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
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
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
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
Other DBP Sources

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

- Bromodichloromethane (Free Chlorination)
- N-nitroso-dimethylamine (NDMA) (Chloramination)
- Bromate (Oxidation)
- Chlorite (Chlorination of Caustic)
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
  – Occurrence levels
  – Toxicological properties
Emerging DBPs

- **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
Possible Target DBPs

Halo-methanes and halo-acids
- Iodoform
  - sub to low µg/L

Halonitromethanes
- Trichloronitromethane
  - low µg/L

Halofuranones

Haloamides
- Chloroacetamide

Haloacetonitriles
- Bromoacetonitrile

Category 1
- human carcinogen
  - Chloroacetaldehyde
  - NDMA

Category 2
- genotoxic
  - Aldehydes
    - rodent carcinogen
    - Chloroacetaldehyde

Roentgen carcinogen

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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
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
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

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)
DBP Research Map

- **DBPs (emerging and traditional)**

  - Is the DBP expected to persist in the environment?
    - Yes
    - No
      - Requirements change with matrix (drinking water vs. wastewater)

  - Toxic to humans or aquatic life?
    - Yes
    - No
      - Already Monitored by USGS?
        - Yes
        - Low Priority For Toxics
        - No
          - Target compound for method development
            - Include in focused research studies
              - If it occurs, include in larger ambient monitoring studies (NAWQA)
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
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