Oxidation-Reduction (Redox) Reactions

- Def'n: Reactions in which one or more electrons is shifted from one element to another
  (Note: In all reactions discussed previously, atoms changed partners, but each atom kept all its electrons)

- **Oxidation** = loss of e^-, hence higher charge;
  Reduction = gain of e^-, hence lower charge;
  Redox = transfer of e^- (simultaneous oxidation and reduction)

Conventions for Assigning Charge to Atoms

- **Rule** (can never be violated): Charge must be conserved, i.e., the charge on a molecule must equal the sum of the charges on the constituent atoms.

- **Conventions**:
  1. H has an oxidation number (charge) of +1.
  2. O has an oxidation number of –2.
  3. N has an oxidation number of –3 when bonded only to H or C, as it is in many organic compounds.
  4. S has an oxidation number of –2 when bonded only to H or C, as it is in many organic compounds.

- **Application:** The above conventions are applied in the order given, but can be violated if necessary to avoid violating the charge conservation rule.

Oxidation Number Calculations

- Oxidation number of C in H_2CO_3:
  $2(+1) + C + 3(–2) = 0$; $C = +4$

  Oxidation number of C in $HCO_3^–$:
  $1(+1) + C + 3(–2) = –1$; $C = +4$
  Same result for CO_2, $CO_3^{2–}$
- Oxidation number of C in glucose ($C_6H_{12}O_6$):
  $6*C + 12(+1) + 6(–2) = 0$; $C = 0$
- Oxidation number of S in $SO_4^{2–}$, H_2S:
  In $SO_4^{2–}$: $S + 4(–2) = 0$; $S = +6$
  In H_2S: $2(+1) + S = 0$; $S = –2$
- Oxidation number of Fe in Fe(*s*), $Fe(OH)_3$(*s*):
  In Fe(*s*)*:* Fe = 0
  In $Fe(OH)_3$(*s*): $Fe + 3(–2) + 3(+1) = 0$; $Fe = +3$

Redox Changes Can Have **Very** Large Effects

- Methane (CH_4 [C=–4]) vs. cellulose (complex, but C≈0) vs. carbonate species (C=+4); In general, metabolism involves oxidation of organic carbon to carbon dioxide, and photosynthesis reverses this process
- Corrosion involves oxidation of pure metals (oxid. state = 0) to metal ions (>0)*
- Chlorine (Cl_2, [Cl=0]) is a disinfectant; chloride (Cl^- [Cl=–1]) is innocuous
- Denitrification reduces nitrate (NO_3^- [N=+5]) to nitrogen gas ($N_2(g)$ [N=0])

(*See picture from p.1 Opflow 2003-09 corrosion scales headloss.pdf)

Balancing Redox Reactions

- Determine oxidation numbers of all atoms in the reaction and identify atoms that undergo oxidization or reduction.
- Choose one of the oxidized or reduced species to have a stoichiometric coefficient of 1.
- Assign other stoichiometric coefficients that are determined unambiguously by the choice made in Step 2.
- Electrons must be conserved. By balancing the number of electrons lost by atoms that are oxidized with the number gained by those that are reduced, determine stoichiometric coefficients for the other oxidized and reduced species.
- Add H_2O to either side of the reaction to balance the oxygen atoms.
- Add H^+ to either side of the reaction to balance charge.
- Hydrogen should automatically balance at this point. Check the H balance to confirm.

Example. Balance the following redox reaction:

$$\underline{a}\mathrm{Fe}^{2+} + \underline{b}\mathrm{Cr_2O_7^{2-}} \leftrightarrow \underline{c}\mathrm{Fe(OH)_3(s)} + \underline{d}\mathrm{Cr}\left(\mathrm{OH}\right)_2^+$$

- Fe(II) is oxidized to Fe(III), and Cr(VI) is reduced to Cr(III)

- Choose *b*=1. Then *d* must be 2 to balance the Cr atoms

$$\underline{a}\mathrm{Fe}^{2+} + \underline{1}\mathrm{Cr_2O_7^{2-}} \leftrightarrow \underline{c}\mathrm{Fe(OH)_3}(s) + \underline{2}\mathrm{Cr}\left(\mathrm{OH}\right)_2^+$$

- Each Cr atom that reacts gains 3 e^-, so for the given coefficients, 6 e^- are transferred. Each Fe(II) releases only 1 e^- when it is converted to Fe(III), so 6 Fe(II) ions must be oxidized. Thus:

$$\underline{6}\mathrm{Fe}^{2+} + \underline{1}\mathrm{Cr_2O_7^{2-}} \leftrightarrow \underline{6}\mathrm{Fe(OH)_3}(s) + \underline{2}\mathrm{Cr}\left(\mathrm{OH}\right)_2^+$$

$$\underline{a}\mathrm{Fe}^{2+} + \underline{b}\mathrm{Cr_2O_7^{2-}} \leftrightarrow \underline{c}\mathrm{Fe(OH)_3}(s) + \underline{d}\mathrm{Cr}\left(\mathrm{OH}\right)_2^+$$

- The reaction has 7 oxygen atoms on the left and 22 on the right. To balance the oxygen, we add 15 water molecules to the left:

$$\underline{6}\mathrm{Fe}^{2+} + \underline{1}\mathrm{Cr_2O_7^{2-}} + \underline{15}\mathrm{H_2O} \leftrightarrow \underline{6}\mathrm{Fe(OH)_3}(s) + \underline{2}\mathrm{Cr}\left(\mathrm{OH}\right)_2^+$$

- The total charge on the left is +10, while that on the right is +2. Adding 8 H^+ to the right balances the charge and, as it must, also balances the H atoms (30 on each side). The final, balanced reaction is as follows:

$$\underline{6}\mathrm{Fe}^{2+} + \underline{1}\mathrm{Cr_2O_7^{2-}} + \underline{15}\mathrm{H_2O} \leftrightarrow \underline{6}\mathrm{Fe(OH)_3}(s) + \underline{2}\mathrm{Cr}\left(\mathrm{OH}\right)_2^+ + \underline{8}\mathrm{H}^+$$

Quantifying Oxidant Concentrations

Concentrations of oxidizing chemicals (“oxidants”) are often expressed in terms of their oxidizing capacity (i.e., the number of electrons they can combine with). The *electron equivalent weight* of an oxidant is defined as the mass (in grams) of the oxidant that can combine with one mole of electrons.

$$e^{-}\text{-equiv wt} = \frac{\text{Molecular wt.}}{\#\text{ of } e^{-}\text{ transferred in redox reaction}}$$

Oxidants Used in Drinking Water Treatment

Oxidant	MW	Reduced	n_e*	Eq. wt.
Cl_2	71	$2Cl^-$	2	35.5
HOCl	52.5	Cl^-	2	26.25
OCl^-	51.5	Cl^-	2	25.75
NH_2Cl	51.5	Cl^-	2	25.75
$NHCl_2$	86	$2Cl^-$	4	21.5
O_3	48	$3H_2O$	6	8
ClO_2	67.5	ClO_2^-	1	67.5
MnO_4^-	119	Mn^{2+}	5	23.8
H_2O_2	34	$2H_2O$	2	17

***n_e = moles of e^-** consumed per mole of oxidant reacting

Quantifying Disinfectant Concentrations

Concentrations of oxidizing disinfectants are frequently expressed in terms of the concentration of Cl_2 that would have the same oxidizing capacity. For example, a concentration of 3 mg/L ClO_2 might be expressed as:

$$3.0\frac{\text{mg ClO}_2}{\text{L}}\left(\frac{1\,e^-\text{ equiv}}{67.5\text{ g ClO}_2}\right)\left(\frac{35.5\text{ g Cl}_2}{1\,e^-\text{ equiv}}\right)=1.58\frac{\text{mg}}{\text{L}}\ \textit{as}\ \text{Cl}_2$$

Jargon for Disinfectant Concentrations

***Dose*: Just what it sounds like. Concentration of disinfectant added, computed as mass per liter of water.**

***Residual*: Concentration of disinfectant remaining and therefore available to combat existing or subsequent microbial contamination. Time of reaction must be specified, since the residual oxidant concentration decreases steadily, albeit slowly.**

***Demand*: Difference between Dose and Residual.**

***Instantaneous Demand*: Concentration of disinfectant that is consumed as soon as it enters the water. Typically attributed to inorganics (Fe^{2+}, HS^{-}) and easily oxidized organics.**

***Note*: All above frequently reported “as Cl_2”**

The Redox Chemistry of Chlorine

- Chlorine gas has the formula Cl_2, so the Cl atoms are in the 0 oxidation state. When Cl_2 dissolves in water, one Cl atom oxidizes the other:

$$\mathrm{Cl_2}\left(g\right) + \mathrm{H_2O} \leftrightarrow \mathrm{HOCl} + \mathrm{HCl}$$

- HOCl is *hypochlorous acid*. At pH>7.5, most HOCl molecules release H^+ to become *hypochlorite ion*, $OCl^–$. HOCl is a better disinfectant than $OCl^–$

- HCl is *hydrochloric acid*. It splits into H^+ and $Cl^–$ under essentially all conditions (regardless of pH).

- The most stable oxidation state for Cl in water is –1 ($Cl^–$). Therefore, both HOCl and $OCl^–$ (which are in the +1 oxidation state) “want” to acquire electrons (i.e., to oxidize something) so that they can become more stable.

Redox Reactions of Chlorine in Drinking Water

- HOCl and OCl^- oxidize many organic compounds, including some that are part of microorganisms and essential for microbial life; hence they serve as disinfectants.
- HOCl and OCl^- also oxidize some inorganic compounds, such as Fe^{2+}, Br^-, Mn^{2+} (slowly at neutral pH, but rapidly at high pH), H_2S, and a few others.

$$2\mathrm{Fe}^{2+} + \mathrm{HOCl} + 5\mathrm{H_2O} \leftrightarrow 2\mathrm{Fe}\left(\mathrm{OH}\right)_3\left(s\right) + \mathrm{Cl}^- + 5\mathrm{H}^+$$

$$\mathrm{Br}^- + \mathrm{HOCl} \leftrightarrow \mathrm{HOBr} + \mathrm{Cl}^-$$

$$\mathrm{Mn}^{2+} + \mathrm{HOCl} + \mathrm{H_2O} \leftrightarrow \mathrm{MnO_2}\left(s\right) + \mathrm{Cl}^- + 3\mathrm{H}^+$$

$$\mathrm{H_2S} + 4\mathrm{HOCl} \leftrightarrow \mathrm{SO_4}^{2-} + 4\mathrm{Cl}^- + 6\mathrm{H}^+$$

Reactions of Chlorine with Ammonia

- HOCl and OCl$^-$ react with some compounds by exchanging Cl$^+$ for an H$^+$. For instance, at low OCl:N ratios, they react with ammonia (NH$_3$) as follows:

$$\mathrm{NH_3 + HOCl \leftrightarrow NH_2Cl + H_2O}$$

$$\mathrm{NH_2Cl + HOCl \leftrightarrow NHCl_2 + H_2O}$$

$$\mathrm{NHCl_2 + HOCl \leftrightarrow NCl_3 + H_2O}$$

- Simultaneously, some N gets oxidized, especially at higher OCl:N ratios, e.g.:

$$\mathrm{2NH_2Cl + HOCl \leftrightarrow N_2 + H_2O + 3H^+ + 3Cl^-}$$

$$\mathrm{NHCl_2 + 2HOCl + H_2O \leftrightarrow NO_3{}^- + 5H^+ + 4Cl^-}$$

Reactions of Chlorine with Ammonia

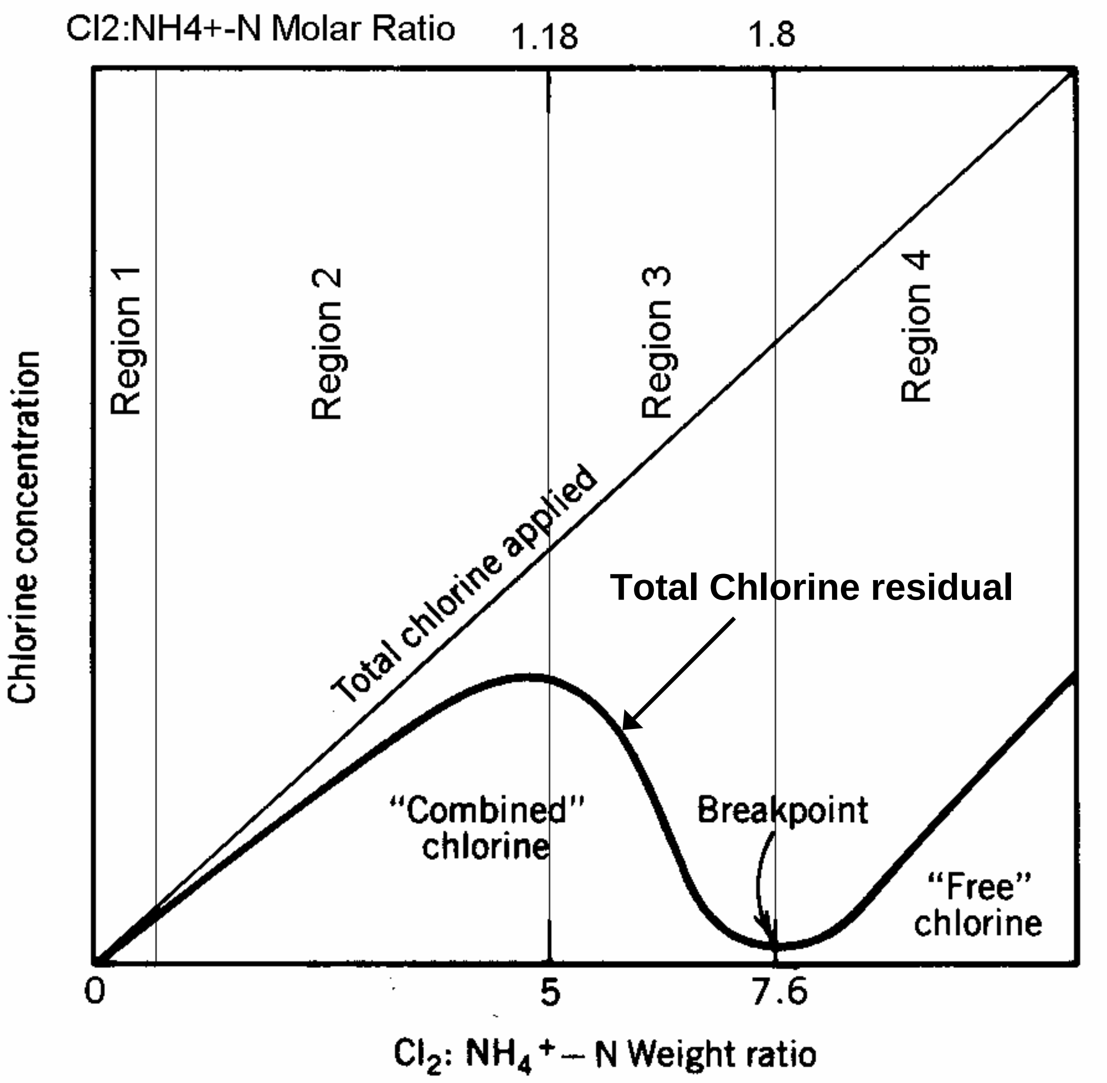
- Chlorinated ammonia species are referred to as mono-, di-, and tri-*chloramine*. Chloramines are referred to collectively as *combined chlorine*, as opposed to HOCl and OCl^- (and Cl_2), which are called *free chlorine*.
- Chlorine is in the +1 oxidation state in chloramines, so it is still unstable (and an oxidant), but less so than in free chlorine. Chloramines are therefore disinfectants, but are weaker than free chlorine.
- The shorthand for all forms of chlorine in the +1 oxidation state is “Cl_2” so free and combined chlorine are written as “free Cl_2” and “combined Cl_2” respectively (not “free Cl” and “combined Cl”)

The “Breakpoint Chlorination” Curve: Reaction of HOCl with Pure H_2O + NH_3

Regions 1 and 2: Formation of combined Cl_2 dominates over oxidation of N; Conc’n of residual Cl_2 increases with increasing Cl_2:N ratio

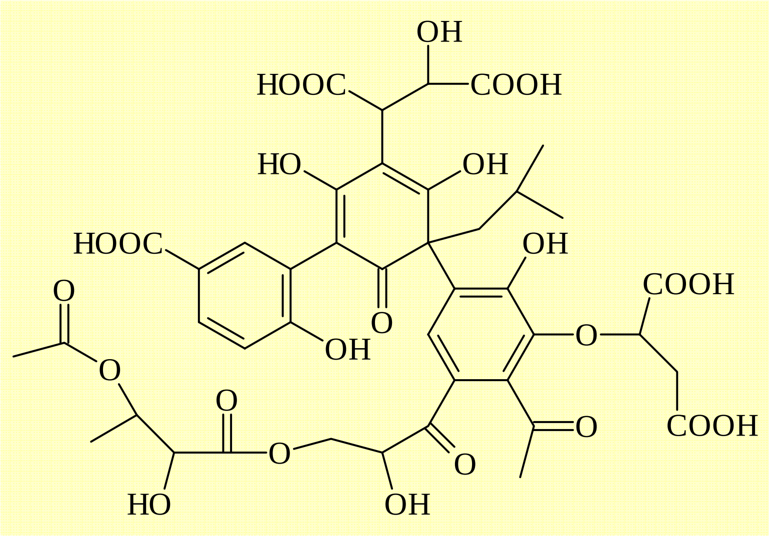
Region 3: Oxidation of N dominates over formation of combined Cl_2; when Cl_2:N ratio increases, more combined Cl_2 is oxidized than is formed

Region 4: All N oxidized; increase in Cl_2:N ratio leads to increase in free Cl_2 residual

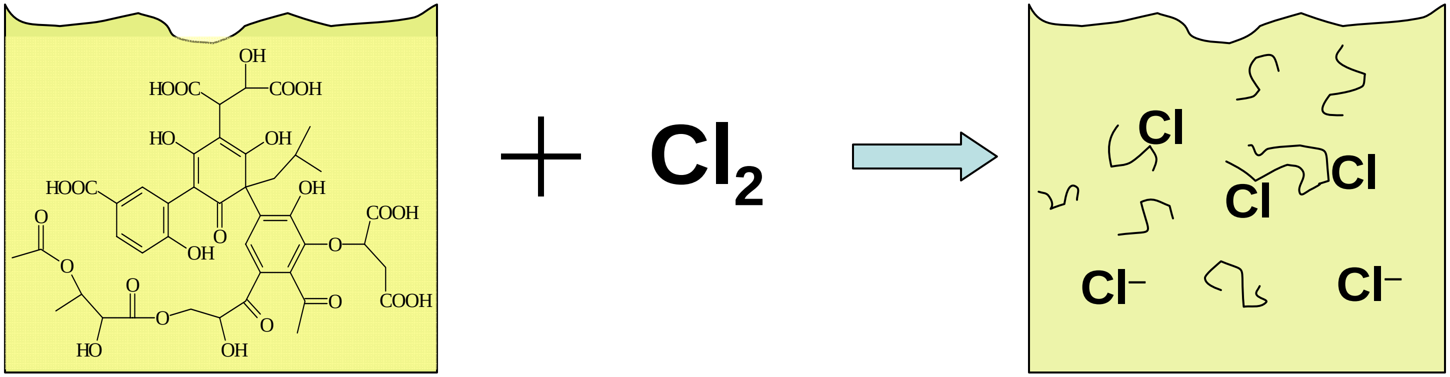


Reactions of Chlorine with Organics (NOM)

One Person's Idea of an NOM Molecule



Free Cl_2 reacts with NOM molecules in two ways: (1) oxidation, generating Cl^-, and (2) substitution to form chlorinated organics.

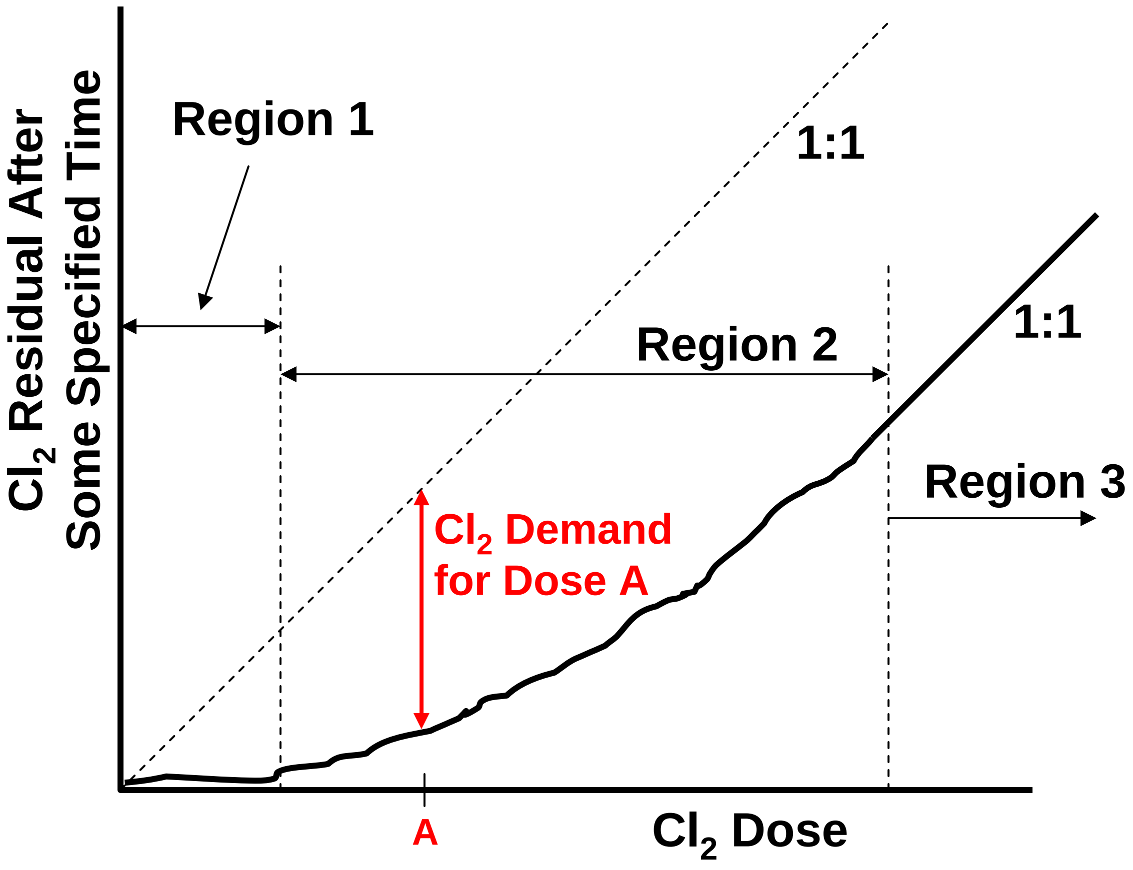


Consumption of Free Cl_2 by Reaction with NOM and Inorganics

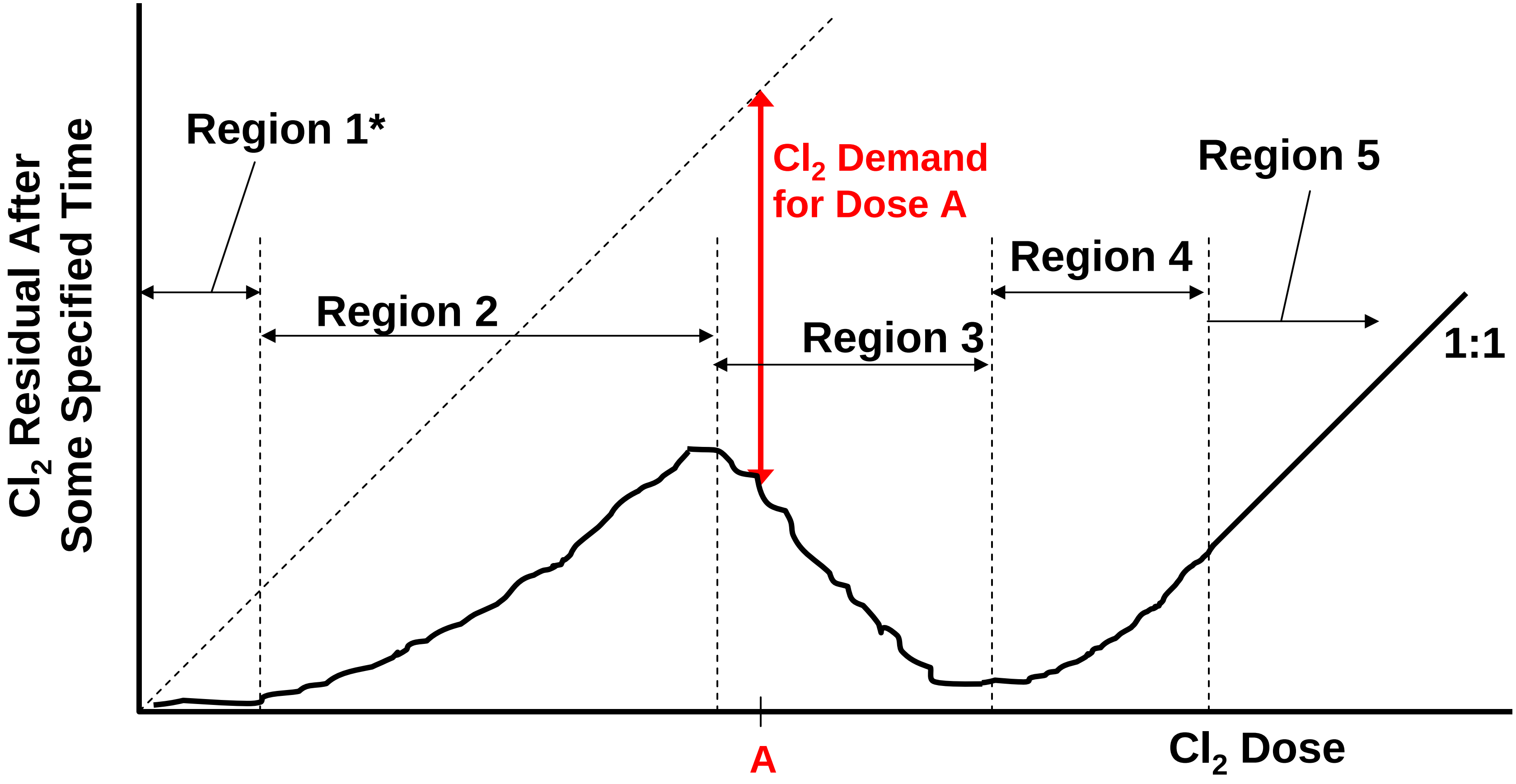
Region 1: Almost all Cl_2 added reacts with NOM or inorganics; negligible residual

Region 2: For each increment of Cl_2 added, some reacts with NOM or inorganics, but some remains as free Cl_2 residual

Region 3: Essentially all of the incremental Cl_2 remains in solution as free Cl_2 residual



Breakpoint Curve for Chlorination of Water Containing NH_3, NOM and Inorganics



*Regions described on following slide

Breakpoint Curve for Chlorination of Water Containing NH_3, NOM and Inorganics

Region 1: Almost all Cl_2 added reacts with NOM or inorganics; negligible residual

Region 2: For each increment of Cl_2 added, some reacts with NOM or inorganics, but most reacts with NH_3 to form combined residual

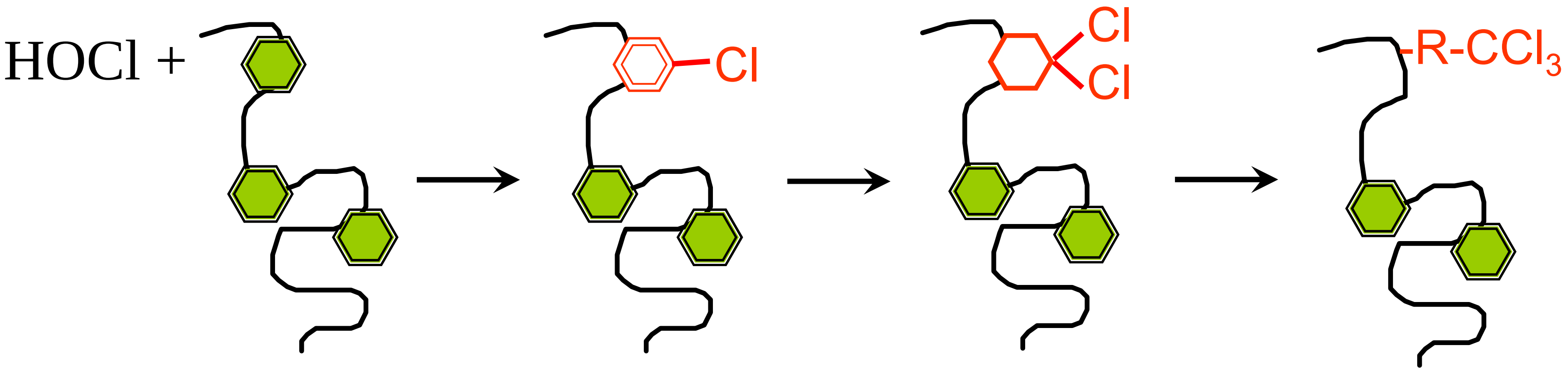
Region 3: Most Cl_2 added oxidizes chloramines, so total Cl_2 residual declines; residual essentially all combined

Region 4: Most Cl_2 added remains as free residual, but some reacts with NOM or inorganics that were unreactive with combined Cl_2

Region 5: Essentially all of the incremental Cl_2 remains in solution as free Cl_2 residual

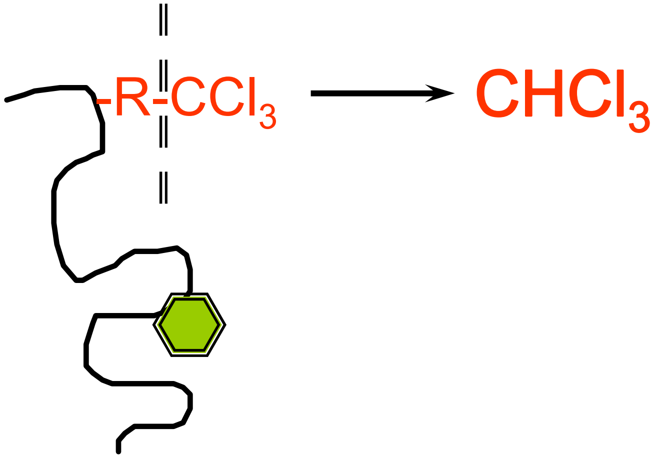
Incorporation of Chlorine into Organics

A portion of the added free Cl_2 (usually <10%) becomes incorporated into NOM molecules. As with substitution into NH_3, multiple substitutions at a single site seem common:

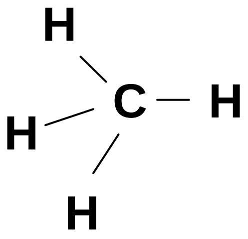


Incorporation of Chlorine into Organics

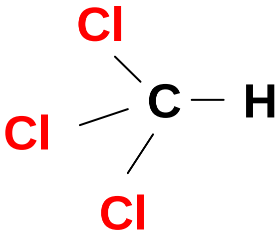
Small segments can break off of the chlorinated NOM to release identifiable compounds. One common product is chloroform ($CHCl_3$):



Chloroform can be thought of as trichloro-methane:



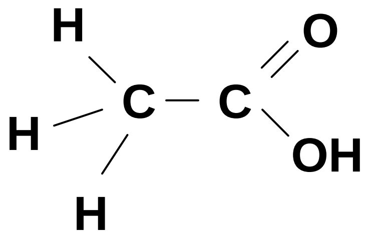
Methane (CH_4)



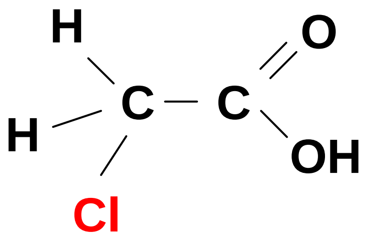
Chloroform ($CHCl_3$)

Formation of HaloAcetic Acids

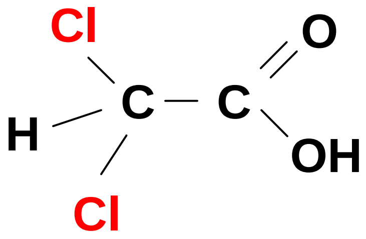
Several other small, chlorinated compounds have been identified, the most significant of which are chlorinated acetic acid (acetic acid is vinegar).



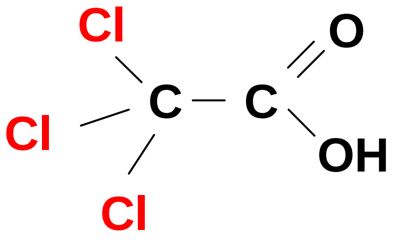
Acetic Acid



Monochloro-acetic Acid



Dichloro-acetic Acid

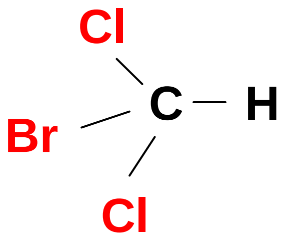


Trichloro-acetic Acid

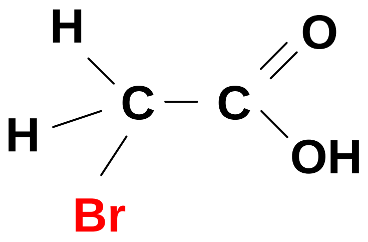
Note: The chlorinated products have the structure of acetic acid, but they form when part of a chlorinated NOM molecule breaks off, not by addition of chlorine to pre-existing acetic acid molecules.

Bromination of NOM

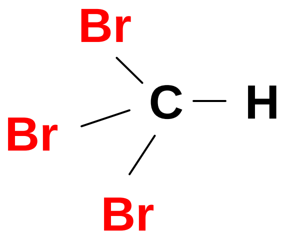
If the raw water contains Br$^-$, it gets oxidized to HOBr by free Cl_2, and then can react with NOM in the same ways that free Cl_2 does. As a result, brominated organics also form:



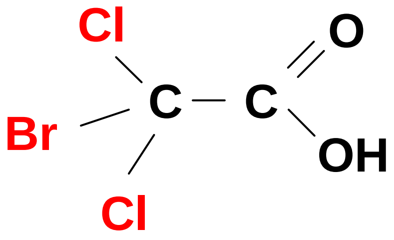
Bromo-Dichloromethane ($CHBr_3$)



MonoBromo-acetic Acid



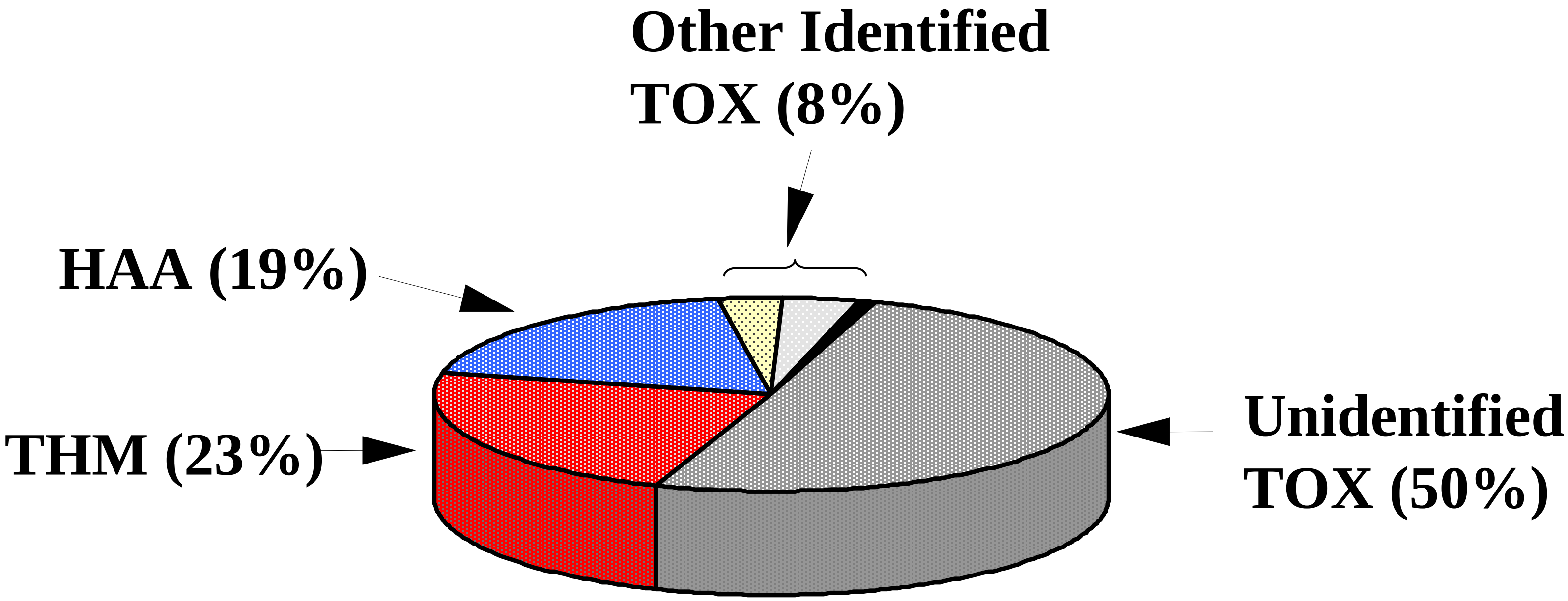
Bromoform ($CHBr_3$)



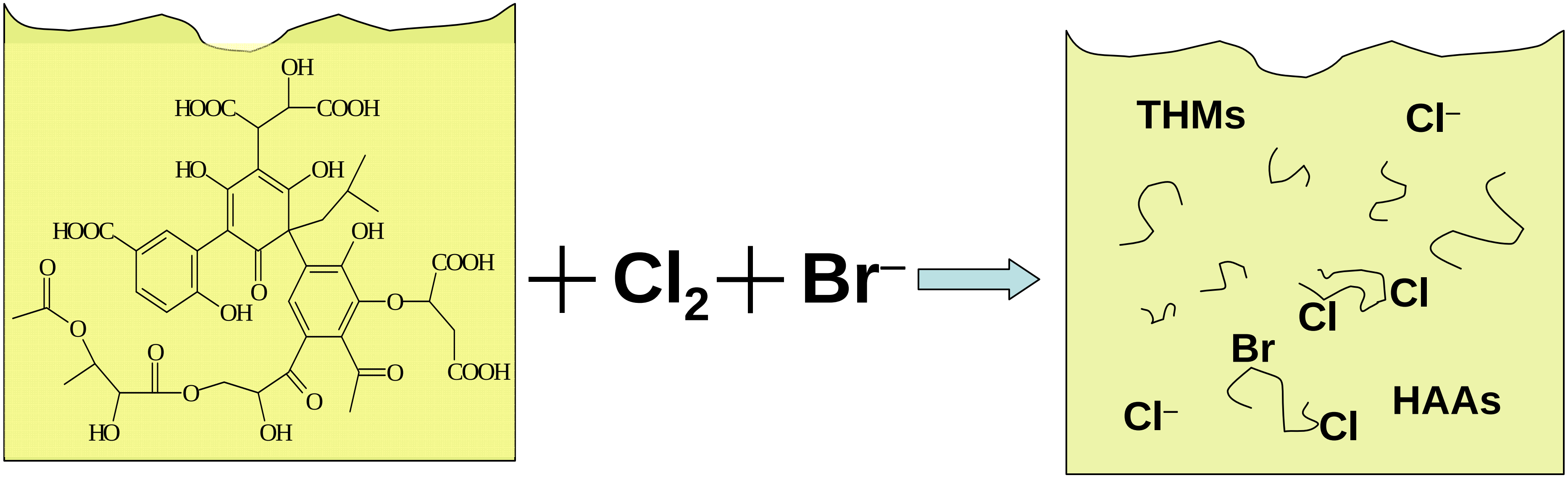
Bromo-Dichloro-acetic Acid

Reactions of Chlorine with NOM

The total conc’n of Cl and Br that gets incorporated into organics is referred to as the *total organic halogen* concentration, TOX. Identifiable molecules account for about one-half of the TOX.



Schematic Summary:
Reactions of Chlorine with NOM



$+ Cl_2 + Br^-$

Regulations for Chlorinated Organics

Maximum Contaminant Levels (MCLs) exist for:

- Total TriHaloMethanes (TTHMs), 80 μg/L
- The sum of five HaloAcetic Acids (HAA_5*), 60 μg/L

Maximum Contaminant Levels Goals (MCLGs) (the “no adverse health effect level”):

- Zero for $CHCl_3$, $CHCl_2Br$, $CHBr_3$, DCAA
- 0.06 mg/L for $CHClBr_2$, 0.3 for TCAA

All chlorinated and brominated organics are referred to as (*halogenated*) *disinfection byproducts*, *DBP*s.

*MCAA, DCAA, TCAA, DBAA, TBAA

Approaches for Reducing DBP Concentrations in Finished Water

- Use a disinfectant that is less likely to form DBPs or forms less problematic ones
- Remove or alter the NOM so that it doesn't react with the free Cl_2
- Remove DBPs after they form

The first two of the above options are employed fairly commonly. Approaches to implement the third option have largely been abandoned.

Alternative Disinfectants

- Chloramines (NH_2Cl and $NHCl_2$)
  - Weaker oxidant than free chlorine; acceptable disinfectant, but higher doses required than for free Cl_2
  - Stable; provides a long-term residual for downstream protection
  - Forms virtually no halogenated DBPs
  - Subject to some biodegradation in presence of O_2, especially in warm water
  - Recent evidence suggests it might allow release of very high concentrations of Pb, if the distribution system has historically been exposed to free Cl_2

Conclusion: Not highly attractive as primary disinfectant, but good for generating long-lasting residual with low DBP formation after an initial dose of some other, stronger disinfectant; concerns about interactions with pipes not yet resolved

Alternative Disinfectants

- Ozone (O_3)
  - Very strong oxidant; excellent disinfectant
  - Unstable; O_3 gas must be generated on-site and used immediately; leaves no stable residual for downstream protection
  - Forms no halogenated DBPs, but reacts with Br^- to form bromate (BrO_4^-), with MCL of 0.01 mg/L, and MCLG of zero
  - Breaks down NOM into more degradable segments (with both good and bad consequences)

Conclusion: Excellent primary disinfectant for many waters; not satisfactory as a sole disinfectant

Alternative Disinfectants

- Chlorine Dioxide (ClO_2)
  - Strong oxidant; better oxidant of Fe^{2+} and Mn^{2+} than free Cl_2. Comparable to free Cl_2 as disinfectant, better for Giardia and Cryptosporidium; insensitive to pH
  - Can transfer from water to gas phase, where it is explosive if highly concentrated or compressed; therefore, ClO_2 generally produced onsite as a concentrated (1-2%) solution
  - Low concentrations of ClO_2 gas can react with household materials to produce offensive odors
  - Seems to form halogenated NOM, but not THMs or HAAs; does form chlorite ($ClO_2^{-,}$) with MCL of 1.0 mg/L, and MCLG of 0.8 mg/L

Conclusion: Good primary disinfectant to avoid DBP formation, but problematic because of ClO_2^- formation; useful in special circumstances (e.g., for Mn^{2+} oxidation)

Removing NOM Before Disinfection

- “Enhanced Coagulation”
  - Add “coagulants” (alum or $FeCl_3$) in doses and at pH values causing precipitation of $Al(OH)_3(s)$ or $Fe(OH)_3(s)$, as in sweep flocculation
  - NOM coats the surface of the particles, as it does to natural particles; with enough artificially produced particles, 30-70% of the NOM attaches to the particles
  - NOM attachment to particle surfaces is sensitive to pH; attachment is extensive at pH~6 or less, but minimal at pH>8
  - When particles are settled or filtered, NOM is removed with them

The Enhanced Coagulation Rule

- Requires NOM removal from many surface waters
- Removal requirement depends on NOM conc'n (quantified as Total Organic Carbon, TOC) and Alkalinity
- "Escape clause" available if a point of diminishing returns is reached
- Enhanced coagulation is a "BAT." If it doesn't work, you are off the hook

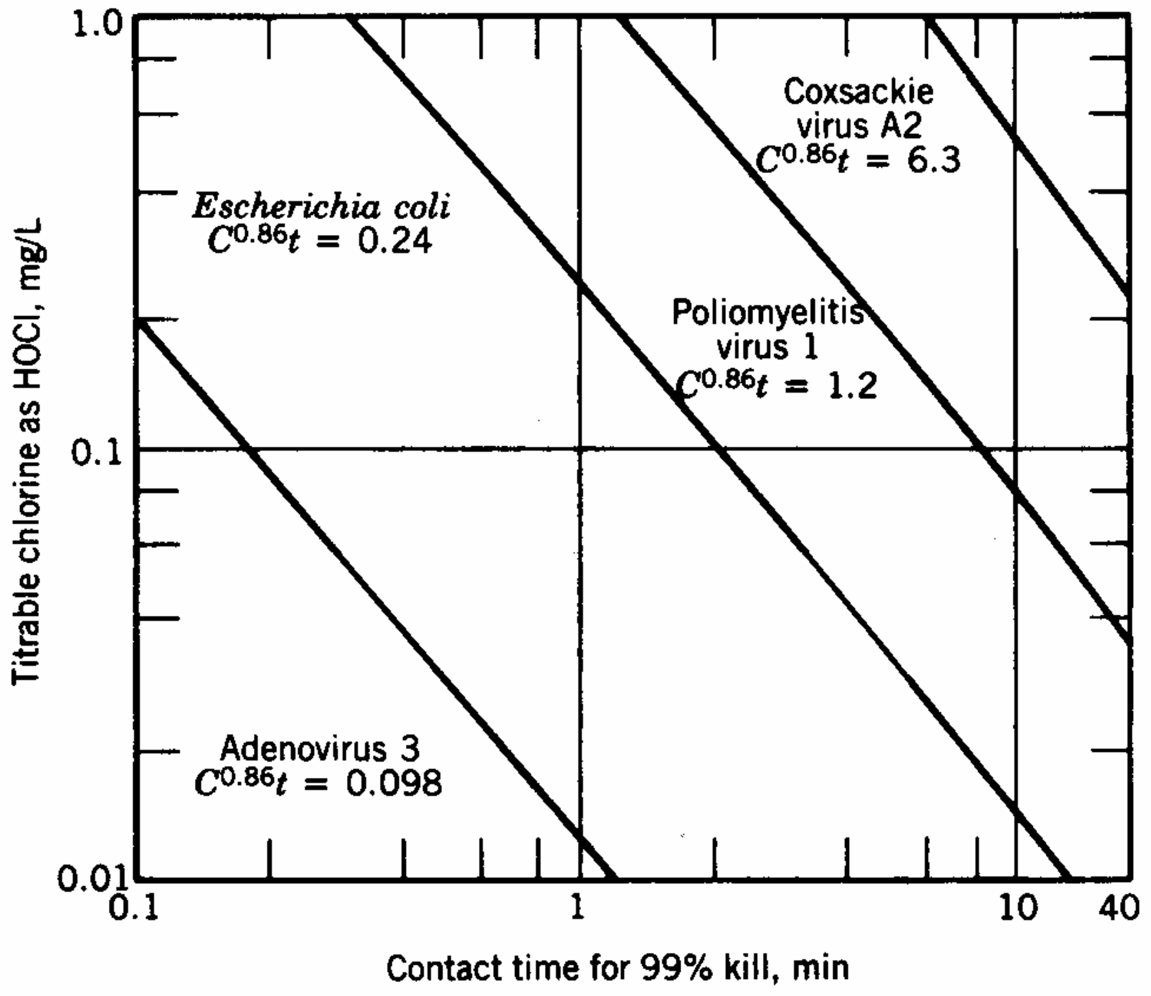
TOC (mg/L)	ALK (mg/L $CaCO_3$)		
	0-60	>60-120	>120
<2	N/A	N/A	N/A
2-4	**35***	**25**	**15**
4-8	**45**	**35**	**25**
>8	**50**	**40**	**30**

*Required percentage reduction in TOC

Disinfection: Characteristics and Regulations

Idealized disinfection curves

- **Same disinfection efficiency (99% here) achieved by any combination of *C* and *t* that gives same $C^{0.86}t$ value.**
- **$C^{0.86}t$ required for given disinfection varies widely for different organisms**



Disinfection: Characteristics and Regulations

The Chick-Watson Law (1908):

$$r_X = -kc_X^a c_D^n$$

a and *n* are often found (or assumed) to be ~1. In that case, if c_D is approximately constant (as in a CMR), the rate expression for killing microorganisms is first order:

$$r_X = -\left(kc_D\right)c_X = -k'c_X$$

PFR: $c_{X,out} = c_{X,in} \exp\left(-k't_d\right) = c_{X,in} \exp\left(-kc_D t_d\right)$

$$\ln \frac{c_{X,out}}{c_{X,in}} = -kc_D t_d; \qquad \log \frac{c_{X,out}}{c_{X,in}} = -\frac{k}{2.303} c_D t_d$$

CMR: $c_{X,out} = c_{X,in} \frac{1}{1+k't_d} = c_{X,in} \frac{1}{1+kc_D t_d}$

$$\frac{c_{X,out}}{c_{X,in}} = \frac{1}{1+kc_D t_d}$$

For both PFRs and CMRs, if c_D is constant during the disinfection process, then log($c_{X,out}/c_{X,in}$) should be constant for a given $c_D t_d$ product. *k* is expected to vary with the disinfectant and organism, temperature, possibly pH, and other water quality characteristics. Larger *k*'s correspond to more effective disinfection.

The $-\log_{10}(c_{X,out}/c_{X,in})$ is commonly called the number of "logs of reduction" of the organism concentration. Thus, $c_{X,out}/c_{X,in}=0.01$ (i.e., 99% kill) represents "two logs of reduction," $c_{X,out}/c_{X,in}=0.001$ (i.e., 99.9% kill) is three logs of reduction, etc.

To achieve two logs of reduction in ideal reactors, the $c_D t_d$ products must be:

PFR: $$-2 = -\frac{k}{2.303} c_D t_d; \qquad c_D t_d = \frac{4.6}{k}$$

CMR: $$\frac{1}{100} = \frac{1}{1+kc_D t_d}; \qquad c_D t_d = \frac{99}{k}$$

- PFR is much more efficient than CMR, as always; PFR advantage increases with increasing removal efficiency
- For PFR, # of logs of removal is proportional to $c_D t_d$; for CMR, # of logs of removal depends on $c_D t_d$, but is not proportional

POTENTIAL ISSUES/CONCERNS

•For CMR, c_D is constant during disinfection, as assumed in the derivation. That assumption is not valid for a PFR, so what value of c_D should be used?

To be conservative, regulations specify that c_D should be the residual as the water leaves the reactor; thus, the actual c_D everywhere in the reactor is greater than the value used in the calculation. In the literature, that value of c_D is just written as "C".

•Most disinfection reactors are designed to be PFRs, but they are not perfect PFRs; how to model them?

To be conservative, but reasonable, regulations specify that the value of t_d used to estimate disinfection efficiency should be the value "T_{10}" such that only 10% of the water has a residence time in the reactor less than T_{10}. This value corresponds to the time when 10% of the tracer mass has exited, if the tracer is input as a spike at $T=0$.

DISINFECTION REGULATIONS

- **For regulatory purposes, disinfection efficiency is computed by treating the reactor as an ideal PFR with $c_D = C$ and $t_D = T_{10}$ (or just *T*):**

$$\#\ \text{logs of removal} = \frac{k}{2.303} CT$$

$$CT = \frac{2.303}{k}\left(\#\ \text{logs of removal}\right)$$

where the second equation indicates the *CT* required to achieve the given # of logs of removal

- **EPA has regulations about the # of logs of reduction required for various organisms (Giardia, Crypto, viruses), and has published tables stating how many logs of "disinfection credit" a utility gets for various *CT* values. Some credit is also given for filtration. A utility can manage its process more or less as it chooses, as long as it accomplishes the regulated number of logs of removal.**

CT values for Giardia and Virus Inactivation Using Chloramines

	Required *CT (mg-min/L)*		
Log Inactivation	**Temperature (C)**		
	5	**15**	**25**
Giardia			
1	**735**	**500**	**250**
2	**1470**	**1000**	**500**
3	**2200**	**1500**	**750**
Viruses			
2	**857**	**428**	**214**
3	**1423**	**712**	**356**
4	**1988**	**994**	**497**

CT values for Inactivation Using Chlorine Dioxide

	Required *CT* *(mg-min/L)*		
Log Inactivation	**Temperature (C)**		
	5	**15**	**25**
Giardia			
1	**8.7**	**6.3**	**3.7**
2	**17**	**13**	**7.3**
3	**26**	**19**	**11**
Viruses			
2	**5.6**	**2.8**	**1.4**
3	**17.1**	**8.6**	**4.3**
4	**33.4**	**16.7**	**8.4**
Cryptosporidium			
1	**429**	**179**	**75**
2	**858**	**357**	**150**
3	**1286**	**536**	**226**

Disinfection and Disinfection By-Products (DBPs)

- Free Cl is an excellent disinfectant for most pathogens; some spore-forming organisms (Giardia and Cryptosporidium) are exceptions. Free Cl also tends to generate chlorinated DBPs

- Combined Cl is a weaker disinfectant than free Cl, but it forms almost no chlorinated DBPs