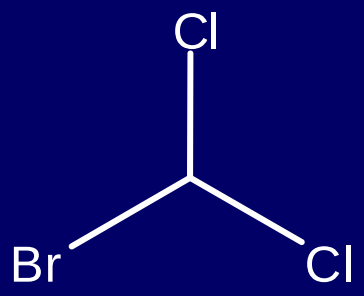
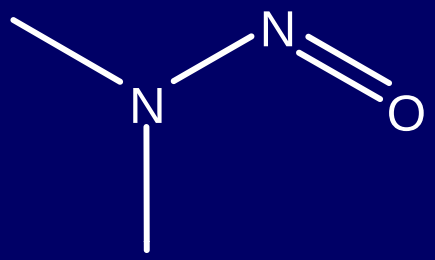
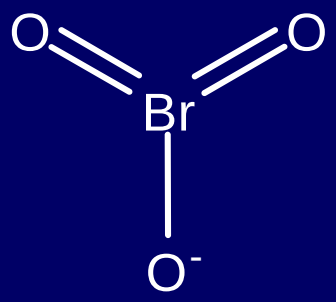
Disinfectant Changes DBPs



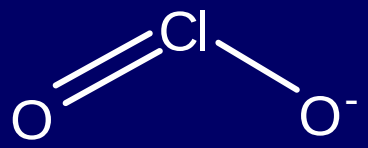
Bromodichloromethane
Free Chlorination



N-nitroso-dimethylamine (NDMA)
Chloramination



Bromate
Ozonation



Chlorite
Chlorine Dioxide

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Unregulated DBPs

- Over 600 DBPs known to form in disinfected water
  - Few have qualitative occurrence or health-effects studies
  - Over half of total organic halides formed not identified
- EPA is considering monitoring more
  - UCMR2 - nitrosamines
  - CCL3 - formaldehyde
- 74 have been tagged as emerging DBPs

  Richardson et al., 2007, *Mut. Res.*, 636, 178-242
  - Occurrence levels
  - Toxicological properties

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Emerging DBPs

(Richardson et al., 2007, *Mut. Res.*, 636, 178-242)

- Category 1- Human carcinogens
  - 8 DBPs; 4 regulated, 4 unregulated
  - Some or all characteristics of human carcinogens
- Categories 2 and 3 – Genotoxic or unknown
  - Moderate occurrence (sub to low µg/L)
  - Category 2: 29 genotoxic compounds; 2 rodent carcinogens
  - Category 3: 14 with little or no toxicological data
- General rule
  - I > Br > Cl for genotoxicity
  - Br > Cl (I?) for carcinogenicity

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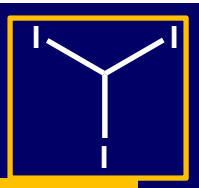
Possible Target DBPs

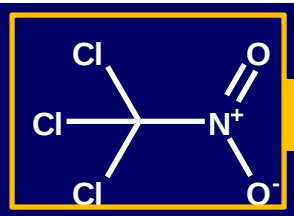
Halo-methanes and halo-acids



Iodoform

sub to low µg/L

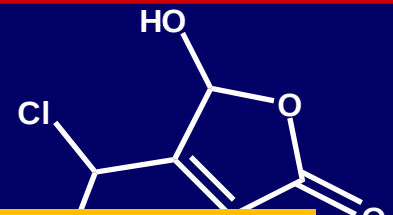
Halonitromethanes



low µg/L

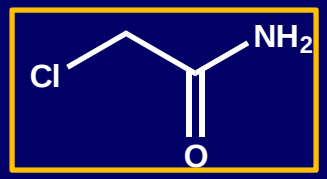
Trichloronitromethane

Halofuranones



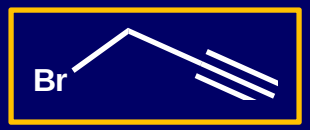
Category 2 genotoxic

Haloamides



Chloroacetamide

Haloacetonitriles



Bromoacetonitrile

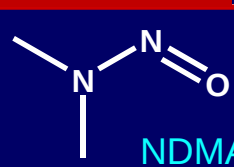
Category 1 human carcinogen

Aldehydes

rodent carcinogen

Chloroacetaldehyde

s



NDMA

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Emerging DBP Sources - Wastewater

- Not traditionally considered a DBP source
- Limited research (Krasner et al., 2009, ES&T, 43, 8320-8325)
  - Nitrification affects DBP formation
    - Poor nitrification with chlorination lead to less halogenated DBPs but higher NDMA
    - Well-nitrified, more halogenated DBPs but lower NDMA
  - Also detected haloacetonitriles and haloacetaldehydes
- Persistence of wastewater DBPs will impact potential affects

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Precursors and DBPs

- Need to understand how compounds present in water affect DBP formation

- Natural organic matter
  - Poorly characterized, varies
  - Links to watershed, soil, landuse
- Transformation products of anthropogenic compounds (pesticides, pharmaceuticals, surfactants)
  - Most current treatment studies only focus on parent removal
  - Products could be more toxic than parent

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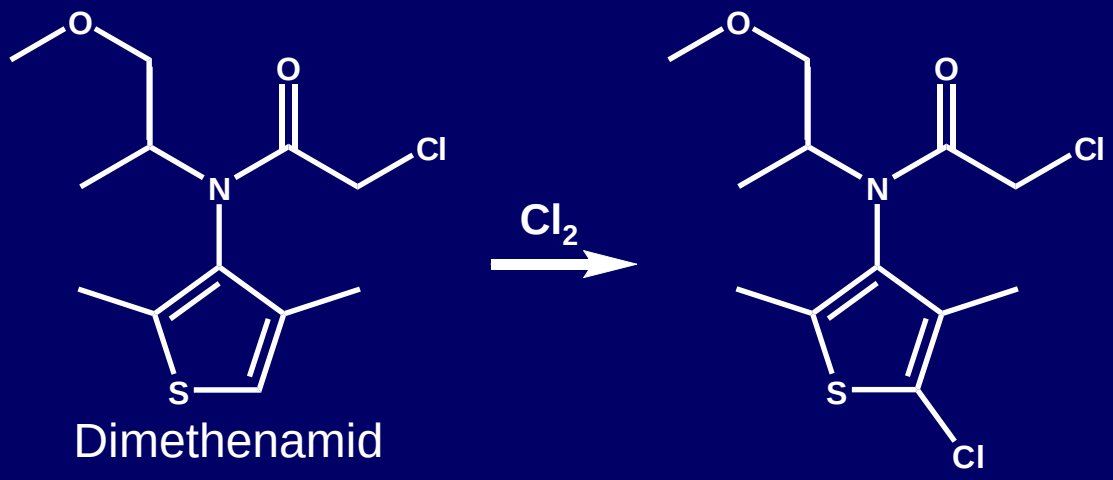
DBP Precursors - Pesticides

- Products not formed in the environment through hydrolysis, photolysis, biodegradation, etc.
- Not included in typical treatment studies -parent disappearance, some environmental degradates



Dimethenamid

Hladik et al., 2005, *Wat. Res.,* 39, 5033-5044

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DBP Prioritization Considerations

- Toxicity (human, ecological)
- Chemical properties (stability, hydrophobicity)
- Disinfection type (chlorination, ozonation)
- Sources/precursors (organic matter, ions)
- Documented occurrence (when available)
- Available methods (instrumentation, detection levels)
- Seek input from other stakeholders (US EPA and AWWA)

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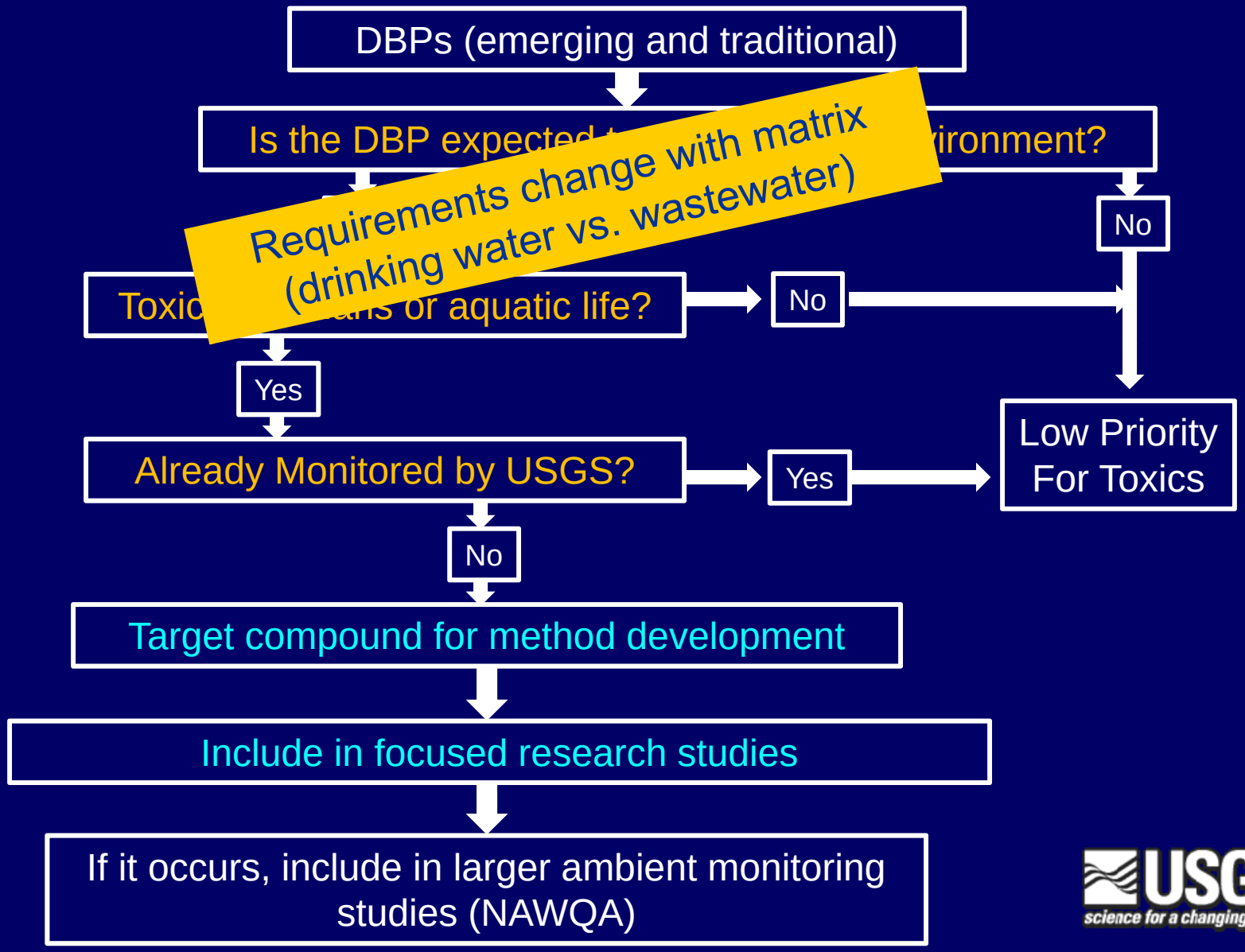
DBP Research Map



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Analytical Methods

- Modify developed DBP methods
  - GC-ECD; GC-MS; with and without derivatization
  - Expand matrices
    - Wastewater more complex than drinking water
    - Possible interferences or poor recoveries
- Develop new methods
  - LC/MS/MS
    - Alternative to derivatization
    - Good for polar compounds
    - Attempt direct aqueous injection (1 mL)

- Look for knowns and unknowns

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Future Plans

- Prioritize DBPs
- Method development
- Reconnaissance – test methods
- Occurrence studies
- Long term
  - Asses DBP behavior in the environment, ecological health studies
  - Identify precursors and sources
- Transfer suitable methods and approaches to monitoring programs

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