Measures of Water Quality Impacting Disinfection

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Washington DC

September, 2008

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Types of Drinking Water Disinfectants

- Free chlorine ($HOCl/OCl^-$)
- Combined chlorine, i.e. monochloramine (NH_2Cl)
- Ozone (O_3)
- Chlorine dioxide (ClO_2)
- Ultraviolet (UV) irradiation

Free Chlorine

- Effective disinfectant
  - For bacteria, viruses, and most protozoan cysts
    - Effectiveness (in the US) is defined by CT values

$$dN/dT = -kC^nN$$

$$\text{Log } N_o/N = kC^nT/2.3$$

CT values (mg-min/L) for Microbial Inactivation by Free Chlorine (pH 7.0, 1.0 mg/L Cl2 residual)*

Temperature °C	<=0.5	5	10	15	20	25
4-log virus inactivation	12	8.0	6.0	4.0	3.0	2.0
3-log Giardia inactivation	210	149	112	75	56	37

*significance of pH, temperature

Source: Water Chlorination/Chloramination Practices and Principles, M20, AWWA, 2006

Water Quality Factors Impacting Disinfection

- Temperature, pH
- Reduced inorganic material
  - Iron and manganese
  - Sulfide
  - Ammonia
- Dissolved organic material (DOM)
- Type of microorganism
  - Bacteria, viruses, protozoan cysts
- State of microorganism
  - Single cell or aggregated (particle-associated)
- Particulate content, e.g. turbidity

Chlorine Demand

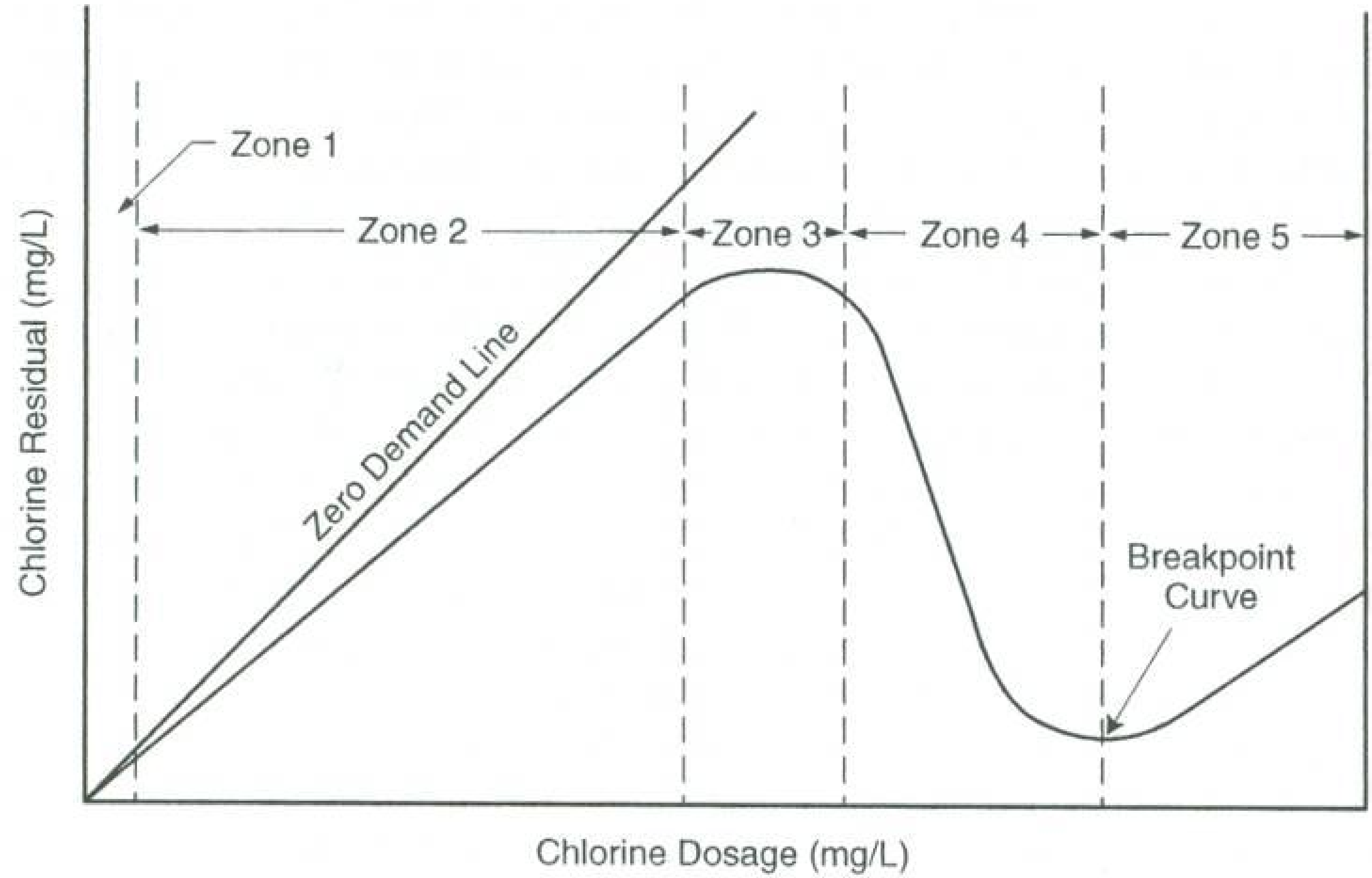
Dose minus residual = chlorine consumed

Chlorine Demand of Various Inorganic Reducing Agents

- $2Fe^{2+} + HOCl + 5H_2O$ **à** $2Fe(OH)_3(s) + Cl^- + 5H^+$
- $Mn^{2+} + HOCl + H_2O$ **à** $MnO_2(s) + Cl^- + 3H^+$
- $H_2S + 4\ HOCl$ **à** $SO_4^{2-} + 4\ Cl^- + 6H^+$
- $2NH_3 + 3HOCl$ **à** $N_2(g) + 3H^+ + 3Cl^- + H_2O$

Chlorine Demand of Various Inorganic Reducing Agents

- 0.64 mg/L of chlorine per mg/L Fe(II)
- 0.93 mg/L of chlorine per mg/L Mn(II)
- 8.86 mg/L of chlorine per mg/L S(-II)
- 7.61 mg/L per mg/L NH_3



Source: Connell, 1996.

Figure 3-2 Breakpoint curve

Source: Water Chlorination/Chloramination Practices and Principles, M20, AWWA, 2006

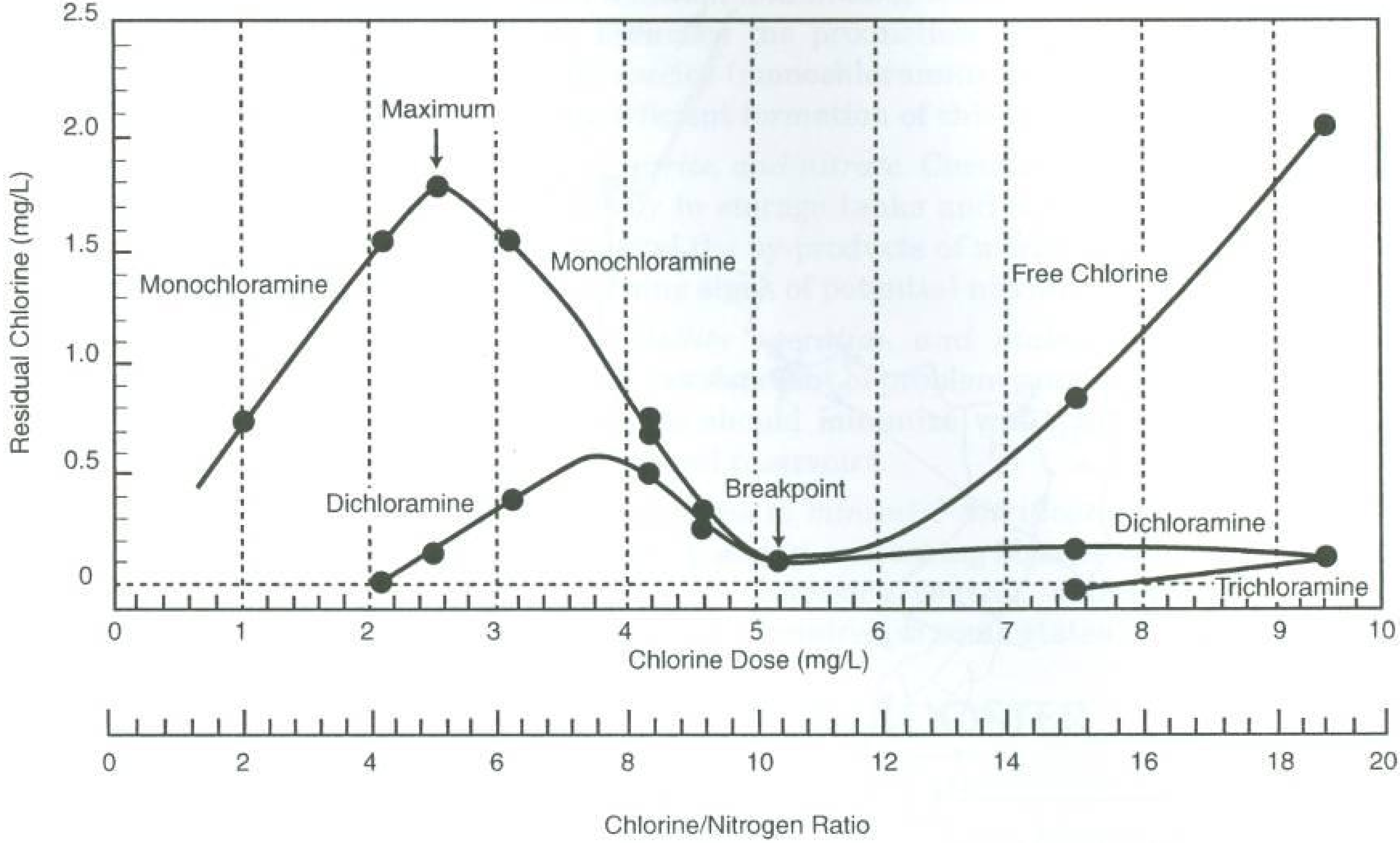


Figure 6-9 Example breakpoint chlorination curve

Source: Water Chlorination/Chloramination Practices and Principles, M20, AWWA, 2006

Chlorine Demand of Dissolved Organic Material

- Chlorine serves as an electron transfer agent (oxidant), but also participates in substitution and addition reactions to form halogenated byproducts (e.g. trihalomethanes).
- On average 1-1.5 mg/L chlorine is consumed per mg/L dissolved organic carbon (DOC) over 24 hours at pH 8 and 25^{o}C.

Summary of Chlorine-Demanding Reactions

For a water containing 0.5 mg/L ammonia and 4 mg/L DOC, the chlorine demand will be on the order of 8.8 mg/L.

For a water containing 0.2 mg/L ammonia and 2 mg/L DOC, the chlorine demand will be on the order of 4.0 mg/L.

For a groundwater with 1 mg/L Fe(II), 0.5 mg/L Mn(II), 1 mg/L DOC, the chlorine demand will be on the order of 2.4 mg/L.

Measurement of Residual Chlorine

- DPD colorimetric/spectrophotometric analysis
  - Most common method of residual chlorine analysis
  - Can distinguish between free and combined chlorine, if done properly
  - But subject to interferences:
    - Combined chlorine may be included as part of the free chlorine residual
    - Some organic chloramines behave like free Cl2 and give an artificially high value
    - 0.2 mg/L “detectable” residual may give misleading information

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- Particulate content, e.g. turbidity
- State of microorganism
  - Single cell or aggregated (particle-associated)

Turbidity (1)

- Can be measured rapidly, easily, cheaply, on-line
- Measures light scattering of particles
- Measured with a turbidimeter (nephelometer)
- Typically measures light scattering at 90^{o} to the incident light

Turbidity (2)

- Degree of scattering is a function of number, size, shape, refraction index of particles, wavelength of incident light, geometry and detection characteristics of instrument, standardization/calibration procedure
- Scattering is maximum for particles of diameter equal to the wavelength of the incident light ($d_p \sim \lambda =$ 0.5 um for white light)
- Typical sizes of microorganisms
  - Viruses: 0.01 - 0.1 um
  - Bacteria: 0.1 - 1 um
  - Giardia cysts: 10-13 um
  - Cryptosporidium oocysts: 4-8 um

Turbidity (3)

- Turbidity is a collective measure, serving as a surrogate parameter for particle content of water, but does not measure particle size, or the nature and morphology of the particle.
  - Small particles scatter more light than an equivalent mass of large particles.
  - Very small particles do not scatter light
- Note: the absence of a measurable turbidity does not mean that a water is free of harmful particulate contaminants.
  - Very small particles (<0.5 um) do not scatter much light.

Particle Size Analysis

- Particle Counters
  - Measure both particle size and particle concentration; particle size distribution
- Optical methods
  - Based on light scattering or blockage
  - Reported size (diameter) based on projected area of particles, i.e. area-equivalent diameter
- Resistivity-based methods
  - Based on volume displacement of water by particles in a salt solution, i.e. volume-equivalent diameter.
- Image analyzers
  - Allows for identification of the type/source/ morphology of particle.

Turbidity/particulate considerations

- Organisms may be single-cell or particle-associated
- If particle-associated, inactivation by chlorine or any oxidant is hindered because the cells are protected.
- Organisms themselves are particulate in nature
  - Viruses: 0.01 - 0.1 um
  - Bacteria: 0.1 - 1 um
  - Giardia cysts: 10-13 um
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UV Irradiation

- Disinfection effectiveness:
  - Compared to chemical disinfectants, not impacted by presence of inorganic reducing agents
  - Impacted by presence of dissolved organic material that absorbs UV light
  - Impacted by nature of microorganisms
    - e.g. protozoan cysts vs bacteria vs viruses
  - Impacted by state of microorganisms
    - particle-associated (aggregated) vs single cell

Filtration

- Because microorganisms are particulate in nature--
- Because microorganisms are often found as aggregates, i.e. associated with particulate material--
- Because microorganisms associated with particulate material are less susceptible to inactivation by disinfectants--

From a public health standpoint, filtration is the first line of defense against microorganisms in drinking water.

Chemical or UV inactivation is most effective in filtered water.

Conclusions

- Many physical and chemical characteristics of water impact the effectiveness of disinfection
- Prediction of an appropriate disinfectant dose and contact time requires knowledge of the chemical composition of the water
- The effectiveness of disinfectants is different for different types of microorganisms
- Disinfection of particle-laden water is problematic; filtration of such waters must be considered prior to chemical or physical disinfection