Presented by
Members of the PHTA Recreational Water Quality Committee (RWQC)

The Impact of Disinfection Byproducts and Combined Chlorine on Air and Water Quality

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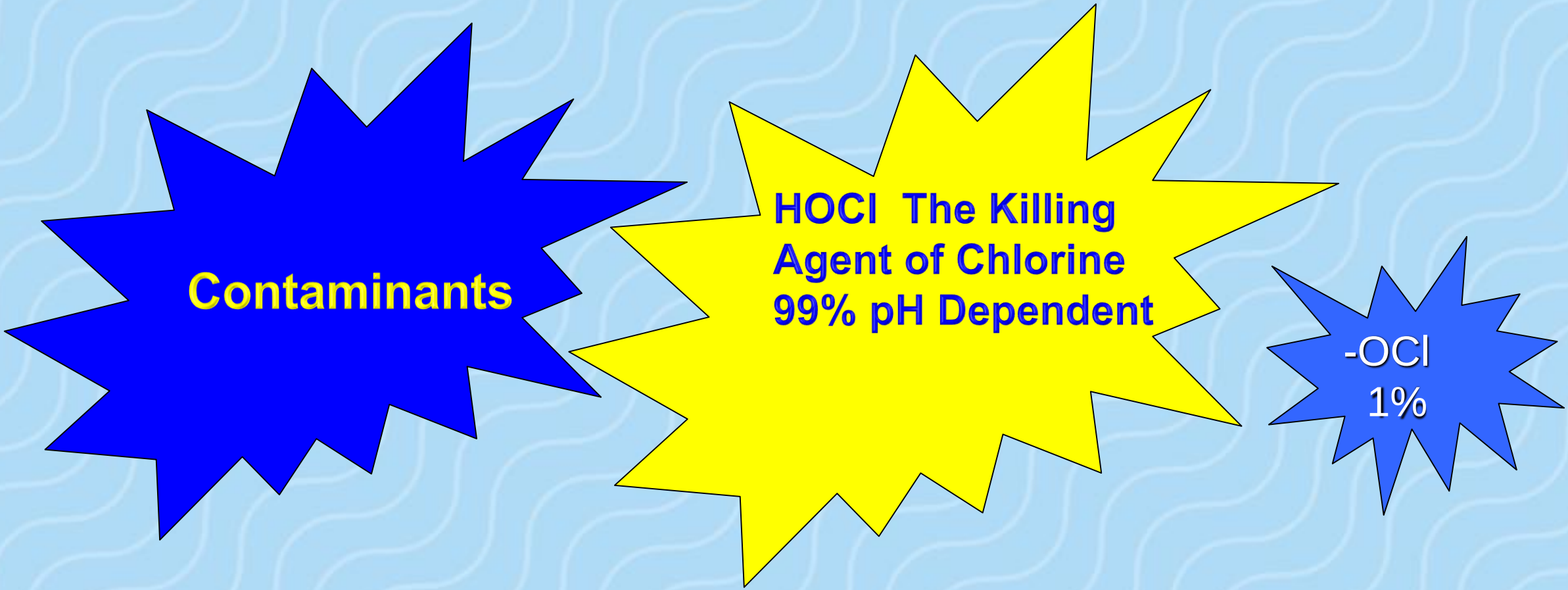
WAHC World Aquatic Health Conference

Chlorine in Pool Water



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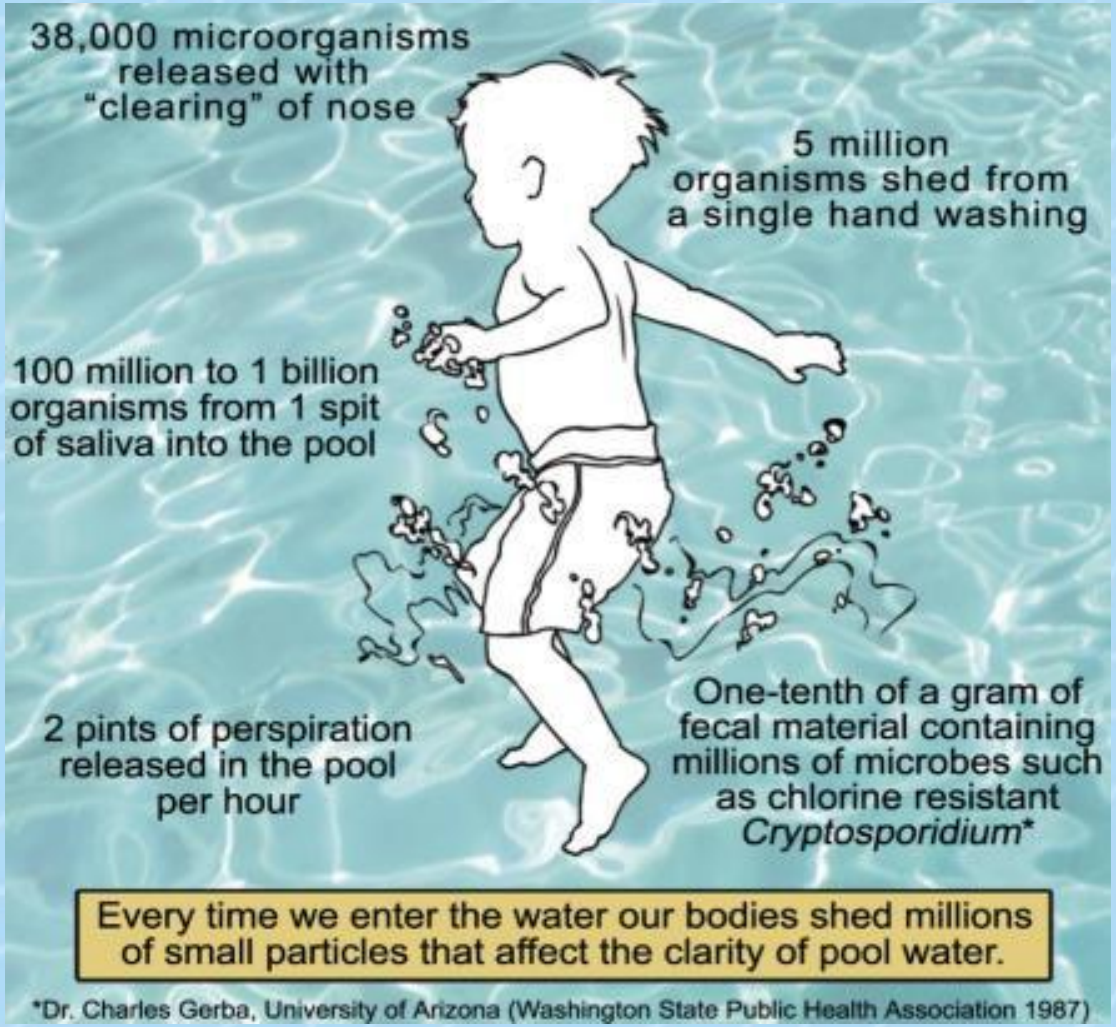
Why Sanitizers are Needed



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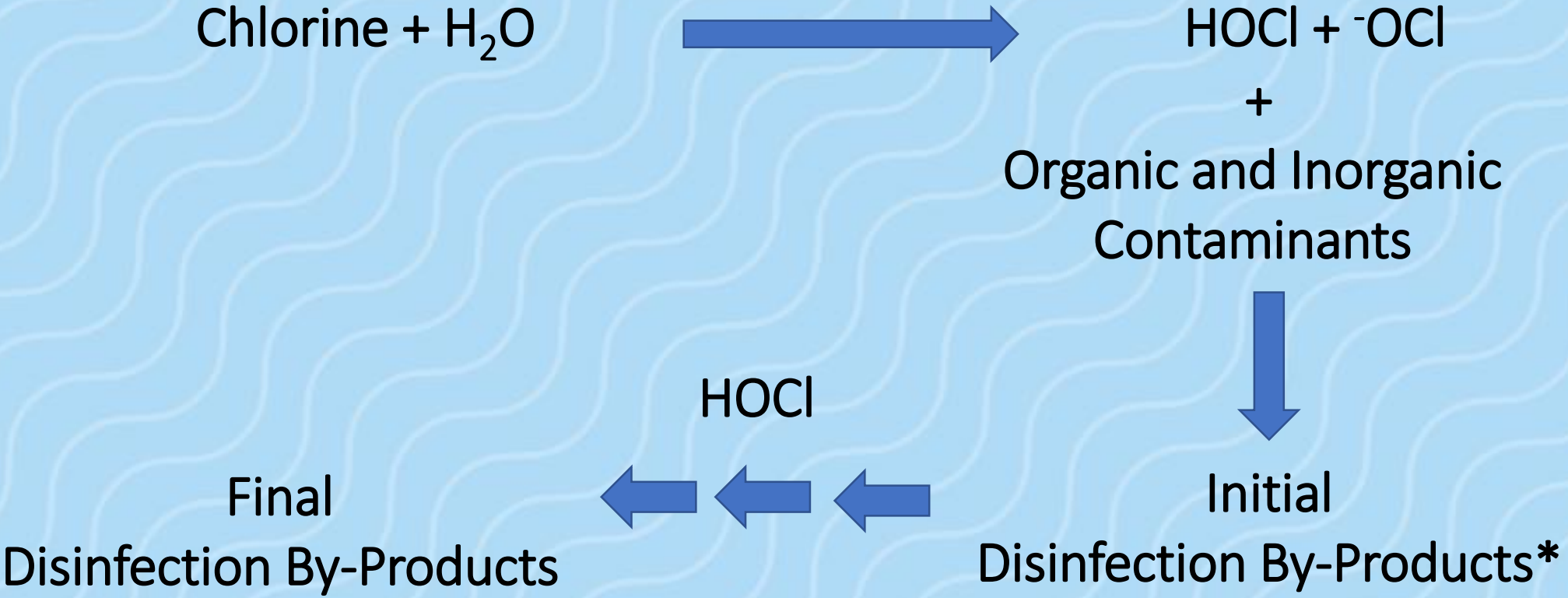

*Disinfection by-products are chemicals produced by the reaction of contaminants with chlorine.

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Contaminants (Precursors) that Produce Disinfection By-Products (DBPs)

- Amino acids
- Creatine
- Urea*
- L-histidine
- L-arginine

Mostly caused from swimmer waste (*perspiration, urine, mucus, skin particles, hair, body lotions, soil etc.).*

*Adult humans produce up to an ounce daily of urea which is dissolved in urine.

Must also consider other organic debris and algae.

Several classes of specialty pool chemicals containing organic compounds (enzymes, sequestering agents, liquid pool covers, etc.) have important applications in pool and spa maintenance, but should be considered as contributing to chlorine demand.

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The Effect of Chlorine on Contaminants

CONTAMINANTS IN POOL WATER

Bacteria, Viruses, Protozoa

Algae, Mold, Bio-Film

Organic and Inorganic Contaminants

Chemicals containing organic compounds

CHEMICAL SUBSTANCE

- Ammonia
- Organic Nitrogen
- Organic Non-nitrogen

HOCl

EFFECT

Destroys Pathogens

Controls and Reduces other microorganisms

Oxidizes organic and inorganic contaminants and chemicals containing organic compounds

OXIDATION

- Inorganic chloramines
- Organic chloramines
- End products primarily NCl_3, $CHCl_3$, HAA, nitrate, N_2, CO_2.

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Inorganic Chloramines

Mono = NH_2Cl

Possible ocular irritant

Di = $NHCl_2$

Respiratory and ocular irritant

Tri =NCl_3

Acute respiratory and ocular irritant

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Organic Chloramines

- Chlorine combines with organic-nitrogen compounds.
  - Proteins / Amino Acids
  - Urea
  - Creatinine
  - Uric Acid
  - Enzymes

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The Effect of Chlorine – 23 Indoor Pool Water Samples

Pool	Temp ° F	pH	FAC ppm	TOC ppm	$CHCl_3$* ppm	Total THM** ppm	Total HAA*** ppm
Median	82.4	7.4	3	7.1	0.062	0.063	0.960
Maximum	93.2	7.8	4	23.6	0.207	0.213	9.005
Minimum	64.4	7.2	0	3	0.025	0.026	0.172

* $CHCl_3$ = chloroform (volatile, primarily from body fluids) is a trihalomethane.

** THM = Trihalomethane
In 30% of the pools, the measured THM was higher than 0.080 ppm (the MCL in US drinking water)

*** HAA = Haloacetic acids (nonvolatile, soluble, primarily from body fluids). The MCL in US drinking water is 0.060 ppm.

Kanan, A.A., Occurrence and Formation of Disinfection By-Products in Indoor Swimming Pool Water, Clemson University, Graduate Dissertation, July 2018.

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The Effect of Chlorine – 6 Pool Water Samples

Pool	FAC ppm as Cl_2	NCl_3* ppm as Cl_2	$CHCl_3$** ppm	Combined Chlorine ppm as Cl_2
Indoor Lap	1.5	0.08	0.07	1.34
Outdoor General Use	1.95	0.07	0.13	0.25
Indoor Lap	0.68	0.09	0.14	1.36
Outdoor Rec Park	6.52	0.16	0.08	1.76
Indoor Lap	5.92	0.10	0.13	1.28
Indoor Lap	1.72	0.07	0.08	0.76

* NCl_3 = Trichloramine (volatile, from inorganic- and organic-N compounds [urea, uric acid, creatinine, etc.]

** $CHCl_3$ = chloroform (volatile, primarily from body fluids)

There is a problem with accurately calculating chlorine demand – magnified in high use pools!

Li & Blatchley, Formation of Volatile Disinfection Byproducts from Chlorination of Organic-N Precursors in Recreational Water, Environ. Sci. Technol. 41:6732-6739 (2007).

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Disinfection By-Products (DBPs)

Inorganic Chloramines (Early DBPs)

- Trichloramine (NCl_3) – Lung and ocular irritant
- N_2, Nitrate

Organic (N-containing and non N-containing contaminants)

- Trihalomethanes (THMs) – Primarily $CHCl_3$ - leads to strong irritant gas off at water surface and in indoor facilities. THMs are lung irritants and exhibit *carcinogenic behavior at high concentrations.*
- Trichloramine (NCl_3) – Lung and ocular irritant
- CO_2, N_2, Nitrate

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Determining Combined Chlorine

- **DPD Method**

Free chlorine **(FC)** determined by liquid DPD #1 & #2 together or DPD #1 tablet. Pink hue compared against a standard for result.

Liquid or tablet DPD #3 is added to treated sample and pink hue is compared against a standard to determine total chlorine **(TC)**.

TC – FC = CC

- **FAS-DPD Method**

Free chlorine **(FC)** determined by DPD Indicator (powder) and titrated to clear endpoint with Ferric Ammonium Sulfate

Liquid DPD #3 (Potassium Iodide or KI) added to treated sample and will indicate the presence of combined chlorine **(CC).** Titrant (FAS) is added again for a direct titration of combined chlorine.

FC + CC = TC

These test methods primarily measure initial and intermediate disinfection by-products

ANSI/APSP/ICC-11 2019 Standard for Water Quality in Public Pools and Spas recommends corrective action when combined chlorine levels reach 0.4 ppm.

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“Breakpoint” Chlorination

- A process to oxidize combined chlorine compounds.
- First introduced in 1940 for the treatment of drinking water.
- Primarily designed for the destruction of ammoniated chlorine in water.
- Introduced to the pool industry to reduce combined chlorine concentrations.
- Standard “breakpoint procedure” for the removal of inorganic ammonia bound chloramines is 10-1 ratio of free chlorine to CC to accomplish “breakpoint.”
- Recent procedures call for subtraction of any residual free chlorine present in pool from the total to be added to achieve “breakpoint.”
- Some organic bound chloramines may require longer reaction time with free chlorine.

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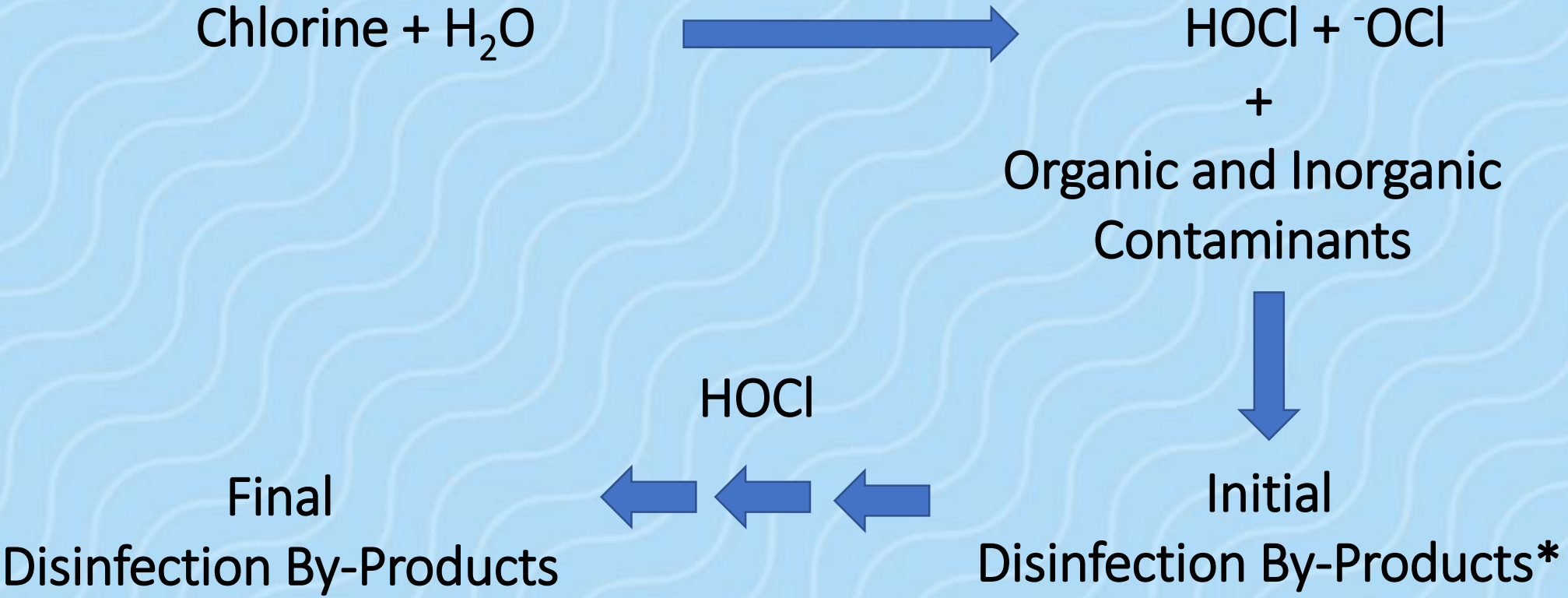
Chlorine in Pool Water



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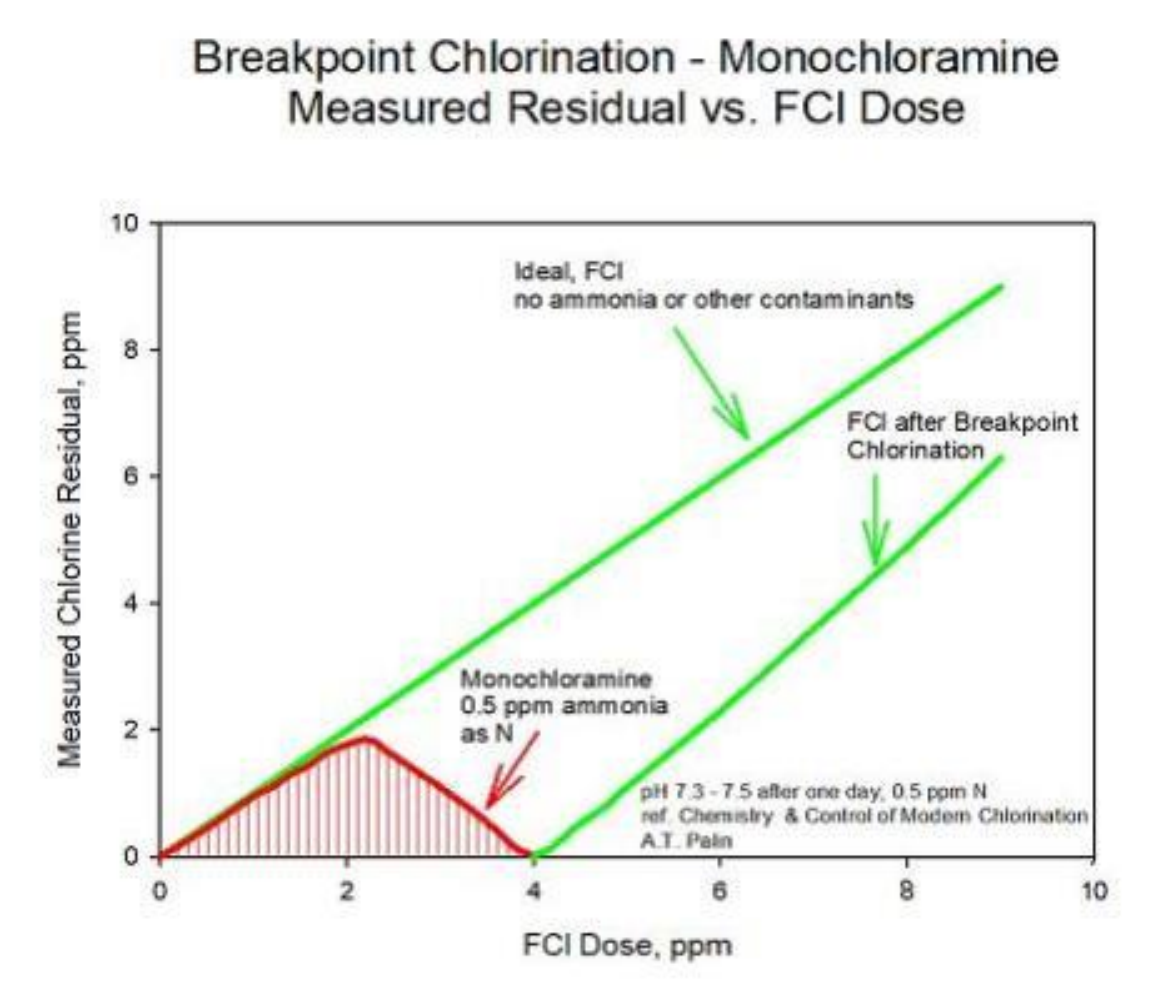
Chlorination of Water Containing Ammonia



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Chlorination of Water Containing Ammonia and Organic-N Compounds

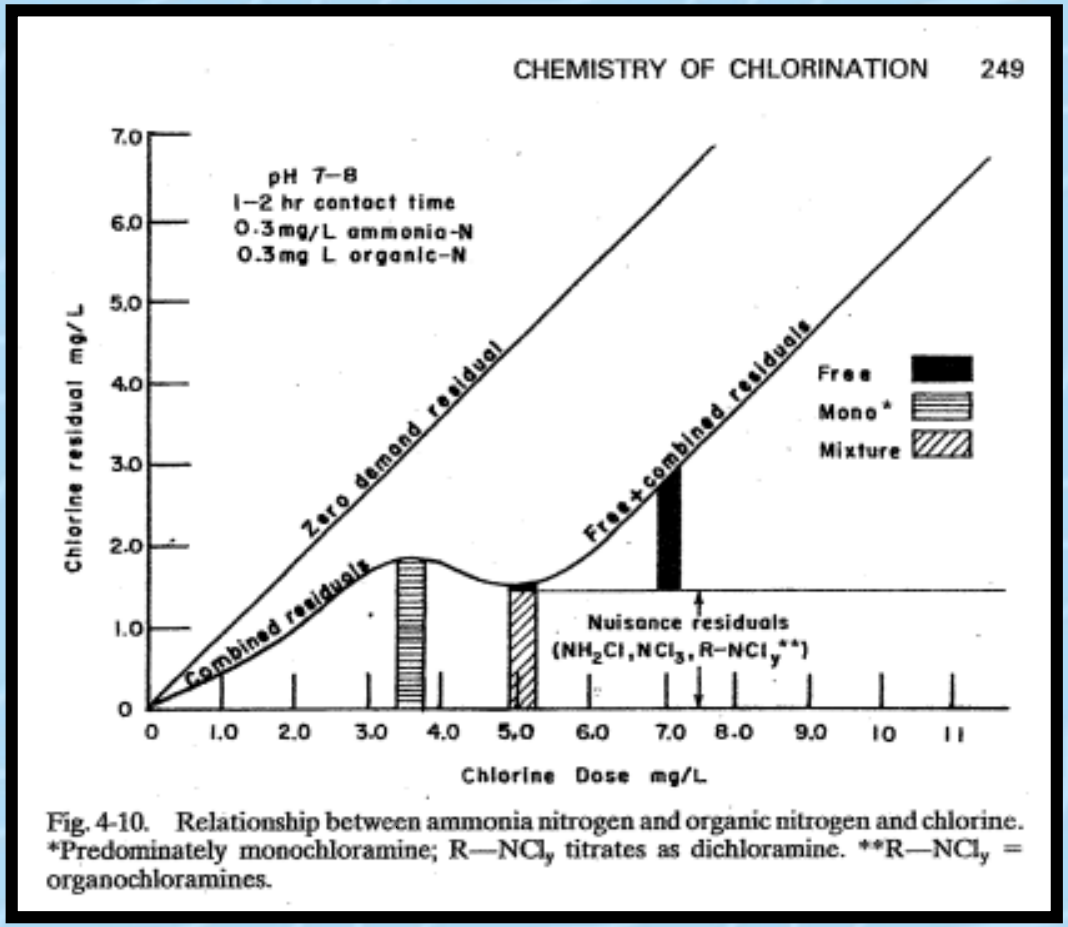

Fig. 4-10. Relationship between ammonia nitrogen and organic nitrogen and chlorine. *Predominately monochloramine; R—NCl_y titrates as dichloramine. **R—NCl_y = organochloramines.

Fig 4-10 illustrates what would be expected with water containing only : 0.3 ppm ammonia nitrogen and 0.3 ppm organic nitrogen

Water containing both ammonia and organic nitrogen does not display the "classic" dip of the breakpoint reaction but rather a small initial dip followed by a plateau AFTER 1-2 HOURS!

The small drop in chlorine residual beyond the hump signifies formation of inorganic and organic chloramines, DBPs, with very little subsequent loss of nitrogen.

White, HANDBOOK OF CHLORINATION, 1999

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Chlorination of Water Containing Ammonia and Organic-N Compounds

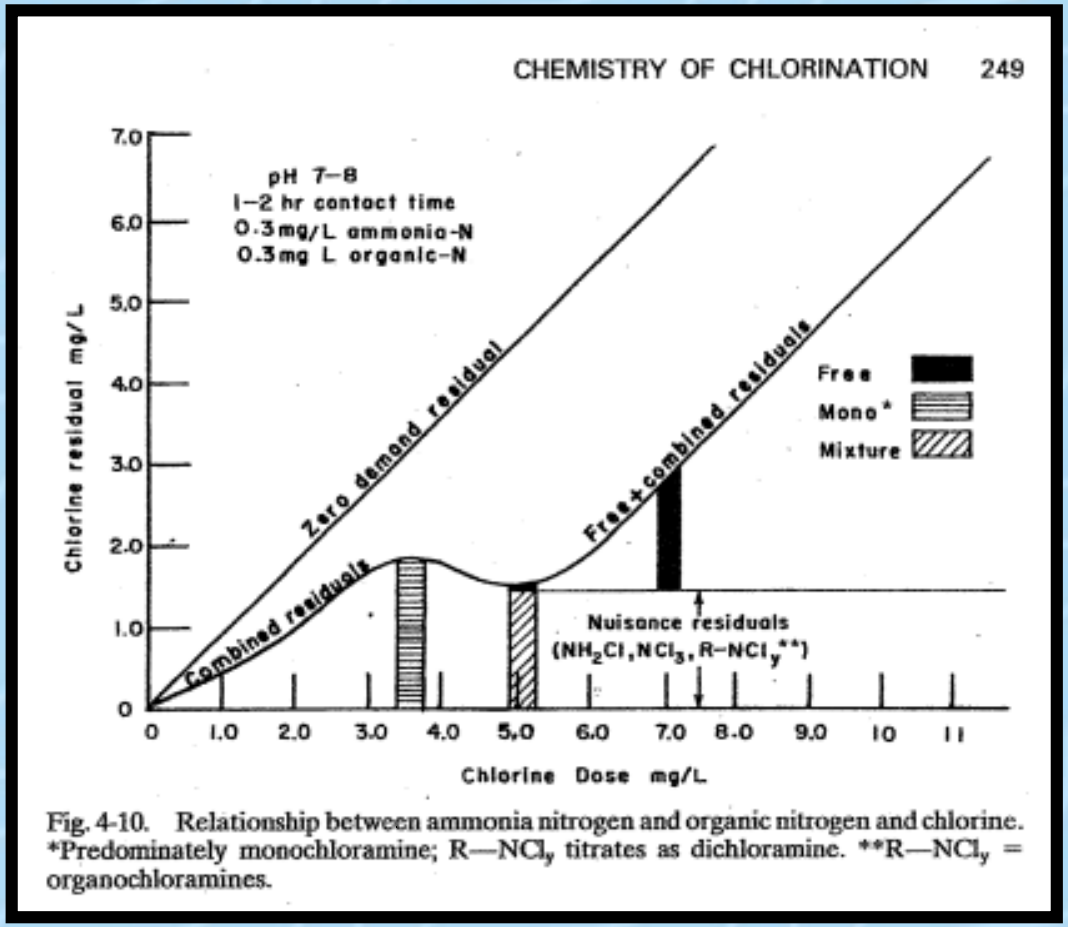

Fig. 4-10. Relationship between ammonia nitrogen and organic nitrogen and chlorine. *Predominately monochloramine; R—NCl_y titrates as dichloramine. **R—NCl_y = organochloramines.

This 1-2 hour reaction figure is NOT representative of what we typically measure in swimming pools.

In the 24-72 hour time frame, the FAC added will be consumed to convert the inorganic chloramines, organic chloramines, and other initial DBPs to NCl_3, $CHCl_3$, HAAs, N_2, CO_2, other DBPs, and nuisance residuals.

IT IS NOT POSSIBLE TO SEGREGATE THE REACTIONS!

THEREFORE, IT IS IMPOSSIBLE TO EXACTLY CALCULATE THE AMOUNT OF CHLORINE NEEDED TO REACT WITH ONLY INORGANIC NITROGEN!

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Reduction of Both Initial and Final DBPs

- Reduce organic and inorganic contaminants.
  - Shower before using pool, frequent bathroom breaks
- Maintain proper water chemistry
  - Reduce algae
  - Maintain equipment integrity
- Do not over-chlorinate!
- Proper filtration and regular cleaning of filters
- Water aeration
- Proper air exchange in indoor facilities
- Pro-active dilution of pool water

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Indoor Air Handling

In order to prevent the detrimental effects of chloramines to facilities and patrons indoor pools must be designed with the following:

- Relative humidity within the building must be maintained at 40 to 60%.
- Proper ventilation and inside/outside air distribution.
- Mechanical cooling systems should have 4-6 air changes per hour.
- Air movement at the water's surface and the deck ANSI/ASHRAE Standard 62.1-2016 requires 0.48 cfm (cubic feet per minute) of outdoor air per square foot on pool and spa deck.
- Chloramines especially dichloramine and trichloramine off gas rapidly. The gas is heavier than air and stays at the water surface. Air velocity of 0.4 feet per second 8 ft above the walking deck should be maintained.

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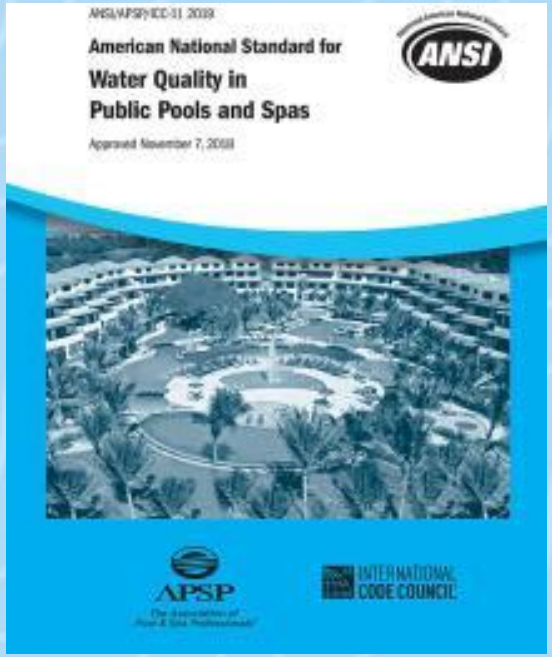
Proper Water Chemistry Ranges - PHTA

- 2-4 ppm Free Available Chlorine (FAC) Pools*
- 2-5 ppm FAC in Spas*
- pH 7.2 – 7.8*



WATER BALANCE

- Calcium Hardness 200-400 ppm Pools 150-250 Spas
- Total Alkalinity 80-120 ppm

TOTAL DISSOLVED SOLIDS (TDS)

- Should not exceed 1500 ppm over initial water. High TDS is a surrogate marker for aged “bad” water. When TDS exceeds 1500 ppm over initial level, chlorine demand may increase 50% and nuisance residuals are likely. Test frequently - at least once a month.

*ANSI/APSP/ICC-11 2019 *Standard for Water Quality in Public Pools and Spas*

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Reduction of DBPs - Insufficient Data to Recommend Use for DBP Reduction

- Ozone or UV units
  - Growing body of evidence to support reduction of chloramines with use, but impact on trihalomethane, haloacetic acid, and other non-chloramine DBPs not completely determined.
- Regular addition of an oxidizer such as MPS
  - No data on DBPs formed in swimming pools when MPS used when chlorine present.

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Reduction of DBPs - Insufficient Data to Recommend Use for DBP Reduction

- Use of Enzymes
  - No data on chloramine, trichloramine, trihalomethane, haloacetic acid, and other DPB concentrations with use.
- Use of Flocculants and Clarifiers
  - No data that exposure to organic material on filter media to a chlorine environment produces different or fewer DBPs than suspended particles exposed to a chlorine environment.

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References

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- *ANSI/APSP/ICC-11 2019 American National Standard for Water Quality in Public Pools and Spas, APSP*
- Natatorium Design Guide – *Seresco 2013*
- UV Photodegradation of Inorganic Chloramines –*Jing Li, Ernest R. Blatchley III School of Civil engineering , Purdue University*
- Effects of UV-based treatment on volatile disinfection byproducts in a chlorinated, indoor swimming pool – *Mehrnaz Zare Afifi, Ernest R. Blatchley III Division of Environmental & Ecological Engineering Purdue University, West Lafayette, IN 2016*
- Disinfection by-product dynamics in a chlorinated, indoor swimming pool under conditions of heavy use: National Swimming competition- *ShihChi Weng, Ernest R. Blatchley III School of Civil Engineering Purdue University 2011*
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Questions and Discussions

2019 Recreational Water Quality Committee (RWQC) Member Companies

American Chemistry Council (ACC)
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Bio-Lab, Inc. – A KIK Custom Products Company
Innovative Water Care
LaMotte Company
NSF International
Pentair Water Quality Systems
Periodic Products
Pure Swim, Inc.
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