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Disinfection By-Products: Formation, Occurrence and Control

Kenan Ozekin¹ and Gary Amy²

¹Awwa Research Foundation

²UNESCO-IHE Institute for Water Education

Outline

- Awwa Research Foundation (AwwaRF)
- Basic concepts
 - Disinfection
 - DBP formation
- Factors Influencing DBP Formation
- Controlling DBP Formation
- Conclusions

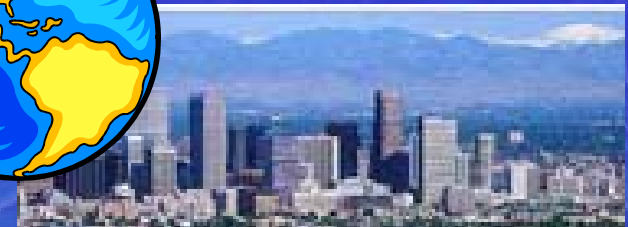


What is AwwaRF

- The Awwa Research Foundation (AwwaRF) is a member-supported, international, nonprofit organization that sponsors research to enable water utilities, public health agencies, and other professionals to provide safe and affordable drinking water to consumers.
- Our Mission: Advancing the science of water to improve the quality of life
 - Sponsoring research
 - Developing knowledge
 - Promoting collaboration

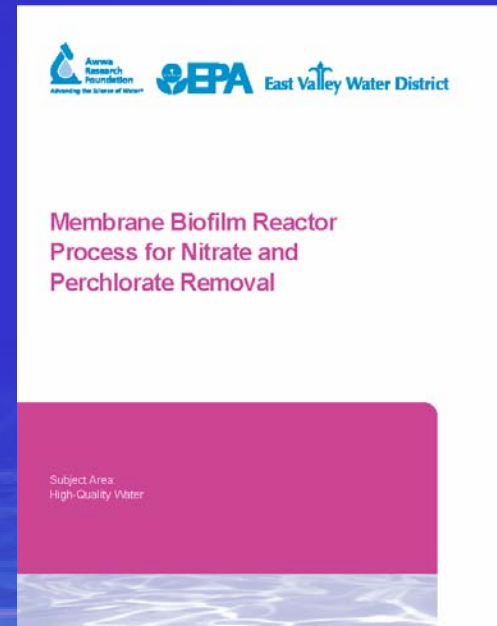


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Sponsored Research

- Total research value > \$340 million
- > 800 research projects total
 - > 500 published reports
 - > 300 projects currently ongoing
- Research Programs
 - Solicited
 - Unsolicited
 - Tailored Collaboration
 - Partnerships



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Subscribers

- ~ 900 utilities
- 50 consultants
- 14 manufacturers
- 34 Partners, e.g.
 - Association of California Water Agencies
 - California Energy Commission
 - KIWA
 - Environmental Protection Agency
 - EAWAG
 - Sandia National Laboratories
 - US Bureau of Reclamation
 - Awwa Research Foundation
 - WaterReuse Foundation



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Disinfection

- Objective - to inactivate pathogenic microorganisms
 - Bacteria, Viruses, Protozoa
- Chlorine - disinfectant most commonly used in US
 - Effective, easy to apply
 - Cheap
 - Most studied
- Disinfection Requirements
 - Based on CT concept (Concentration x Time)

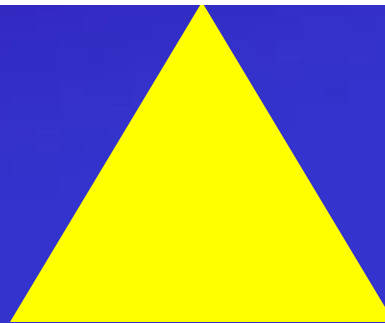


Disinfection vs By-Product Formation

Disinfection

Disinfection By-products

Microbial Risk



Long-Term (Cancer) and Short-Term (Reproductive) Effects

- Overall risk assessment
- Dangers in developing countries (Peru)



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DBP Formation

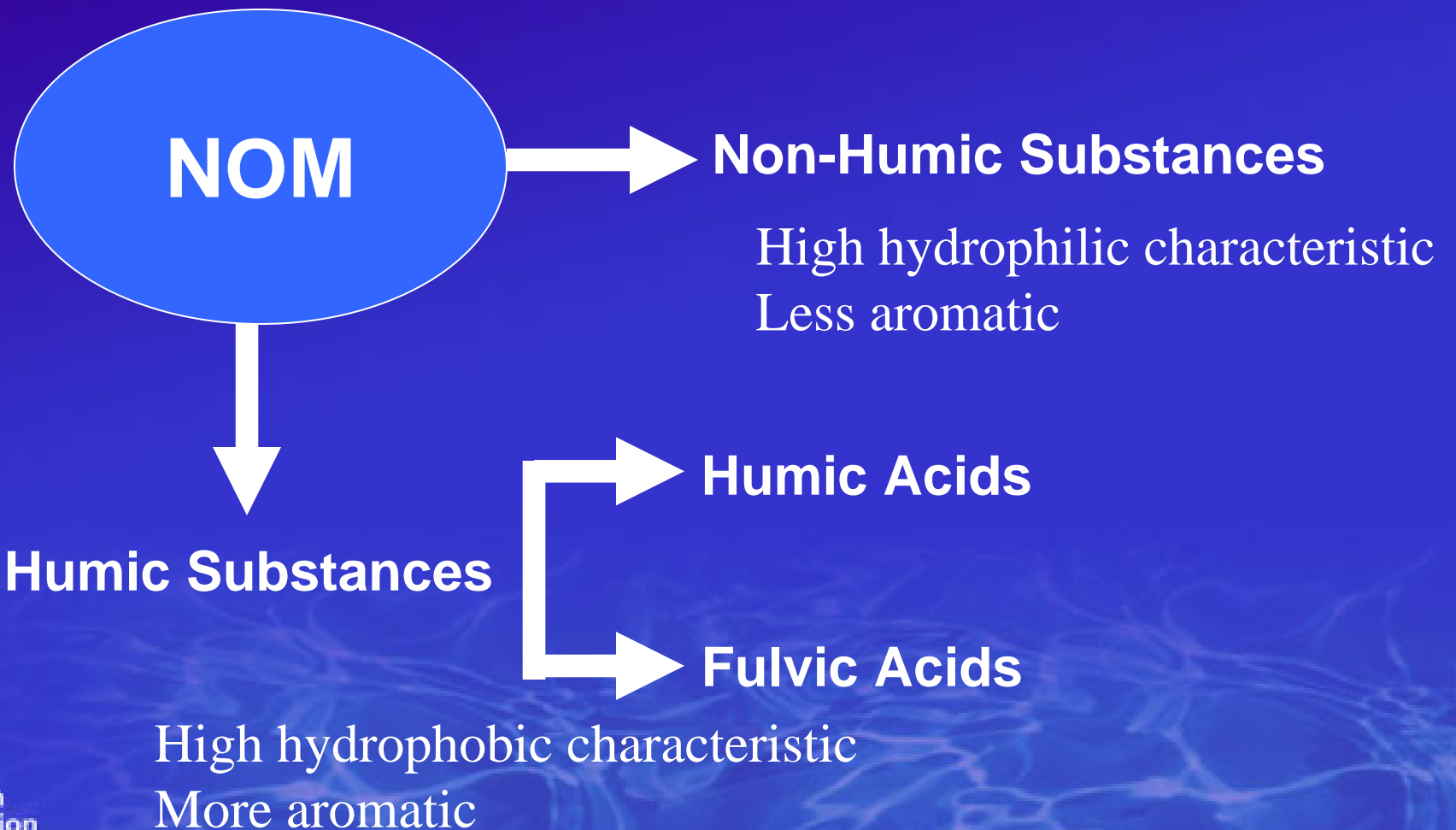
- Disinfectant + Precursor \longrightarrow DBPs
- Disinfectants
 - Chlorine
 - Chloramine
 - Ozone
 - Chlorine Dioxide
- Precursors
 - Natural Organic Matter (including algae)
 - Bromide



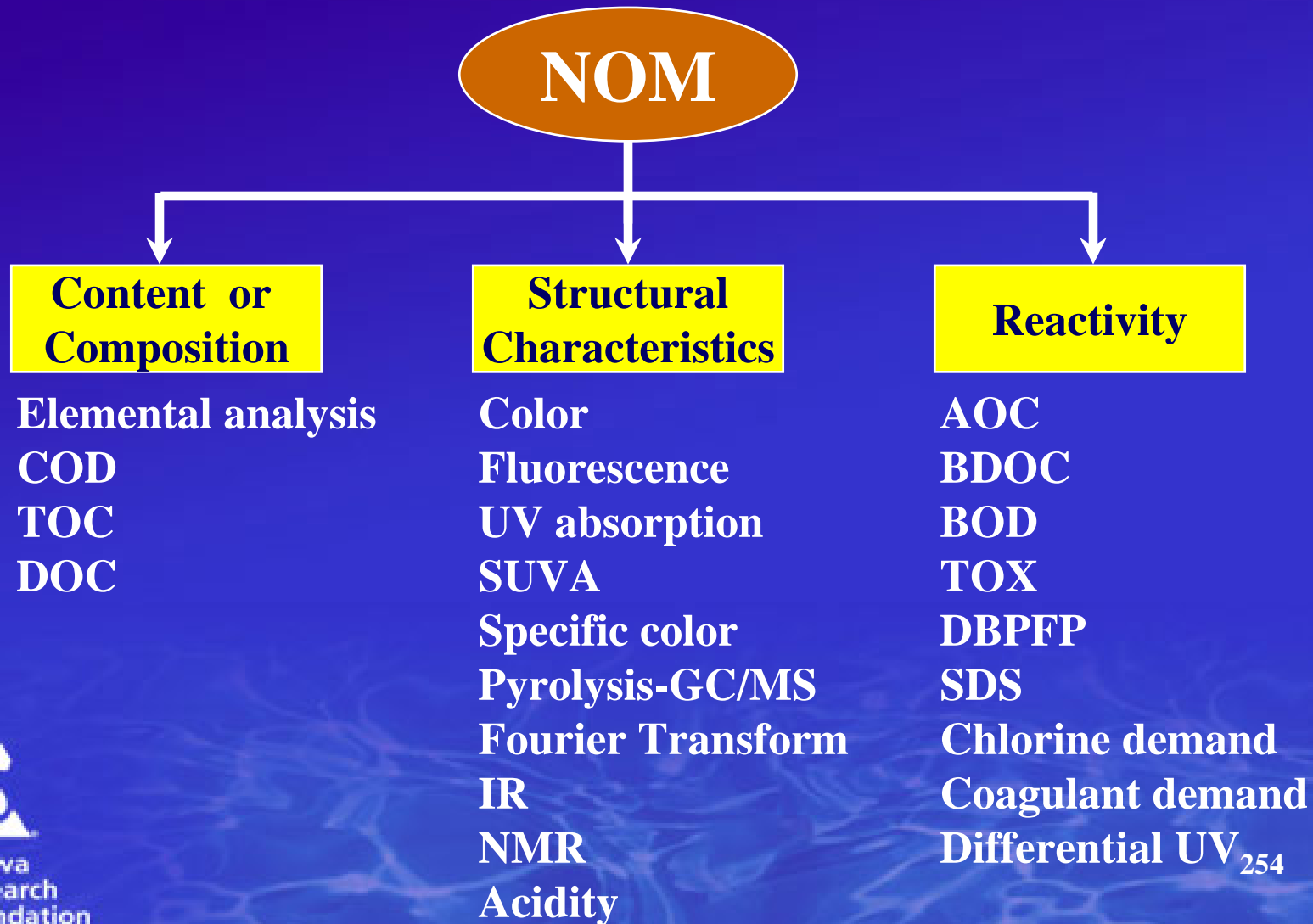
What is NOM

- A complex mixture of compounds formed as a result of the breakdown of animal and plant material in the environment
- Composition of mixture is dependent on the environmental source
- Mainly consists of carbon, oxygen and hydrogen, but may contain nitrogen and sulphur.

Natural Organic Matter



Characterization Techniques



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Adapted from: Kornegay, 2001 NOM Workshop

Chlorination DBPs

- Trihalomethanes (THMs);
 - Four species (TTHM*)
- Haloacetic Acids (HAAs)
 - Nine species (HAA₉ vs. HAA₅* vs HAA₆)
- Haloacetonitriles (HANs)
 - Five species; DHANs (Three)
- Haloketones (HKs)
- Halonitromethanes (HNMs)
- Chloral Hydrate (CH)
- Chloropicrin (CP)
- Cyanogen Chloride (CNCl)
- Aldehydes (non-halogenated)



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Regulated in USA

Formation of Chlorination DBPs

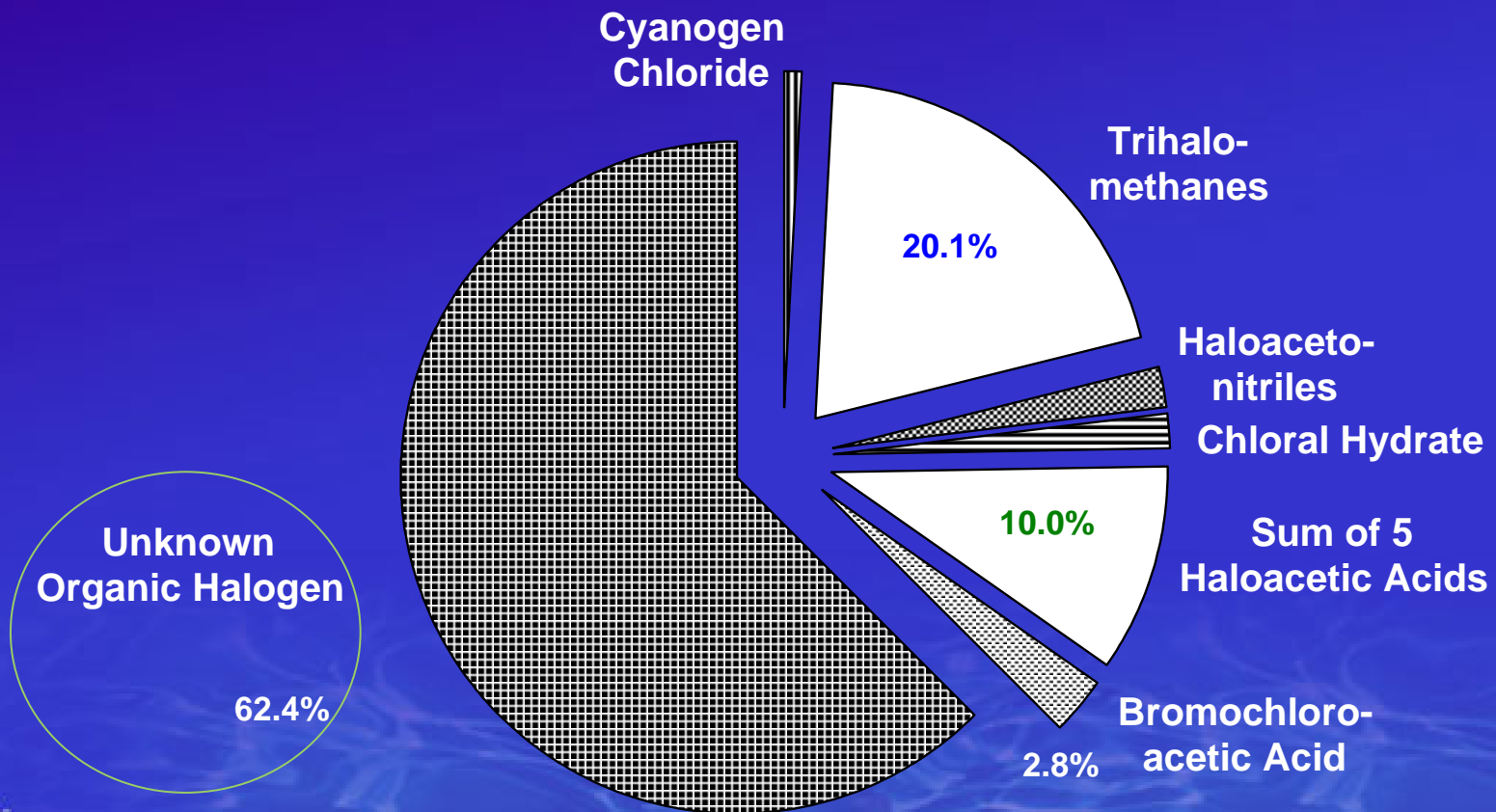
- $\text{NOM} + \text{Cl}_2 \rightarrow \text{TOCl}$
- $\text{Br}^- + \text{Cl}_2 \rightarrow \text{Br}_2$
- $\text{NOM} + \text{Br}_2 \rightarrow \text{TOBr}$
- $\text{TOX} = \text{TOCl} + \text{TOBr}$

Identifiable Compounds Comprise Less Than 50 % of TOX

Bromide Incorporation Can Range Up To 75 %



Percentage of Total Organic Halogen (TOX) Accounted for by Known DPBs (molar basis) (Krasner, 1996)



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***California water, 1997 (raw-water bromide = 0.15 mg/L):
Total organic halogen = 172 µg/L**

Influential Water Quality Factors

■ pH

- THM formation increases with increasing pH
- Mixed effect on HAA species
- TOX concentration decreases at higher pH

■ Temperature (seasonal parameter)

- DBP formation increases with increasing temperature
- Higher chlorine demand at higher temperatures

■ NOM Properties

- Halogenated DBP formation increases with the activated aromatic content of NOM
- UV_{254} or UV_{272} or SUVA is a good surrogate for DBPs

■ Bromide

- In the absence of bromide, only chlorinated by-products are formed
- In the presence of bromide, mixed chloro-bromo substitution products are formed
- In waters with high bromide concentrations, it is possible to form primarily the brominated species



Influential Treatment Factors

- Cl₂ Dose
 - ⇒ Higher Doses Promote HAAs over THMs
- Hydraulic Residence Time (HRT)
 - ⇒ In-Plant vs. Distribution-System HRT
 - ⇒ Brominated Species Form More Rapidly Than Chlorinated;
 - ⇒ HAAs Form More Rapidly Than THMs;
Stability of Brominated HAAs?



Chloramination

- Weaker disinfectant than chlorine
- Requires higher concentration and longer time
- May cause nitrification problems
- Corrosion and lead release

(water systems > 10,000 people)

	<u>1978</u>	<u>1989</u>	<u>2005</u>
Chlorine	91%*	87%*	68%#
Chloramines		20%*	29%#



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AWWA WWA Disinfection Committee Survey (2000)
Seidel et al. (2005)

Chloramination

- Approaches:

- ⇒ Cl_2 vs. NH_3 Sequence:

- $\text{Cl}_2 \rightarrow \text{NH}_3$ (Some Free- Cl_2 CT)

- $\text{NH}_3 \rightarrow \text{Cl}_2$

- $\text{Cl}_2 + \text{NH}_3$ (pre-formed)

- ⇒ Cl_2/NH_3 Ratio:

- Generally Form NH_2Cl



Chloramination DBPs

- HAA
 - Lower than chlorination except DXAA
- THM
 - Lower than chlorination
- TOX
 - THM and HAA constitute less than 20% of TOX.
The rest of TOX is unknown
- Iodoacetic Acid (?)
- NDMA



NDMA

- CA-DEP has developed a proposed Public Health Goal of 3 ng/L
- Organic nitrogen containing precursors play an important role on the formation
- Formation is pH dependant (mixed results)
- Cl_2 vs. NH_3 sequence is important (addition of Cl_2 first decreases the formation)



Ozonation

- Most effective disinfectant - lowest CT
- Good primary disinfectant, it must be used in conjunction with a persistent secondary disinfectant
- Ozone generation systems are very reliable
- Oxidizes color causing compounds
- Decreases the chlorine demand
- Improves coagulation and flocculation

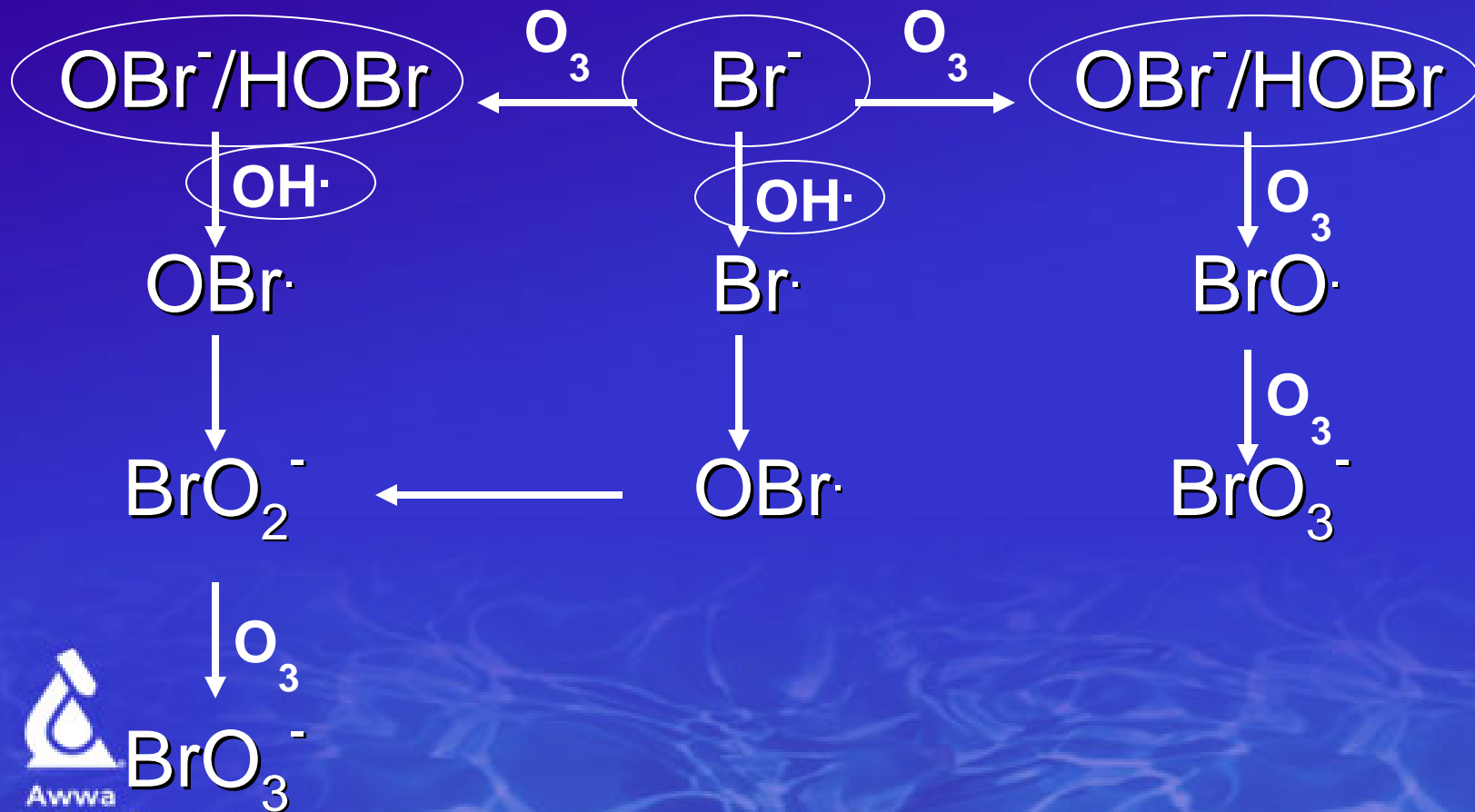


Ozonation By-Products

- **Non-Brominated Compounds:**
 - ⇒ Aldehydes (4 dominant species)
 - ⇒ Ketoacids (3 dominant species)
 - ⇒ Carboxylic Acids (3 dominant species)
- **Brominated Compounds:**
 - ⇒ **Bromate (BrO_3^-)**
 - ⇒ TOBr (e.g., Bromoform, Dibromoacetic Acid, Dibromoacetonitrile)



Bromate Formation



Important Water Quality & Treatment Factors: BrO_3^-

- pH (+)
- Temp (+)
- Carbonate Alkalinity (+)
- Br^- (+)
- NH_3 (-)
- NOM (-), on O_3 Dose Basis
- O_3 (+)
- H_2O_2 (+/-)
- Hydraulic Residence Time (HRT) (+)
- Pre-oxidation with Cl_2 or NH_2Cl (-)

Chlorine Dioxide

- Effective disinfectant - low CT values
- Effective for taste and odor control
- Successful in removing color causing compounds
- Can oxidize iron and manganese
- Chlorine demand could be decreased because of the oxidation of inorganic and organic compounds by chlorine



Chlorine Dioxide DBPs

Chlorite (ClO_2^-)

- ⇒ 50 – 70 % of $\text{ClO}_2 \rightarrow \text{ClO}_2^-$; Relatively Stable
- ⇒ $\text{ClO}_2^- \rightarrow \text{ClO}_3^-$ if Cl_2

Chlorate (ClO_3^-)

- ⇒ Formed During ClO_2 Production
- ⇒ Impurity of NaOCl Solutions

U.S. (ICR) Database (n = 29)



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- ⇒ Avg. ClO_2 and ClO_2^- = 0.97 mg/L and 0.38 mg/L

Controlling DBP Formation

Disinfectant + Precursor \longrightarrow DBPs



Use an
Alternate



Remove/Reduce
Before Formation



Remove/Eliminate
After Formation



Chlorination DBP Control

- **Watershed Management**

- ⇒ Algae (Autochthonous NOM) Control by Nutrient Limitation
- ⇒ Bank Filtration for BOM Removal (EU Approach)
- ⇒ Br⁻ Control (e.g., Salt Water Intrusion)

- **Precursor Removal**

- ⇒ Enhanced/Optimized Coagulation (up to 50 % DOC removal);
- ⇒ GAC (GAC₁₀ to GAC₂₀) (up to 70% DOC removal);
Non-Adsorbable NOM Fraction
- ⇒ Membranes (NF, Fe + MF) (up to 90 % DOC removal);
- ⇒ Ion Exchange (e.g., MIEX): DOC (NOM Acids) and Br⁻
- ⇒ Goals: Reduce TOC (or DOC); UVA; SUVA; Higher MW NOM; Humic NOM
- ⇒ Br⁻ Passes conservatively through coagulation and GAC;
some removal (e.g., 50 %) by NF



Conclusions

- Disinfection is necessary to inactivate pathogenic microorganisms
- DBPs form
- Water Quality (pH, temperature, precursor concentration, bromide ion) and Operating Parameters (disinfectant dose, contact time) are important parameters of DBPs formation
- *Balance* Disinfection (CT) Requirements vs. DBP Control
- *Balance* DBP Risk; Chemical vs. Microbial Risk



Questions



**For further information on DBP formation
contact:**

**Kenan Ozekin, Ph.D.
Senior Project Manager
Awwa Research Foundation**

kozekin@awwarf.org

(303) 734-3464



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