

Water Quality Problems in Distribution Systems

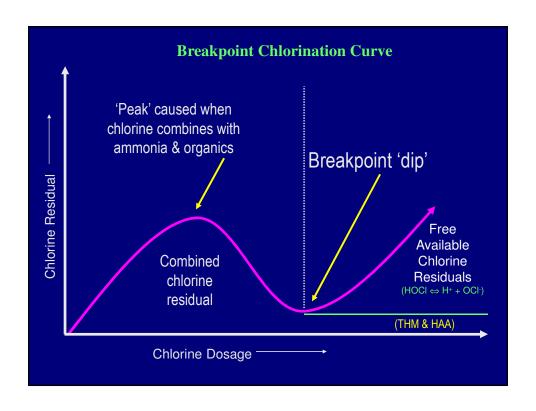
- 160 responses to AWWA survey indicates % of annual reported problems:
- 44% Taste & Odor
- 43% Color & Turbidity
- 5% High Heterotrophic Plate Count
- 5% DBP's, coliforms, corrosion, misc.
- 3% Loss of disinfection residual

Do you have a free Cl₂ residual?



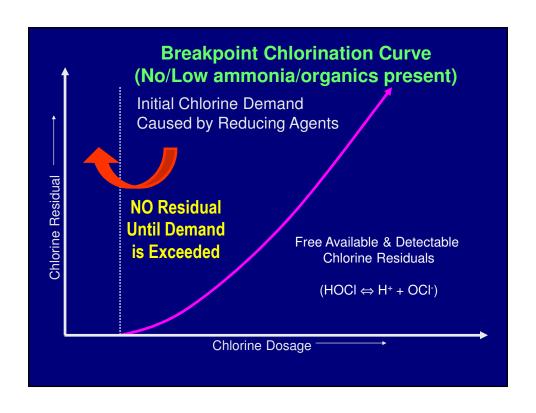


- Chlorine in 'pure' H₂O = HOCl + OCl
- HOCI = Hypochlorous Acid
- OCI⁻ = Hypochlorite Ion
- Free chlorine residual = HOCI / OCI-
- Free 'available' chlorine is very reactive
- Total Chlorine Free = Combined
- Minimum system chlorine residuals:
- IL EPA: 0.2 free / 0.5 mg/L total
- IA DNR: 0.3 mg/L free / 1.5 mg/L total
- FL DEP: 0.2 mg/L free / 0.6 mg/L total



What is Chlorine Breakpoint?

- The initial point where free 'available' chlorine residual is present / detected
- Breakpoint residual occurs after the chlorine dosage rate exceeds the demand created by reducing agents, ammonia, and organics
- B.P. curve-shape is determined by contact time, temp, chlorine and ammonia concentration, pH, and water quality





- Cl₂ dosage Demand = Residual
- 1 mg/ 0.8 mg/L = 0.2 mg/L
- Initial demand = Reducing Agent mg/L
 (Fe⁺², Mn⁺², H₂S, NO₂⁻)
 - (Fe⁺², H₂S, NO₂-) may reappear in plant/system
- If Dosage </= Demand then '0' residual</p>
- If Dosage > Demand then free residual exists
- Reducing Agents donate / lose electrons (consume oxidizing agents such as chlorine)

Reducing Agent Reactions with Chlorine

(Demand & Destroy Chlorine Residual)

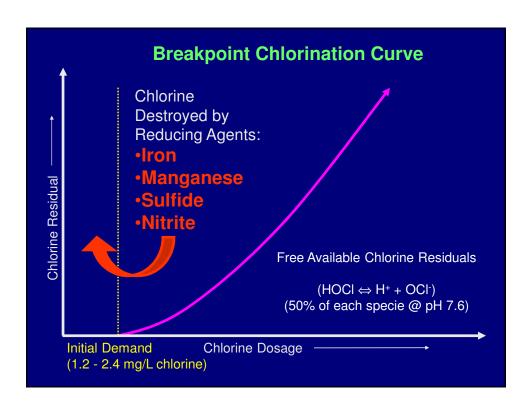
$$2Fe(HCO_3)_2 + Cl_2 + Ca(HCO_3)_2 \Rightarrow$$

$$2Fe(OH)_3 \downarrow + CaCl_2 + 6CO_2$$

$$Cl_2 + MnSO_4 + 4NaOH \Rightarrow$$
 $MnO_2 \downarrow + 2NaCl + Na_2SO_4 + 2H_2O$

$$H_2S + CI_2 \Rightarrow 2HCI + S \downarrow 0$$

$$NO_2^- + HOCI \Rightarrow NO_3^- + H^+ + CI^-$$





Calculate Initial Demand (Reducing Agent Demand)

Water Quality (Example mg/L)	Free Chlorine Demand Factor	Cl ₂ Demand
Iron 0.3 mg/L	X 0.64 =	0.192 mg/L
Manganese 0.05 mg/L	X 1.3 =	0.065 mg/L
Sulfide 0.2 mg/L	X 2.08 to S =	0.416 mg/L
(optional factor) 0.2	$X 8.32 \text{ to } SO_4 =$	(1.664 mg/L)
Nitrite-N 0.1 mg/L	X 5.0 =	0.5 mg/L
	Total Reducing Agent Demand =	1.173 mg/L Demand (2.421 mg/L)

Free Chlorine vs Lack of Cl₂

Oxidation potential: ORP

Disinfection Protection
Taste & Odor Control
Fe/Mn Oxidation

H₂S Destruction Bleaching of Colo

Algae/ Microbe Contro

Byproducts-THM/HAA

- Reduction potential:
- Disease potential
- Taste & Odor events
- Staining & Deposits
- Sulfur bacteria +
- Color Organics
- Biofilm / Corrosion
- No/low DBPs

What does chlorine do to cells?

- HOCl enters cell wall efficiently- permeates & pokes holes in cell wall of exposed bacteria
- Enzyme systems of microbes are affected, deactivating organisms & ability to reproduce
- In most bacteria, HOCl causes adverse reactions of respiratory, transport, nucleic acid-DNA systems, protein coating of virus deactivated?
- Microbes hiding in biofilm less vulnerable
- HOCl unable to penetrate pipe scale, NH₂Cl longer lasting & reacting against microbes
- Chlorine is similar to...

Free Chlorine Solutions

Concentration (% available)
Chlorine Gas / Liquid 100%
Calcium Hypochlorite 65%
Sodium Hypochlorite 12.5%
a.k.a. Clorox bleach 5.25%+



Chlorine + Water = ? Chlorine + Water = ? Cl₂ + H₂O ⇒ HOCl + HCl (< pH 6) HOCl (Hypochlorous Acid) 'Biocidal' HOCl ⇔ H + OCl (> pH 9 complete) OCl (Hypochlorite Ion) 'Oxidative'

• (%HOCl = %OCl⁻) @pH 7.6 / 20C

Combined Chlorine Demand-Combining Agents

- Cl₂ Dosage Demand = Residual
- Combining agents = ammonia, NOM (TOC/DOC), organic nitrogen, decayed plant/animal (proteins, amino acids)
- Combined chlorine residuals are byproducts of ammonia-N and organic contaminants (tannins, lignins, color)
- Chloramines / chlororganic compounds

Calculate Secondary Demand (Combined Demand)

Water Quality (Example mg/L)	Free Chlorine Demand Factor	Cl ₂ Demand
Ammonia-N 0.1 mg/L	X 10 to12 =	1.2 mg/L
Organic-N 0.05 mg/L	X 1.0 =	0.05mg/L
Total Organic Carbon 1.0 mg/L	X 0.1 =	0.1mg/L
	Total Combined Demand =	1.35 mg/L Demand

CT Values for Virus Inactivation

Disinfectant	2-log inactivation (99%)	3-log inactivation (99.9%)
Chlorine mg-min/L	3	4
Chloramine mg-min/L	643	1,067
Chlorine Dioxide mg-min/L	4.2	12.8
Ozone mg-min/L	0.5	0.8
UV mW-s/cm ²	21	36

¹ CT values based on 10C, pH range 6-9, free chlorine residual 0.2-0.5 mg/L

² CT values based on 10C, pH 8

³ CT values based on 10C, pH range 6-9

CT Values for Inactivation of Giardia Cysts

Disinfectant	2-log inactivation (99%)	3-log inactivation (99.9%)
Chlorine mg-min/L	69	104
Chloramine mg-min/L	1,230	1,850
Chlorine Dioxide mg-min/L	15	23
Ozone mg-min/L	0.95	1.43

¹ CT values based on 10C, pH range 7, free chlorine residual less than or equal to 0.4 mg/L

Disinfection Byproducts (DBP) are formed when . . .

- Chlorine and bromide (Br-) reacts with natural organic matter (NOM) in source waters to create DBPs
- HOCl + Br⁻ + NOM ⇒ Halogenated DBPs
- Bromide comes from mineral deposits and salt water intrusion
- NOM from decaying vegetation and algae

² CT values based on 10C, pH range 6-9

³ CT values based on 10C, pH range 6-9

Total Organic Carbon (TOC) analysis primary measurement for natural organic matter (NOM, TOC, DOC, UV254) in source and system drinking water

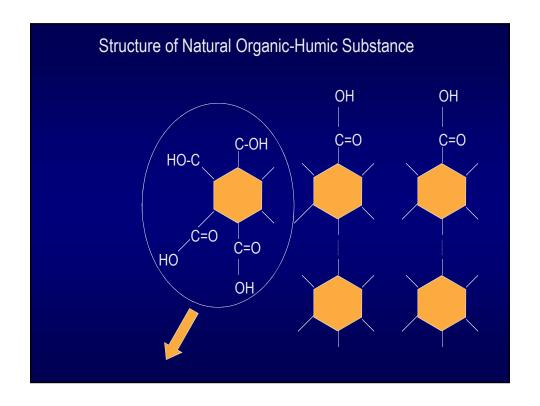
D/DBP Rule includes TOC as a compliance parameter

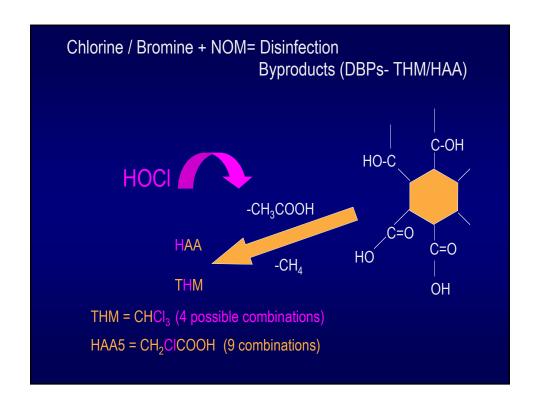
TOC / DOC is an indicator of potential for DBP formation

Free Chlorine + Natural Organics (humic, fulvic, tannin / lignin, color) ⇒ Chlororganics (TOX) DBP, THM, HAA

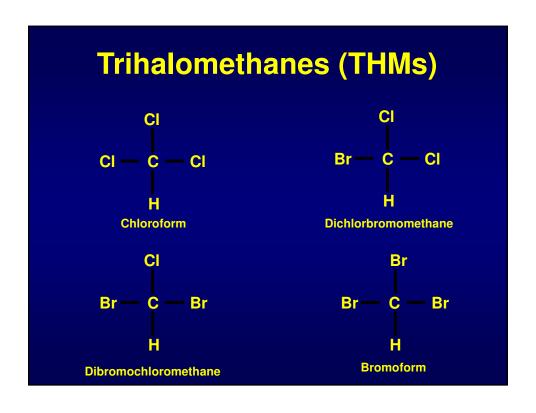
HOCl + Br + Natural Organic Matter (NOM) ⇒
Halogenated Disinfection Byproducts (DBPs)

O3 + Br + (NOM) ⇒ Brominated organics, AOC, BDOC, bromate





Trihalomethanes (THM) / HAA Chloroform CHC₁₃ Bromoform CHBr₃ Chlorodibromomethane CHCIBr₂ CHBrCl₂ Bromodichloromethane Locational Running Annual Average- LRAA MCL at each sample pt. in distribution system (TTHM) MCL = 0.080 mg/L (HAA) MCL = 0.060 mg/L MRDL 4.0 mg/L Chlorine, chloramines, MRDL CIO2 (0.8 mg/L) MCL's: Chlorite 1.0 mg/L, bromate 0.01 mg/L



Haloacetic Acids (HAA5)			
Monochloroacetic Acid	CH ₂ CICOOH		
Dichloroacetic Acid	CHCl₂COOH		
Trichloroacetic Acid	CCI ₃ COOH		
Monobromoacetic Acid	CH ₂ BrCOOH		
Dibromoacetic Acid	CHBr ₂ COOH		



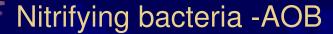
Location on Breakpoint curve

- Analyze ammonia NH₃-N
- Analyze monochloramine NH₂CI
- Total NH₃ NH₂Cl = Free NH₃
- When free NH₃ is near zero then NH₂Cl is near optimal peak at top of 'hump'
- Compare to chlorine dosage & residuals
- Does Cl₂ dose change ↑↓ residuals?

Chloramination— (intentional) Advantages Disadvantages

- Minimal THMs
- Fewer HAAs
- Persistent residual
- Better protection against bacterial regrowth
- Higher taste & odor threshold from monochloramine

- Added NH₃ in water
- Higher chlorine dose to maintain residual
- Worse Byproducts (Nitrosoamines-NDMA, IO-iodoform
- Nitrifying bacteria-AOB ⇒ nitrites
- $NH_3 + O_2 \Rightarrow NO_2$



- Recycle organic nitrogenous materials from ammonium (endpoint for decomposition of proteins) to nitrates, in aerobic process
- Nitrifying bact. indicate latter stages of aerobic decay of N-rich organic matter
- NROM from compromised septic tanks, sewage systems, industrial sites, ag, haz.
- Nitrification (ammonium-nitrite-nitrate)
- $NH_4^+ \to NO_2^- \to NO_3^-$ (-3, +3, +5 valence)
- Denitrification NO₃⁻ → NO₂⁻ → N₂

Chloramination Exposure

- USEPA estimates 30% of surface water use chloramines- secondary disinfection
- 60% projected use- comply with Stage 2 DBPR- applies to all surface waters and groundwater 'under the direct influence'
- MCL / RAA of 4.0 mg/L chloramines
- Theorized lead release in DC, elevated water & blood lead levels due to chloramination treatment

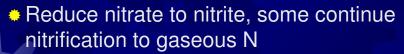


Which comes 1st (NO₂-/NO₃-)

- Nitrite NO₂ (as N)
- Not in source water
- Intermediate stage in nitrification
- MCL 1 mg/L
- May form nitrosoamines in gut
- Destroyed by free chlorine 5:1

- Nitrate NO₃⁻ (as N)
- Ag. Runoff into H₂O
- End pt of nitrification
- MCL 10 mg/L
- Methemoglobinemia (Blue Baby Syndrome) diuresis from NO₃ or NO₂





 DN indicate high concentrations of nitrate, sample anaerobic, rich in NOM

 DN signal latter stages of decay of Nrich sewage or septic wastewaters

Limited by availability of fractions

 \bullet NO₃ $^{-}$ \rightarrow NO₂ $^{-}$ \rightarrow NO \rightarrow N₂O \rightarrow N₂

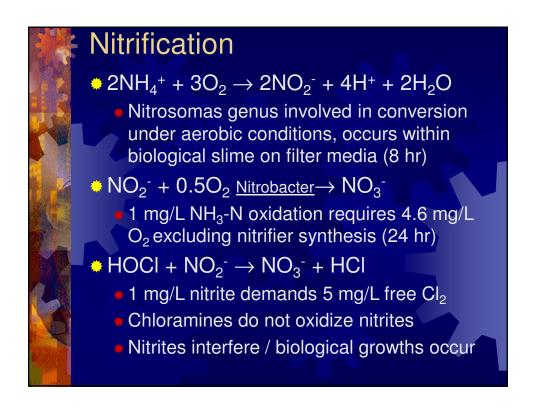
NO₃⁻ → methemoglobinemia (BBS)

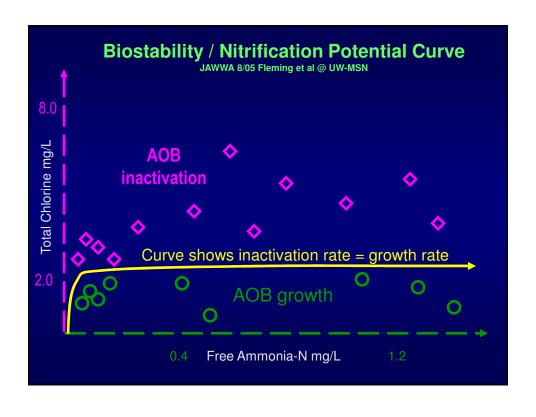
N relationship in 'polluted' water under aerobic conditions

- Water containing only nitrates is rather remote in time from any pollution (30-60 days)
- Containing nitrites is highly suspicious (mid pt)
- Shallow waters of mostly organic N and NH3 has been subjected to recent pollution (0-mid)
- Organochloramines are nongermicidal and appear in total chlorine residual, in potable water O-N ranges (0.3-0.6 mg/L) ? 3 mg/L max
- > 0.25 mg/L Organic-N = T&O problems

Nitrification- by AOB

- NH₃ (Nitrosomonas) ⇒ Nitrite (NO₂)⁻
- Resistant to chlorine/chloraminesNitrite oxidized by free chlorine
- Nitrite (Nitrobacters) ⇒ Nitrate (NO₃)²
- Less resistant, so (NO₂)⁻ accumulates
- NH3 and Cl2 stress nitrobacters
- Thrive in reservoirs during summer
- Byproducts can support coliforms
- Free ammonia generates more nitrites





Steps to control nitrification

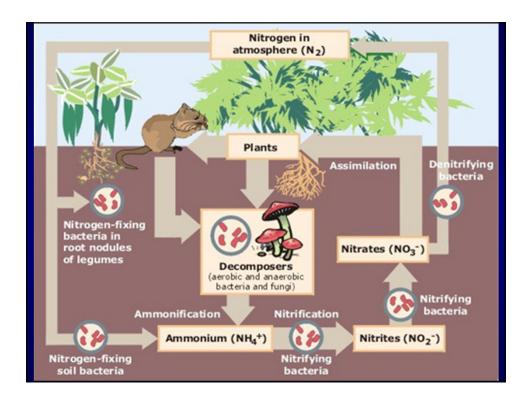
- Maintain Total NH₂Cl residual > 2 mg/L
- Free chlorinate (periodic), if TOC is low
- Remove more TOC in raw H₂O
- More turnover of reservoirs / tanks
- Flushing / cleaning of system & tanks
- Boost Cl₂ re-chlorinate free residual in system
- Free residuals annually, few days, flushing
- Increase chloramine dosage initially
- Optimize ratio of CI : NH₃ for chloramines
- Adjust water to pH > 8.0 (8.3 optimal)
- Monitor with BART test kits (N & DN)

Nitrification (partial) Critical Threshold Concept (Article JAWWA 7/05)

- Increased use of monochloramination
 Huron, SD THM 154 ug/L down to 37 ug/L
- Excess NH₃ released during monochloramine use and decay (free)
- Promotes growth of AOB → nitrification
- $NH_3 \rightarrow AOB \rightarrow NO_2^- \rightarrow NO_3^-$
- Monitor NO₂ to detect nitrification
- 0.05 mg/L NO₂ -N as critical threshold



- Nitrification occurs when NH2Cl decomposes
- 0.05 mg/L NO₂ too high to predict nitrification
- If NO₂ detected, too late to prevent nitrification (2-3 months after loss of Cl₂)
- Loss of total Cl₂ or monochloramine residuals gives early warning of nitrification
- Sodium chlorite (0.1 mg/L) inhibits nitrification
- Chlorite MCL 1 mg/L, byproduct of Cl02 use
- IA- 0.3 mg/L chlorite, PO3 0.9 mg/L = stable residuals, <0.01 NO₂-, 0.6 mg/L NH3 stable & no signs of nitrification in consecutive systems





Nitrogen fertilizer- NH₃ / NO₃

- Des Moines river in Ottumwa, IA yields springtime NH₃ & summer NO₃⁻
- Anhydrous NH₃ converts to NO₃ runs off or into aquifer if ground (frozen), cool soil hold tends to hold N, too hot evaporates (IA State) 55F soil temp
- NH₃ /NH₄+ bonds to soil, NO₃- repels charge
- Soil microbes convert N to NO₃- (water soluble used by plants)
- Fall fertilizer application up to 70% N loss
- IA DNR has opinions on fall NH₃ applications



Chloramination Controls

- Maintain 3-4 mg/L chloramine at plant
- Keep chlorine / ammonia 4-5:1
- Minimize free ammonia < 0.1 mg/L</p>
- Keep filter media clean, shock Cl₂ + PP
 Unless media is bioactive NH₃ → NO₃
- Monitor chlorine / chloramine, ammonia, nitrite, biofilm, water quality
- Keep residuals or boost up in system.

Demand versus Decay

- Demand = loss of residual after chloramine reaction with reducing agents (iron, manganese, sulfide, nitrite) and NOM in distribution system
- Decay = loss of chloramine residual due to automatic decomposition as follows:
- $3NH_2CI \Rightarrow N_2 + NH_3 + 3HCI$
- (NH₃↑ as pH ↓ (8.3 optimal), T ↑, CO₃↑, DO↓

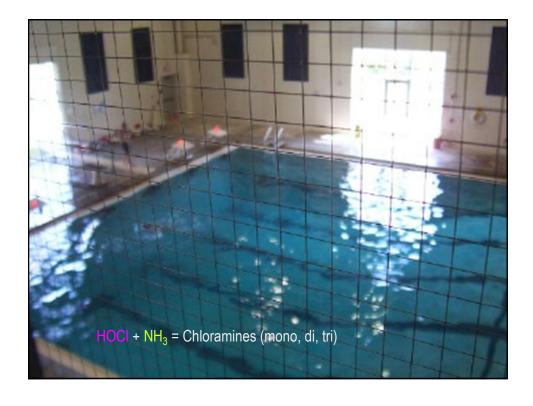
Polyphosphate treatment

- Sequesters iron Fe⁺² (rusty water control)
 - Reduces apparent color/turbidity of Fe⁺³ particles
- Suspends manganese Mn+2 (black/brown water)
- May sequester/chelate metal from pipes
 - Overdose disrupts pipe surface & byproducts
- Prevents scale formation
 - 'Thresholding' calcium Ca+2 carbonate formation
 Removes existing scale and corrosion deposits reducing chlorine demand & regrowth potential
- Reduced THM's (HOCl demand & pH operation)
 - Less chlorine available for THM formation and less byproducts NOM in distribution system

Effects of Polyphosphate

- Study examined disinfection ability of free chlorine and monochloramine for controlling biofilm and effect on corrosion control
- Application of corrosion inhibitors improved chlorine disinfection, allowing for penetration of pipe scale and biofilm removal
- Polyphosphate application resulted in 1,000 fold decrease of biofilm counts (∴ reduces DBP precursors and formation potential)
- Chlorine alone reacts with surface of scale

LeChevallier, Mark W.;Lowry, Cheryl D.;Lee, Ramon G., Disinfecting Biofilms in a Model Distribution System, JAWWA Vol. 82 - No. 7, 1990



Free Chlorine + Ammonia-N = Combined Residuals			
$CI_2 + H_2O = HOCI + HCI$	ODOR LIMIT 20 mg/L		
HOCI + NH ₃ = Chloramines (mono, di, tri)	30 mg/L taste		
$HOCI + NH_3 \Leftrightarrow NH_2CI$ (monochloramine) + H_2O	5.0 mg/L		
$HOCI + NH_3 \Rightarrow NHCl_2$ (dichloramine)	0.8 mg/L		
HOCI + $NH_3 \Rightarrow NCI_3$ (trichloramine)	0.02 mg/L		

What is total residual?

- Total Chlorine = Free + Combined
- Chlorine in 'contaminated' H₂O = chloramines & chlororganics (combined)
- Chloramines = mono, di, tri
- Chlororganics = DBP, THM, HAA
- Combined residual is less reactive
- Combined chloramine residual is formed before reaching the breakpoint, a nuisance trace remains after



What are phantom residuals?

- False positive results- NOT VALID
- Observed in DPD free chorine analysis
- Interference from chloramine residuals in the water sample, while free not really present
- "3 mg/L monochloramine will cause increase of < 0.1 mg/L free chlorine reading" (per DPD low range method 0-2 mg/L -Handbook)
- Contradicted by the DPD high range 0-5 mg/L



Why do phantoms exist?

- Natural ammonia in raw water is primary problem, often unrecognized
- Monochloramine residuals 'bleed over' into the DPD free test results
- As the water sample ages, the free chlorine DPD results drifts higher indicating nearly the same result as the total chlorine test



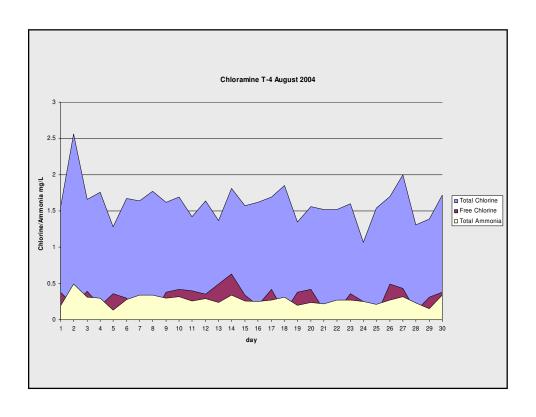
When do phantoms exist?

- Chloramine interferes with the DPD free chlorine reagents
- Sample may turn faint pink to dark magenta color (0.1-1.0+ mg/L) free chlorine.
- Sample turns pink over time indicating a phantom residual (seconds minutes)
- Free DPD analysis should be rejected if the color drifts higher over time

Interference from monochloramine on 1 minute DPD free chlorine test

(per DPD high range 0-5 mg/L method Hach Analysis Handbook)

NH ₂ Cl mg/L	5C temp	10C	20C	30C
1.2 mg/L	+0.15	+0.19	+0.30	+0.29
2.5 mg/L	+0.35	+0.38	+0.56	+0.61
3.5 mg/L	+0.38	+0.56	+0.69	+0.73
5.0 mg/L	+0.68	+0.75	+0.93	+1.05

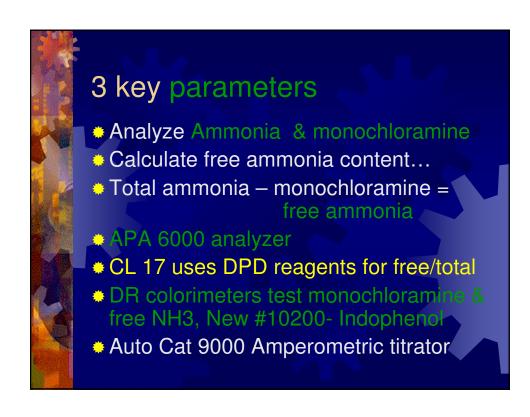


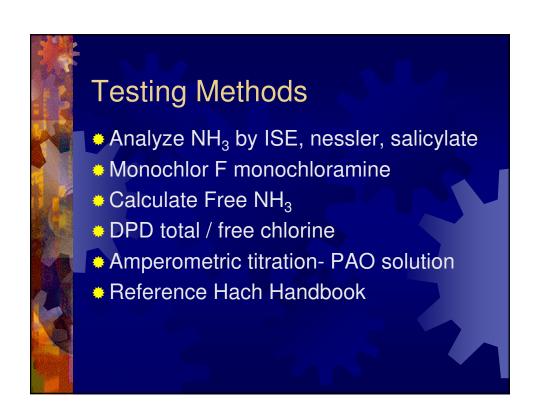


- Perform DPD free chlorine test, measure results 'immediately'
- Allow sample to age and continue analyzing DPD free chlorine residual
- If results drift higher over time, it maybe a phantom – false positive result
- Compare with DPD total chlorine test

What to do next?

- Analyze water for ammonia (ISE) and monochloramine (Hach Monoclor F)
- If ammonia exists (> 0.5 mg/L) then sufficient combined residual may interfere with the Free DPD test
- Calculate Free ammonia = (Total ammonia monochloramine)
- Determine location on breakpoint curve







PWS, MS (DPD analysis)

- 1.67 mg/L total chlorine residual
- 0.52 mg/L free chlorine residual
- 1.67-0.52 = 1.15 combined (calculated)
- 9 mg/L Cl₂ dosage (75 lb Cl₂ / MG water)
- Where are they on the breakpoint curve? Do they have a free residual?
- Do they have ammonia?
- Fe/Mn/Sulfide negligible



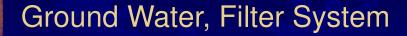
Sampling suggestions

- Perform free chlorine test immediately after adding DPD reagents
- Minimize sample storage time
- Use separate sample cells (free/total)
- Do both tests (free/total) per quality
- Record and plot results to isolate decay rates and location of decomposition

Treatment steps to improve system chlorine residuals

- Remove Fe/Mn, organics, precursors
- Sequester Fe/Mn with polyphosphate
- Corrosion control keeps pipes cleaner and free of biofilm, byproducts, organics
- Pre-oxidize with permanganate / ozone to destroy DBP precursors and demand
- Pre-aerate to release hydrogen sulfide
- Consider Chloramination (Cl₂ + NH₃-N)





- Natural occurring ammonia in 8 wells
 (0.1 5 mg/L) supplying pressure filters
- Ammonia fluctuates (10-400% weekly)
- Pre/post chlorination (1-12 mg/L)
- Very high TOC (1-8 mg/L), color
- Bacterial fouling, taste/odors, hydrogen sulfide, slime in toilet bowls, complaints

Problems & treatment change

- Unable to maintain free chlorine residuals, Fe breaking through filters, mud balls, media fouling, flow decreased & backwash frequency increased, water quality poor
- Switched from free chlorine to chloramine (3-4 mg/L residual) by reducing chlorine dosage (moved back up the breakpoint curve)

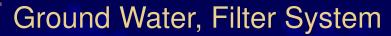


Treatment & Results

- Wells & filters cleaned regularly / Qtr.
- Permanganate / chlorine soak
- Sand/anthracite media cleaned / topped
- Filter flow at designed rate 3 gpm/ft²
- THMs low at plant 10 ug/L
- TTHM low in system 7 ug/L average
- Water quality improved, residents now calling asking what happened, 'water is great'

Suggestions

- Keep monochloramine high (3-4 mg/L)
- Keep free ammonia low < 0.1 mg/L</p>
- Flush yearly, free chlorinate, monitor
- Clean & flush wells, filters, tanksCheck filters for AOB, if so leave alone?
- Inhibit corrosion, sequester Fe/Mn
- Monitor regrowth & deterioraton



- Wells, pre-aeration, chlorination, pressure filters Fe-removal, ion exchange softening, post chlorination, O-P corrosion inhibitor, fluoridation
- Not aware if NH₃ present in wells
- Variable Cl₂ residuals in plant/system, pre/post chlorination
- Moderate N-bacteria in filters
- Prior filter cleaning = loss of free Cl₂

Source	Ammonia	Nitrite	Total Cl2	Free Cl2
Well	1.1-1.2	0.001	pre 2.2 dose	
Booster	1.05 well off	0.118	0.89/0.88 monochl	0.03 Not valid
Fe filter discharge	0.7 off 1.3 on	0.227	post 10 dose	
Finished tap	0.0 off 0.05 on	.007	3.8	3.8
Other wells	0.5-1.2		2.9	0.16 phantom

Options & Changes Made

- Switch pre/post chlorination dosages-destroy ammonia with pre, adjust free residual in post
- Utilize natural ammonia for seasonal combined residuals in summer
- Free residuals in fall prior to hydrant flushing and maintain post spring flush
- Blending of system waters compatible
- Top off lost filter media with 9" anthracite
- Evaluate filter/well rehabilitation methods
- Monitor total/free ammonia, Pb/Cu, Fe, corrosion, biofilm, and chlorine residuals

FYI

- Waste influent 8-10 mg/L P, effluent limit 1-2 mg/L P
- NH3 inflow 20-25 mg/L, outflow 1.2-2 mg/L discharge
- Limit on fish kill from NH3
- Anaerobic digesters concentrate NH3 to 600-1000 mg/L

