Advanced Chemistry and Its Impact on Disinfection

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Roy D. Vore, Ph.D., NSPF®I, CPO® Certification, CPI™
BioLab Inc.
roy.vore@biolabinc.com
Since 1900 a few things have changed . . . . .

- Filtration systems have changed – in more ways than recognized
- The focus of chlorination changed from oxidation to disinfection
- Test methods for chlorine have changed
- The list of pathogens have expanded
- The concentration of chlorine used has increased
- Water balance parameters have narrowed
- Now we have Model Aquatic Health Code (MAHC)
- Have we now arrived?
Status of rec water today – my view

- Operators are still focused on water quality with lesser concern about recreational water illnesses
- Inspectors are focused on comparing test results to rigid parameters

As we continue to revise our pool codes as well as the Model Aquatic Health Code I suggest we ask:

1. What lessons from the past have been lost?
2. Are our basic assumptions on treatment too restrictive?
Three areas I think we should revisit:

1. Examine how filtration has evolved
2. Investigate RWI outbreaks to see if we are using the correct pathogens as targets in establishing disinfection
3. Consider how normal variations in water parameters are impacting disinfection
Filtration
Slow rate sand filters – in the beginning

- **Gravity flow** – very slow
- **Multi-layers of fine sand, larger sand, and gravel** (top to bottom)
- **Early 1900s**, not used in pools today
- Typically used with ammoniated alum \((\text{NH}_4\text{Al(SO}_4)_2)\)
- Biologically active slime bed on top metabolized organics

www.slideshare.net/drsanat81/water-filtration-plant
Rapid rate sand filters – 2nd generation

- **3 gpm/square foot of filter area**
- Multi-layers of gravel, sand, fine sand
- Early 1900s, decreasing in use after 1950, still around but quite rare today
- Commonly used with alum \((\text{Al}_2(\text{SO}_4)_3)\)
- Deep floc layer on top significantly improved filter efficiency

NSPF
High rate sand filters – 3rd generation

<table>
<thead>
<tr>
<th>High-rate sand filter</th>
</tr>
</thead>
<tbody>
<tr>
<td>5-20 gpm/ square foot of filter area</td>
</tr>
<tr>
<td>Single layer of sand of uniform size</td>
</tr>
<tr>
<td>Introduced in 1950s, dominate type used in pools today</td>
</tr>
<tr>
<td>Flocculants not typically used</td>
</tr>
<tr>
<td>Filter aids used only as needed to polish water</td>
</tr>
</tbody>
</table>

www.poolspanews.com/
## Summary of sand filters

<table>
<thead>
<tr>
<th>Slow rate sand filter</th>
<th>Rapid rate sand filter</th>
<th>High-rate sand filter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gravity flow – very slow</td>
<td>3 gpm/square foot of filter</td>
<td>5-20 gpm/ square foot of filter</td>
</tr>
<tr>
<td>Multi-layers of fine sand, larger sand, and gravel</td>
<td>Multi-layers of gravel, sand, fine sand</td>
<td>Single layer of sand of uniform size</td>
</tr>
<tr>
<td>Early 1900s, not in pool today</td>
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</tr>
<tr>
<td>Typically used with ammoniated alum $(\text{NH}_4\text{Al(SO}_4)_2$)</td>
<td>Commonly used with alum $(\text{Al}_2(\text{SO}_4)_3$)</td>
<td>Flocculants not typically used</td>
</tr>
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<td>Biologically active slime layer metabolized organics</td>
<td>Floc layer significantly improved filter efficiency</td>
<td>Filter aids used only as needed to polish water</td>
</tr>
</tbody>
</table>
Overview on sand filters

➢ What we know
  • Filters work better being a little dirty, or with a flocculent
  • Filters contain $>10^6$ bacteria per gram of sand
  • Filters with microbial beds are called fixed-bed bioreactors
  • Fixed-bed bioreactors are commonly used to bacteria digest organics
  • Chlorinated organics are much more intractable to biological digestion than non-chlorinated organics

➢ What we might think about
  • Would a slow-rate filter on a side stream increase DBP removal?
    • Would post-filter chlorination control *Pseudomonas* release?
    • Would post-filter chlorination increase DPBs?
  • Would routinely using floc with current filters increase DBP removal?
Pathogens in treated recreational water
Evolution of pathogens of concern

- Fecal indicators – the list came from drinking water
- *Staphylococcus* and coliforms – 1950s (White, 1972)
- *Shigella* – 1969
- *Giardia* – 1985 (MMWR V47, SS-2)
- *E. coli* O157:H7 – 1998 Atlanta water park outbreak
- *Cryptosporidium* – 1992 (MMWR v 42; SS-5, 1993)
- Viruses have been mentioned for >60 years but less is known on their abundance or role in RWIs
Overview on pathogens of concern

What we know

- CDC reports do not contain outbreaks of chlorine-sensitive pathogens when the free chlorine is >1.0 ppm
- This has been confirmed in an extensive field study (Esterman, 1984)
- Impacting bather behavior is very difficult - many still swim while ill
- Hyperchlorination is hard to employ, reactive, and not used until we are in the middle of a serious community health crisis

What we might think about

1. Requiring full time on-site CPOs or remote monitoring for all facilities to reduce the incidence of chlorine-sensitive RWI outbreaks
2. Requiring secondary disinfection on all facilities to reduce Crypto outbreaks
Disinfection concentration
## Chlorination type and levels

<table>
<thead>
<tr>
<th>Pre-1941</th>
<th>1945-1969</th>
<th>1969-present</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>“Token” chlorination</strong></td>
<td><strong>“High free residual”</strong></td>
<td><strong>Current U.S. system</strong></td>
</tr>
<tr>
<td>Measured by orthotolidine (O-T aka OTO)</td>
<td>Measured by orthotolidine (O-T aka OTO)</td>
<td>Measured by DPD</td>
</tr>
<tr>
<td>Used with ammonia supply</td>
<td>Total chlorine: 3.0 – 5.0 ppm</td>
<td>Combined chlorine &lt;1.0 ppm, preferably &lt;0.4 ppm</td>
</tr>
<tr>
<td>Total chlorine typical &lt;1.0 ppm; monochloramine was primary disinfectant</td>
<td>Free chlorine: 1.0 – 2.0 ppm was primary disinfectant</td>
<td>Free chlorine: 1.0 – 4.0 ppm is mandated by EPA label</td>
</tr>
<tr>
<td>Limited ammonia supply in WWII reduced use</td>
<td>Required frequent superchlorination</td>
<td>Some states still listing &lt;1.0 ppm free as minimum</td>
</tr>
<tr>
<td>Phased out once breakpoint was understood</td>
<td>Phased out because O-T is a carcinogen</td>
<td>MAHC 2016 lists: 1.0-10.0 ppm (without CYA) 2.0-10.0 ppm (with CYA)</td>
</tr>
</tbody>
</table>

**White, 1972; MAHC 2016**
Disinfection standards today

- Based on assumption that a broad-spectrum, rapid-acting disinfectant must be in the water at all times
- Disinfection testing method was drafted by USDA pesticides group (this was fore runner of US EPA)
- Method was published in 1964 (Ortenzio and Stuart, 1964)
- Method relied on the same bacteria used as indicators of fecal contamination of drinking water.
- Method was formalized as AOAC 965.13 and has not be updated since 1970
Conditions used in AOAC 965.13
Specified by US EPA in OCSPP 810.2600 as the laboratory presumptive method

- Glassware washed with chromic acid, triple rinsed and baked at 180°C for >2 hours
- Bacteria rinsed twice in a sterile solution and centrifuged to remove miscellaneous organic matter
- Sterilized distilled water with phosphate buffering
  - Plus it is treated to have ZERO chlorine demand
- Chlorine concentrations used:
  - 0.6 ppm at time zero
  - 0.4 ppm at ten minutes
- Kill times
  - *E. coli* 6 log reduction in \( \leq 30 \) seconds
  - *Enterococcus faecium* 6 log reduction in \( \leq 2 \) minutes
Before you adopt a 30 second kill rate

- Are your pool surfaces washed with chromic acid?
- Are your bacteria free of organic matter (e.g. feces, vomit, slime)?
- Did any soil get blown into the pool?
- Did any bather sweat or urinate in the pool?
- Did any bather carry sunscreen into the pool?
- In the official test method 1 bacteria is killed at 30 seconds and the other at 120 seconds. Why do we only quote 30 seconds as the performance standard?

Are you still certain that you want a rigid 30 seconds for a kill time in a real world setting?
## Comparison of various codes/guidelines

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>FC (no CYA)</td>
<td>1.0 - 4.0</td>
<td>1.0 – 10.0</td>
<td>2.0 - 4.0</td>
<td>&gt;1.0 @ &lt;30°C 2.0 @ &gt;30°C</td>
<td>0.3 – 1.5</td>
</tr>
<tr>
<td>FC (+ CYA)</td>
<td>1.0 - 4.0</td>
<td>2.0 – 10.0</td>
<td>2.0 - 4.0</td>
<td>&gt;1.0 @ &lt;30°C 2.0 @ &gt;30°C</td>
<td>1.0 – 3.0</td>
</tr>
<tr>
<td>CC</td>
<td>Not covered</td>
<td>≤0.4</td>
<td>≤0.4</td>
<td>Lowest possible</td>
<td>≤0.5</td>
</tr>
<tr>
<td>ORP (mV)</td>
<td>Not covered</td>
<td>Only specified with ozone</td>
<td>650 – 720</td>
<td>≥770 @ 0.3 ppm FC 700 @ 0.5 ppm FC</td>
<td>≥650</td>
</tr>
<tr>
<td>pH</td>
<td>7.2 - 7.8</td>
<td>7.2 - 7.8</td>
<td>7.2 - 7.8</td>
<td>6.8 – 7.6</td>
<td>6.8 – 7.6</td>
</tr>
<tr>
<td>Turbidity</td>
<td>Not covered</td>
<td>Must see bottom</td>
<td>Must see bottom</td>
<td>≤0.5 NTU</td>
<td>≤1.5 NTU</td>
</tr>
<tr>
<td>Flocculants</td>
<td>Not covered</td>
<td>Optional</td>
<td>Optional</td>
<td>Not covered</td>
<td>Optional</td>
</tr>
<tr>
<td>Bacteria testing</td>
<td>Not required (1)</td>
<td>Not required</td>
<td>Not required</td>
<td>Required</td>
<td>Optional</td>
</tr>
</tbody>
</table>

**Notes:**
FC: free chlorine; CC: combined chlorine; (1) chlorine/bromine are grand fathered and efficacy data is not required for new formulations.
## Comparison of various trade guidelines

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>FC (no CYA)</td>
<td>1.0 - 5.0</td>
<td>1.0 - 4.0</td>
<td>0.5 - 2.0</td>
</tr>
<tr>
<td>FC (+ CYA)</td>
<td>1.0 - 5.0</td>
<td>1.0 - 4.0</td>
<td>2.5 - 5.0</td>
</tr>
<tr>
<td>CC</td>
<td>&lt; 0.2</td>
<td>&lt; 0.2</td>
<td>&lt;50% of FC</td>
</tr>
<tr>
<td>ORP</td>
<td>“Calibrate to disinfectant level”</td>
<td>Not covered</td>
<td>Set per DPD results</td>
</tr>
<tr>
<td>pH</td>
<td>7.2 - 7.8</td>
<td>7.2 - 7.8</td>
<td>7.2 - 7.8</td>
</tr>
<tr>
<td>Turbidity</td>
<td>Drain clearly visible from deck</td>
<td>Bottom clearly visible</td>
<td>Not specified</td>
</tr>
<tr>
<td>Flocculants</td>
<td>Optional</td>
<td>Not covered</td>
<td>Optional</td>
</tr>
<tr>
<td>Bacteria tests</td>
<td>Not required</td>
<td>Not required</td>
<td>APC/coliforms recommended</td>
</tr>
</tbody>
</table>

**FC**: free chlorine; **CC**: combined chlorine;
Let’s examine a hypothetical pool

- Assumptions:
  - Chlorine source: pool bleach
  - Free chlorine by DPD: 2.0 ppm
  - Combined chlorine by DPD: 0.3 ppm
  - pH (probe calibrated 1 hour ago): 7.5
  - ORP (probe calibrated 1 hour ago): 780 mV
  - Temperature: 77°F
  - Cyanuric acid: 0.0 ppm
  - TDS: 1000 ppm
  - Ozone: not used
  - Potassium monopersulfate: not used

Exactly what is your disinfectant level?
What happens if you keep the free chlorine at 2.0 ppm by DPD but your pH is unstable?

<table>
<thead>
<tr>
<th>Free chlorine by DPD</th>
<th>pH</th>
<th>HOCl</th>
<th>OCl-</th>
<th>mV (Chemtrol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0 ppm</td>
<td>6.6</td>
<td>1.77 ppm</td>
<td>0.23 ppm</td>
<td>849 mV</td>
</tr>
<tr>
<td>2.0 ppm</td>
<td>6.9</td>
<td>1.58 ppm</td>
<td>0.42 ppm</td>
<td>833 mV</td>
</tr>
<tr>
<td>2.0 ppm</td>
<td>7.2</td>
<td>1.31 ppm</td>
<td>0.69 ppm</td>
<td>815 mV</td>
</tr>
<tr>
<td>2.0 ppm</td>
<td>7.5</td>
<td>0.97 ppm</td>
<td>1.03 ppm</td>
<td>793 mV</td>
</tr>
<tr>
<td>2.0 ppm</td>
<td>7.8</td>
<td>0.64 ppm</td>
<td>1.36 ppm</td>
<td>766 mV</td>
</tr>
<tr>
<td>2.0 ppm</td>
<td>8.1</td>
<td>0.39 ppm</td>
<td>1.62 ppm</td>
<td>734 mV</td>
</tr>
<tr>
<td>2.0 ppm</td>
<td>8.4</td>
<td>0.21 ppm</td>
<td>1.79 ppm</td>
<td>694 mV</td>
</tr>
</tbody>
</table>

- As pH goes down HOCl and mV increase – and the kill rate increases accordingly
- As pH goes up HOCl and mV decrease – and the kill rate decreases accordingly

Data courtesy of Richard Falk
But you want to maintain HOCl at 1.0 ppm. How do you adjust your DPD readings?

<table>
<thead>
<tr>
<th>HOCl (ppm)</th>
<th>pH</th>
<th>Free chlorine by DPD (ppm)</th>
<th>OCl- (ppm)</th>
<th>mV</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>6.6</td>
<td>1.13</td>
<td>0.13</td>
<td>799</td>
</tr>
<tr>
<td>1.0</td>
<td>6.9</td>
<td>1.26</td>
<td>0.26</td>
<td>793</td>
</tr>
<tr>
<td>1.0</td>
<td>7.2</td>
<td>1.53</td>
<td>0.53</td>
<td>786</td>
</tr>
<tr>
<td>1.0</td>
<td>7.5</td>
<td>2.05</td>
<td>1.05</td>
<td>779</td>
</tr>
<tr>
<td>1.0</td>
<td>7.8</td>
<td>3.10</td>
<td>2.10</td>
<td>773</td>
</tr>
<tr>
<td>1.0</td>
<td>8.1</td>
<td>5.20</td>
<td>4.20</td>
<td>766</td>
</tr>
<tr>
<td>1.0</td>
<td>8.4</td>
<td>9.37</td>
<td>8.37</td>
<td>759</td>
</tr>
</tbody>
</table>

- In this case HOCl concentration is the dominant parameter
- **But** - you cannot directly measure HOCl. You calculate with a complex equation
- **Further** - the equation changes with changes in water chemistry parameters – and they are many

Data courtesy of Richard Falk
But we should not simplify this too much. Applying the same Free Chlorine vs. ORP curve to all pools will NOT work.

Data courtesy of Richard Falk and Jeff Luedeman.
If you can develop a method to compare HOCl to ORP the fit is much better.

The $R^2$ improves substantially to “$R^2 = 0.736$”.

Data courtesy of Richard Falk and Jeff Luedeman
Overview on disinfection

What we know

- In chlorine treated pools, HOCl is the only chlorinated species that is an effective disinfectant
- Using old studies is problematic because different test methods (OT, thiosulfate, DPD) were used at various times
- The disinfectant concentration, HOCl in our case, is impacted by numerous parameters including sunlight, temperature, pH, and organics
- Measuring HOCl is very difficult but it can be calculated, if you factor in the appropriate parameters

What we might think about

1. Focusing on HOCl, not free chlorine as measured by DPD
2. Considering wider water parameters that recognize HOCl chemistry
Issues with *Crypto* in bromine pools
Methods to produce hypobromous acid

Regardless of the source, HOBr is the primary disinfectant
Reactions of bromine during disinfection

\[ \text{HOBr} + \text{Organic matter} \]

\[ \text{Br}^- + \text{Oxidized products} + \text{Inorganic/organic combined bromine} \]

The ONLY way to eliminate the bromide salt (Br-) is to COMPLETELY drain and refill the pool.
Hyperchlorinating a bromine pool

Adding chlorine results in the regeneration of hypobromous acid
- This reaction occurs almost instantaneously
- Because there is so much Br\(^-\) this reaction continues until all the hypochlorous acid is depleted

The net result: it is extremely unlikely that you would ever be able to establish any appreciable amount of free chlorine in a bromine pool

White, Handbook of Chlorination, 4\(^{th}\) ed
Hyperchlorinating a bromine pool

- If the Br- to HOBr reaction consumes all the HOCl then you are hyperbrominating **NOT** hyperchlorinating the pool
- DPD *cannot* distinguish HOBr, combined chlorine, and combined bromamines easily or quickly
- If you have a *Crypto* outbreak in a bromine pool and decide to treat it with chlorine, how do you test to ensure that you have achieved the correct CT target?
  - *You cannot!*
- For *Crypto* you have only two effective options
  - A *COMPLETE* drain and refill (partial refills may not be effective)
  - Secondary disinfection systems
Finally, five thoughts to consider

1. If someone proposes a filtration system that has demonstrated DPB reduction would you consider it? What if it’s unconventional?

2. If a pool is operating well at pH 6.6, zero cyanuric acid, has balanced water and 1.1 ppm free chlorine by DPD with no eye/skin complaints should it be closed by an inspector? If yes, why?

3. If a pool is operating well at pH 8.1, zero cyanuric acid, has balanced water and 5.2 ppm free chlorine by DPD with no eye/skin complaints should it be closed by an inspector? If yes, why?

4. How do you treat a *Crypto* outbreak in an outdoor bromine pool?

5. What if 2, 3, or 4 occurred in a splash pad with a UV system?
References

- PWTAG. 1999. Swimming Pool Water: Treatment and quality standards. (this is not the most current)