

# The Chlorine / Cyanuric Acid Relationship and Implications for Nitrogen Trichloride

by Richard A. Falk

## Abstract

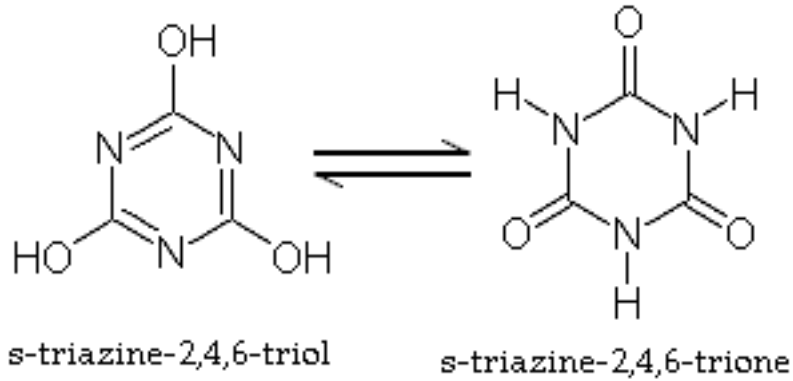
The amount of hypochlorous acid (HOCl) in water with Cyanuric Acid (CYA) at typical pool pH is proportional to the FC/CYA ratio and is orders of magnitude lower than the FC level itself. The primary oxidizing and sanitizing compound is hypochlorous acid while hypochlorite ion and the chlorinated isocyanurate compounds (chlorine attached to CYA) have orders of magnitude lower oxidizing or sanitizing capability.

The rate of production and total amount of nitrogen trichloride produced from the oxidation of ammonia by chlorine is related to the hypochlorous acid concentration and not to the FC level directly. Though the precise mechanism of oxidation of urea by chlorine is unknown, proposed mechanisms lead to the same conclusion of nitrogen trichloride quantities being proportional to the hypochlorous acid level, all else equal. Therefore, the use of a small amount of CYA in indoor pools should significantly lower the amount of nitrogen trichloride produced in such pools and result in lower rates of outgassing of chlorine, corrosion of metal directly exposed to water and oxidation of skin, swimsuits and hair.

## The Hypochlorous Acid / Cyanuric Acid Equilibrium

Cyanuric Acid (CYA, aka stabilizer or conditioner) is used in pools to protect chlorine breakdown from sunlight. Though CYA absorbs ultraviolet (UV) radiation directly thus shielding the lower depths of water and protecting chlorine in those depths from breakdown, the primary result of having CYA in the water with chlorine (hypochlorous acid) is that it combines with chlorine to form a set of chemical species collectively called chlorinated isocyanurates. These compounds also absorb UV without breaking down as quickly as chlorine. The full chemistry is complicated (well, tedious) because there are 6 different species of chlorinated isocyanurates (that is, chlorine attached to CYA) and 4 different species of Cyanuric Acid and its dissociated ions. There are 13 simultaneous chemical equilibrium equations of the CYA, chlorinated isocyanurates, hypochlorous acid and their combinations though only 10 of these are independent from each other.

Look at the chemical structure for CYA here (diagrams from Wikipedia)

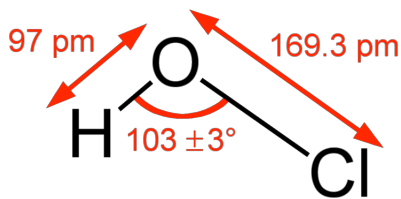


and that of Trichlor and Dichlor here

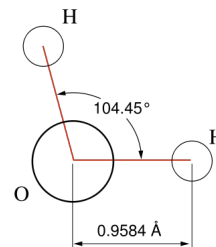


and notice that essentially the Nitrogen can have either hydrogen or chlorine attached to it and that there are three such sites. Qualitatively, **chlorine combines with CYA to form new chemicals that are essentially not disinfectants nor oxidizers** (to be demonstrated later in this paper). CYA has a moderately strong affinity for chlorine such that when CYA >> FC (when both are measured in their respective ppm), then most of the chlorine is attached to CYA. For example, when the pH is 7.5 and the FC is 3.5 ppm and the CYA is 30 ppm, then 97% of the chlorine is attached to CYA. Nevertheless, the chlorine attached to CYA gets measured in the FC test because the chlorine gets released from the CYA quickly enough to replenish the chlorine that is consumed by the test (by reacting with dye).

In a very real sense, CYA acts as a hypochlorous acid buffer holding chlorine in reserve, but significantly lowers its concentration which determines the rate of any reaction in which chlorine participates. You can see from the structure of Hypochlorous Acid (on the left) that it looks similar to water (on the right) with a chlorine atom substituting for a hydrogen atom.



Hypochlorous Acid



Water

When chlorine combines with CYA, this is a chlorine substitution for a hydrogen atom or essentially an exchange of the chlorine atom to the CYA and the hydrogen atom from the CYA to make water. When chlorine is released from CYA, then the opposite exchange occurs.

The definitive scientific paper that determined the equilibrium constants between hypochlorous acid, cyanuric acid, and the chlorinated isocyanurates was presented at a conference in 1973 and published in 1974. The reference is the following:

J. O'Brien, J. Morris and J. Butler, "Equilibria in Aqueous Solutions of Chlorinated Isocyanurate", Chapter 14 in A. Rubin, ed., *Chemistry of Water Supply, Treatment and Distribution*, 1973 Symposium, (published 1974), Ann Arbor Science, Ann Arbor, MI, pp. 333-358.

This book is out-of-print, but I received permission to reprint/post it and you can retrieve a PDF of this paper at the following web page and I strongly encourage you to read at least the INTRODUCTION and SUMMARY sections of this document (note that the term "Free Chlorine" is not as it is used today and that the FC test really measures "reservoir chlorine" as described in the paper:

<http://richardfalk.home.comcast.net/~richardfalk/pool/OBrien.htm>

I have created a spreadsheet that calculates the various chemical species including hypochlorous acid concentration given standard water chemistry parameters. This spreadsheet may be found at the following link:

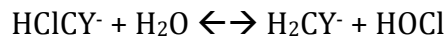
<http://richardfalk.home.comcast.net/~richardfalk/pool/PoolEquations.xls>

One can, of course, use any of a number of standard chemical equilibrium programs to compute the concentrations of chemical species using the equilibrium constants from O'Brien and concentrations converted from standard ppm units. Such programs include CHEMQL, EQS4WIN, MINEQL+, among others.

## The FC/CYA Ratio as a Proxy for Equivalent FC with no CYA

### Simplified Chemical Equations

To simplify the description, I will only write about the most dominant chemical species found at the pH of pool water. For Cyanuric Acid (which I designate as  $H_3CY$ ), the species at highest concentration is the one that has dissociated one hydrogen ion which I will designate as  $H_2CY^-$ . For the chlorinated isocyanurate species, it is CYA with one hydrogen, one chlorine, and one open slot so is negatively charged which I will designate as  $HClCY^-$ . The following is the primary relevant chemical equation to focus on:



"Chlorine bound to CYA" + Water  $\leftrightarrow$  "CYA ion" + Hypochlorous Acid

Hypochlorous Acid is the strongly disinfecting and oxidizing form of chlorine so is all I will write about (as opposed to hypochlorite ion). The chlorinated isocyanurates show little if any disinfecting capability and minimal oxidation power. The above equation is described by a chemical equilibrium constant as shown by the following:

$$[H_2CY^-] * [HOCl] / [HClCY^-] = 10^{-5.62} = 2.4 \times 10^{-6}$$

At 3.5 ppm Free Chlorine (FC), this is equivalent to  $4.9 \times 10^{-5}$  moles/liter concentration while 30 ppm CYA is  $2.3 \times 10^{-4}$  concentration. Since the CYA concentration is much higher than the FC concentration, even if all the chlorine could attach to CYA via the above equation, the net effect is that the total amount of "chlorine bound to CYA" can't be more than the amount of FC and the  $H_2CY^-$  does not drop very much. Rearranging, we have:

$$[HOCl] = 2.4 \times 10^{-6} * [HClCY^-] / [H_2CY^-]$$

Hypochlorous acid (HOCl) is also in equilibrium with hypochlorite ion ( $OCl^-$ ) where at a pH of 7.5 this is roughly split 50/50 between these two species. So we can rewrite the above in terms of measured concentrations as follows where CYA and FC are total concentrations:

$$FC = [HOCl] + [OCl^-] + [HClCY^-]$$

$$CYA = [H_2CY^-] + [HClCY^-]$$

$$[HOCl] = 2.4 \times 10^{-6} * ([FC] - [HOCl] - [OCl^-]) / ([CYA] - [HClCY^-])$$

and at a pH near 7.5,

$$[HOCl] = 2.4 \times 10^{-6} * ([FC] - 2*[HOCl]) / ([CYA] - [FC] + 2*[HOCl])$$

For practical purposes, because CYA is much larger than FC, the  $HClCY^-$  can be initially ignored in the above. The above equation implies that the HOCl concentration must be very small and that most of the chlorine is bound to CYA. The following is an approximation we can test:

$$[HOCl] \text{ is approximately } 2.4 \times 10^{-6} * [FC] / [CYA]$$

The chlorine values of [HOCl] and [FC] can be measured in the same units (as they are on both sides of the equation so any factors cancel), but we can convert the [CYA] concentration into ppm by multiplying the right hand side (numerator) by the molecular weight of CYA, 129.075 g/mole, and 1000 mg/g (multiplying the denominator by this number converts CYA into ppm) resulting in:

$$\text{HOCl is approximately } 0.3 * \text{FC} / \text{CYA}$$

The above approximation isn't terribly far off from the accurate calculation. At an FC of 3.5 ppm and a CYA of 30 ppm, the actual HOCl is 0.051 ppm while the above approximation gives 0.035 ppm. You can see where the FC/CYA ratio comes from -- it is a direct result of the chemical equilibrium between chlorine attached to CYA vs. separate chlorine and CYA. A more accurate approximation is given by modification of the formula not removing the [FC] term in the denominator (which results in a factor that is the ratio of CYA and Cl<sub>2</sub> molecular weights):

$$\text{HOCl is approximately } 0.31 * \text{FC} / (\text{CYA} - (1.8 * \text{FC}))$$

$$\text{or } 0.31 * (\text{FC}/\text{CYA}) / (1 - (1.8 * (\text{FC}/\text{CYA})))$$

which with the FC of 3.5 ppm and CYA of 30 ppm results in 0.046 which is within 10% of the correct result. However, the above approximation falls apart rather quickly when the CYA/FC ratio is less than 5 and it is still pH dependent (the assumptions were at a pH of 7.5 for the dominant species which determines the equilibrium constant).

At a pH of 7.5, there is roughly an equal amount of hypochlorous acid and hypochlorite ion so the 3.5/30 ratio of 0.117 is close to the FC that produces the same amount of hypochlorous acid if there was no CYA, namely 0.106. The following table shows how the FC/CYA ratio can be used as a reasonable proxy for FC with no CYA when the pH is near 7.5.

<b>FC as % of CYA</b>	<b>FC/CYA</b>	<b>Equivalent FC with no CYA (based on 30 ppm CYA)</b>	<b>Equivalent FC with no CYA (based on 50 ppm CYA)</b>	<b>Equivalent FC with no CYA (based on 100 ppm CYA)</b>	<b>2.06 * 0.31 * (FC/CYA) / (1 - (1.8 * (FC/CYA)))</b>
1%	0.01	0.0075	0.0075	0.0076	0.0065
2%	0.02	0.0152	0.0153	0.0154	0.013
5%	0.05	0.0396	0.0400	0.0404	0.034
10%	0.10	0.0854	0.0866	0.0874	0.078
20%	0.20	0.202	0.206	0.208	0.20
30%	0.30	0.36	0.37	0.38	0.42
40%	0.40	0.60	0.62	0.64	0.91
50%	0.50	0.92	0.98	1.02	3.2
60%	0.60	1.39	1.50	1.61	N/A

FC as % of CYA	FC/CYA	Equivalent FC with no CYA (based on 30 ppm CYA)	Equivalent FC with no CYA (based on 50 ppm CYA)	Equivalent FC with no CYA (based on 100 ppm CYA)	$2.06 * 0.31 * (FC/CYA) / (1 - (1.8 * (FC/CYA)))$
70%	0.70	2.03	2.27	2.50	N/A
80%	0.80	2.89	3.35	3.88	N/A
85%	0.85	3.41	4.05	4.84	N/A
90%	0.90	4.00	4.87	6.02	N/A
95%	0.95	4.66	5.81	7.49	N/A
100%	1.00	5.38	6.90	9.30	N/A

You can see from the above that a constant FC/CYA ratio results in the same hypochlorous acid concentration (or equivalent FC with no CYA which is about double at pH 7.5) independent of CYA level (from 30 to 100 ppm) even when the FC as a % of CYA is up to around 50% at which point the error is around 10% of the hypochlorous acid concentration (or equivalent FC with no CYA). This is why 3 ppm FC with 30 ppm CYA is the same as 6 ppm FC with 60 ppm CYA is the same as 10 ppm FC with 100 ppm CYA. **As the CYA level climbs, the FC must also be increased proportionately in order for the hypochlorous acid concentration to remain constant.**

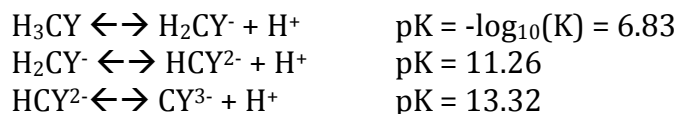
The FC/CYA ratio itself as a proxy for the equivalent FC is a rough guide when the ratio is 20% or less, but you can see that it's only rough since 1 ppm FC at 100 ppm CYA is not equivalent to 0.0100 but rather to 0.0076 ppm. Nevertheless, it does give an order-of-magnitude sense for the effect of CYA. The more accurate formula shown in the last column, still based on the FC/CYA ratio (the 2.06 factor converts HOCl to equivalent FC at a pH of 7.5), is reasonably accurate up to an FC/CYA ratio of 30%.

### Complex Chemical Equations

So how can one conclude what the dominant species are since that is the assumption I started with above? Let's look at the detailed equations and go through a process of elimination based on the pH. We'll start with the easier case to analyze, namely CYA and its dissociated species. Some of the following equations use an adjusted equilibrium constant for the ionic strength in typical pool water at 300 ppm CH, 100 ppm TA, 30 ppm CYA and 525 ppm TDS. All of the equilibrium constants come from the 1974 O'Brien paper, but you can also see these constants (with some minor errors due to using slightly different sources) in the following link

<http://www.epa.gov/hpv/pubs/summaries/tricltrz/c14659rr.pdf>

on document page 12 ( PDF page 18 ).



Let's take a look at the first reaction's equilibrium expression:

$$[\text{H}^+] * [\text{H}_2\text{CY}^-] / [\text{H}_3\text{CY}] = 10^{-6.83}$$

Taking the negative  $\log_{10}$  of both sides gives:

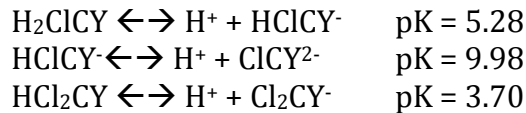
$$\begin{aligned} \text{pH} - \log_{10}([\text{H}_2\text{CY}^-] / [\text{H}_3\text{CY}]) &= \text{pK} \\ \log_{10}([\text{H}_2\text{CY}^-] / [\text{H}_3\text{CY}]) &= \text{pH} - \text{pK} \end{aligned}$$

So from the above, and generalizing, one can see that when  $\text{pH} < \text{pK}$  then the ratio in the  $\log_{10}$  is less than 1 while when  $\text{pH} > \text{pK}$  the ratio in the  $\log_{10}$  is greater than 1. So this means that at a pH of 7.5, the following are true:

$$\begin{aligned} [\text{CY}^{3-}] &\ll [\text{HCY}^{2-}] \\ [\text{HCY}^{2-}] &\ll [\text{H}_2\text{CY}^-] \\ [\text{H}_2\text{CY}^-] &> [\text{H}_3\text{CY}] \end{aligned}$$

So this is where we get our initial assumption of  $\text{H}_2\text{CY}^-$  being the dominant cyanurate species where we can see that the next most dominant cyanurate species is  $\text{H}_3\text{CY}$ .

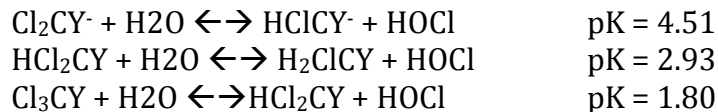
For the chlorinated isocyanurates, we have the following (the pK are adjusted for ionic strength):



where we can conclude the following at a pH near 7.5:

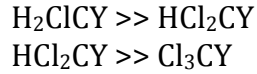
$$\begin{aligned} \text{HClCY}^- &\gg \text{H}_2\text{ClCY} \\ \text{ClCY}^{2-} &\ll \text{HClCY}^- \\ \text{Cl}_2\text{CY}^- &\gg \text{HCl}_2\text{CY} \end{aligned}$$

So of the above species,  $\text{HClCY}^-$  and  $\text{Cl}_2\text{CY}^-$  are dominant, but we cannot yet tell which is more dominant between these two. There are additional chemical equations relating to the interaction of chlorine with the chlorinated isocyanurates as follows:



Because the HOCl concentration is relatively small ( $\text{pHOCl} > 4.6$ ; actually  $> 6$ ), this implies the following:

$$\text{HClCY}^- > \text{Cl}_2\text{CY}^-$$

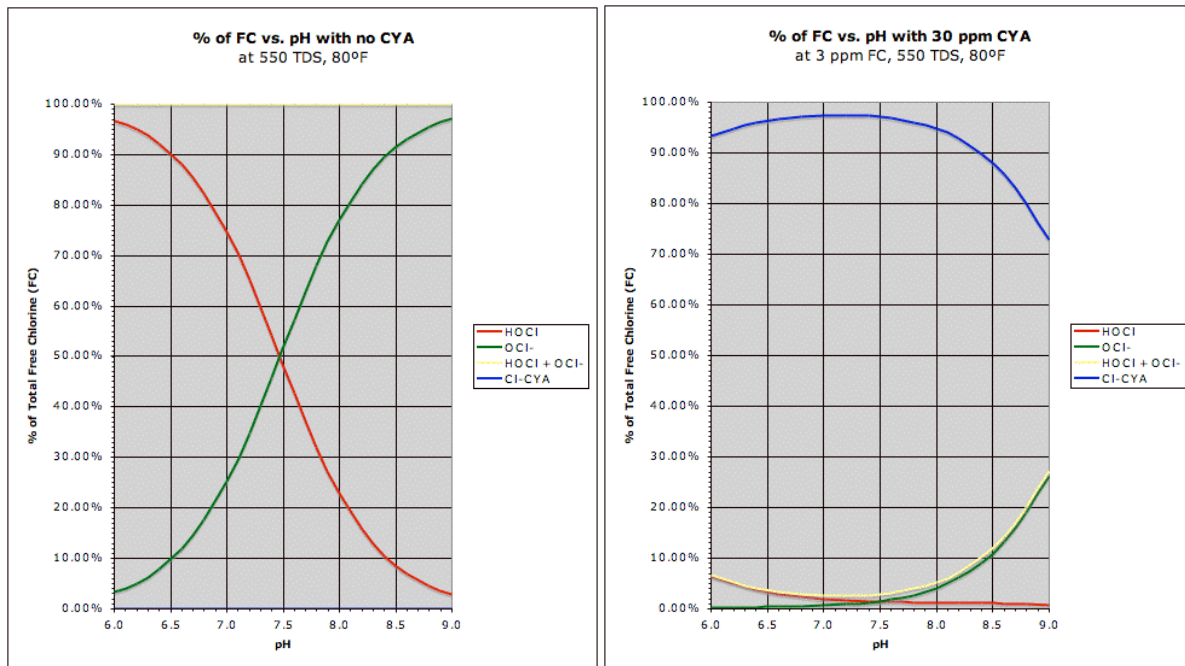


So the assumption that  $HClCY^-$  is the dominant chlorinated isocyanurate species is reasonable and the next most dominant chlorinated isocyanurate species is  $Cl_2CY^-$ .

In spite of the above equilibrium, the rate of release of chlorine from CYA is rather fast (see the half-life constants in the aforementioned EPA link) so all of the chlorine attached to CYA measures as FC in the FC test because the  $HOCl$  gets used up reacting with the dye in the test and more  $HOCl$  is released from that attached to CYA (or is converted from hypochlorite ion) in the time of the test. Essentially, the FC test mostly measures the amount of chlorine in “reserve” and does not measure the amount of active disinfecting and oxidizing chlorine alone.

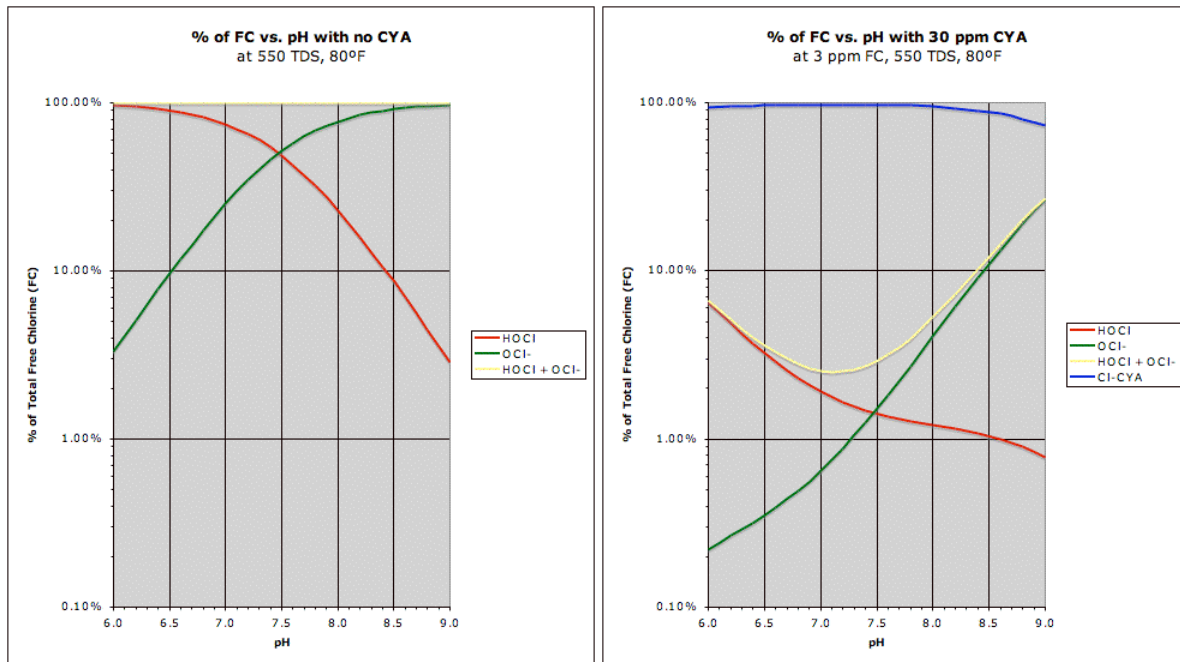
### Graphs of Chlorine vs. pH

The traditional industry graph showing hypochlorous acid and hypochlorite ion as a function of pH is incorrect in the presence of Cyanuric Acid (CYA). The traditional graph and the correct graph when CYA is present are shown below:



Since it is hard to see the proportional effects of pH, the following are the equivalent graphs using a log scale for FC concentration:





If you look carefully, you will see that the log graph on the right is the same as shown in the O'Brien paper in Figure 14.5 on page 352 except that my pH range is narrower and I have combined multiple chlorinated cyanurate species into one "Cl-CYA" curve. In particular, the shape of the HOCl (red) and OCl<sup>-</sup> (green) curves is the same as in the O'Brien paper. This, of course, is not a surprise since I used the O'Brien equilibrium constants to generate the graph from a spreadsheet that computes chemical species concentration.

The above graphs show that CYA buffers hypochlorous acid such that the effect of pH on hypochlorous acid level is not as strong as without CYA (i.e. the red curve is more "flat", especially above pH 7.5).

### Effects of Cyanuric Acid on Disinfection and Oxidation

Though the above chemistry demonstrates the very low level of hypochlorous acid in the presence of Cyanuric Acid (CYA), how do we know that chlorine attached to CYA is not as effective? There have been numerous scientific studies to answer this question so let's look at ones readily available online and most being free of charge.

If one calculates the hypochlorous acid concentration when there is hard data for kill times (not just "< 30 seconds"), one is able to predict the kill times within a factor of 2 in most cases thus demonstrating that hypochlorous acid is the primary disinfecting agent and that the chlorinated isocyanurates have a much diminished capacity except as a reservoir for hypochlorous acid.

## Bacteria

The following four papers published from 1965 to 1969 show the significant reduction in bacterial kill times when chlorine is in the presence of Cyanuric Acid (CYA). Note that the fourth reference demonstrates how ammonia in water reduces some of the apparent effect of CYA on chlorine kill rates, most likely due to the formation of monochloramine which is not moderated in strength by CYA (though is a less powerful bactericide than hypochlorous acid). It should also be noted that the presence of organic matter in the water can consume chlorine such that low FC levels can become ineffective. This is where CYA can become helpful, where higher FC levels can be used to not “run out” of chlorine while having moderated strength in spite of the higher FC level.

<http://www.pubmedcentral.nih.gov/picrender.fcgi?artid=1256554&blobtype=pdf>

<http://www.pubmedcentral.nih.gov/picrender.fcgi?artid=377704&blobtype=pdf>

<http://www.pubmedcentral.nih.gov/picrender.fcgi?artid=546955&blobtype=pdf>

<http://www.pubmedcentral.nih.gov/picrender.fcgi?artid=1227093&blobtype=pdf>

## Viruses

The following 1988 paper demonstrates the significant reduction in virus activation time when chlorine is in the presence of Cyanuric Acid (CYA).

<http://www.jstor.org/pss/3863297>

## Protozoan Oocysts

The following two papers in 1983 and 2009 demonstrate the significant reduction in inactivation of protozoan oocysts when chlorine is in the presence of Cyanuric Acid (CYA).

<http://www.pubmedcentral.nih.gov/picrender.fcgi?artid=239534&blobtype=pdf>

<http://www.iwaponline.com/jwh/007/jwh0070109.htm>

## Algae

The following 1981 paper does not demonstrate any significant affect of Cyanuric Acid (CYA) on chlorine effectiveness against killing algae. This is not only inconsistent with all previous studies as shown above, but it is inconsistent with the experience of over 20,000 (mostly residential) pool owners reporting at The PoolForum and over 10,000 pool owners reporting at Trouble Free Pool where the chlorine/CYA relationship has successfully kept these pools free of algae using chlorine alone. I can only speculate that the growth media used to culture the algae may have contained ammonia-like compounds that created

compounds (such as monochloramine) that inhibited algae growth and were not affected by CYA level.

<http://www.pubmedcentral.nih.gov/picrender.fcgi?artid=241858&blobtype=pdf>

### Organics

The following 2001 paper demonstrates that for the oxidation of monochlorodimedone (MCD), the rates with chlorinated cyanurates were estimated to be 1/150<sup>th</sup> that of the free chlorine solution (hypochlorous acid plus hypochlorite ion; mostly the former as the pH was 7.0).

[http://dx.doi.org/10.1016/S0043-1354\(01\)00482-1](http://dx.doi.org/10.1016/S0043-1354(01)00482-1)

U.S. Patent 5,591,692 issued in 1997 and assigned to Bio-Lab (now part of Chemtura) demonstrates a significant reduction in the rate or production of chloroform (trihalomethane, THM) from humic acid reacting with chlorine when either Cyanuric Acid or glycoluril was present. Glycoluril is very similar to CYA in that it binds to chlorine, but does so somewhat more strongly than CYA.

<http://www.google.com/patents?vid=USPAT5591692>

### Real-Pool Studies on Disinfection and ORP

Though some of the scientific studies noted above used real pool water in addition to chlorine demand-free water, there has been a controversy in the industry as to whether the chemistry of chlorine and CYA applies to “real pools”. The following two studies using real pools attempt to answer this question.

#### Pinellas County, Florida Pool Study 1992 (1994)

The following is a link to the main page for the Pinellas study with links under the heading “Florida Study Details Microbicidal Properties of Chlorine”.

<http://www.nspf.com/Research Archives.html>

One of the conclusions of this study was that Free Chlorine (FC) had by far more influence on the bacteria populations (disinfection conditions) than any other variable. However, the study did not look specifically at calculated hypochlorous acid concentration so I decided to do that myself. First, I put all of the raw data into a spreadsheet which can be viewed in HTML at the following link:

<http://richardfalk.home.comcast.net/pool/Pinellas.htm>

I extracted relevant columns of data and sorted by Free Chlorine (FC) and by calculated hypochlorous acid (HOCl) concentrations as shown in the following links and highlighted in red the bacteria and algae counts that were considered to be a problem according to study criteria.

<http://richardfalk.home.comcast.net/pool/PinellasFC.htm>

<http://richardfalk.home.comcast.net/pool/PinellasHOCl.htm>

To see the effects of FC and calculated HOCl, I reorganized the data into groups increasing in a logarithmic fashion. Let's first look at the data using FC. Due to space limitations, I only show bacteria and not algae, but the algae data didn't make any sense anyway with only 4 pools with green algae and that pools with no FC and high bacterial counts had no green algae.

Count	FC	HPC	TCOLI	FCOLI	NCOLI	PSEUD	TSTAPH	FSTREP
49	< 0.1	48.98%	36.73%	20.41%	57.14%	6.12%	6.12%	2.04%
4	0.1-0.19	25.00%	0.00%	0.00%	75.00%	0.00%	0.00%	0.00%
14	0.2-0.39	14.29%	7.14%	7.14%	14.29%	7.14%	28.57%	0.00%
35	0.4-0.79	8.57%	11.43%	5.71%	20.00%	2.86%	11.43%	0.00%
44	0.8-1.59	9.09%	6.82%	4.55%	9.09%	2.27%	2.27%	0.00%
111	1.6-3.19	4.50%	6.31%	4.50%	9.01%	0.00%	7.21%	0.00%
189	3.2-6.39	4.76%	5.82%	3.70%	12.17%	0.00%	3.17%	0.53%
29	6.4-12.79	0.00%	6.90%	3.45%	0.00%	0.00%	3.45%	0.00%
11	> 12.8	0.00%	9.09%	0.00%	0.00%	0.00%	0.00%	0.00%
486	Overall	9.88%	9.67%	5.76%	15.84%	1.23%	5.56%	0.41%

You can see an S-curve like effect where a threshold FC roughly at 0.2 results in a significant drop in the percentage of pools with bacteria counts, though there is no level of chlorine that has no counts whatsoever though pool #318 had an HPC of 31000 and an NCOLI of 320 (and 2 TSTAPH) and yet had 5 ppm Free Chlorine (FC) with a pH of 7.2 and no Cyanuric Acid. So there are clearly no absolutes.

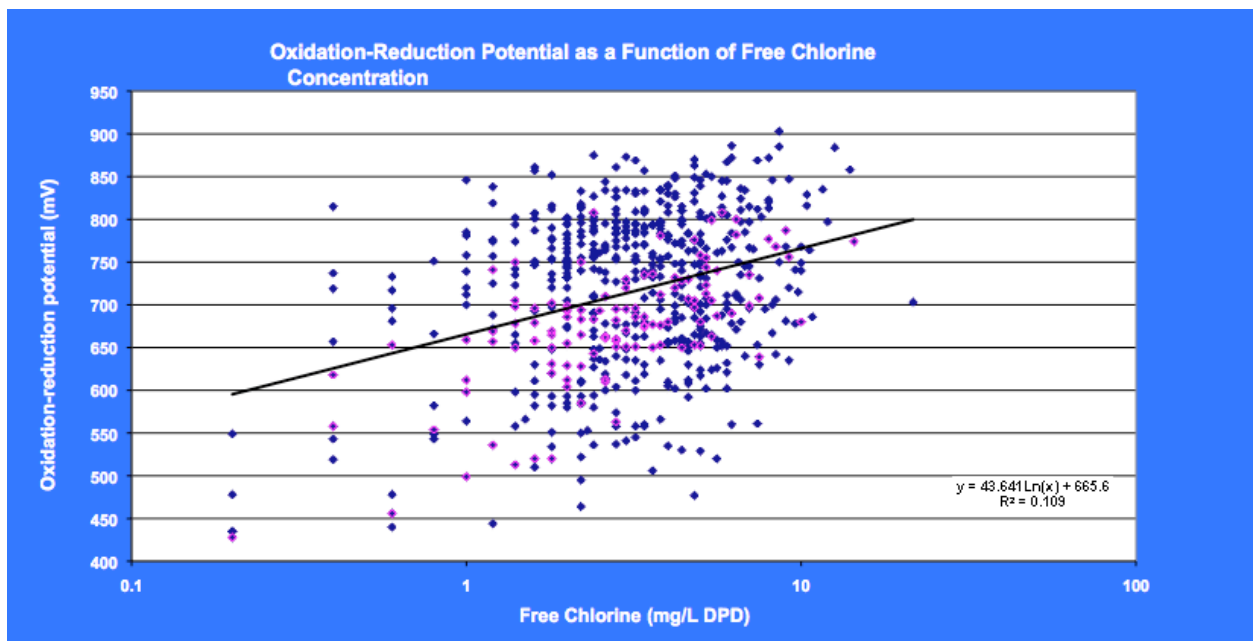
Now let's look at something the report didn't examine - calculated hypochlorous acid concentration.

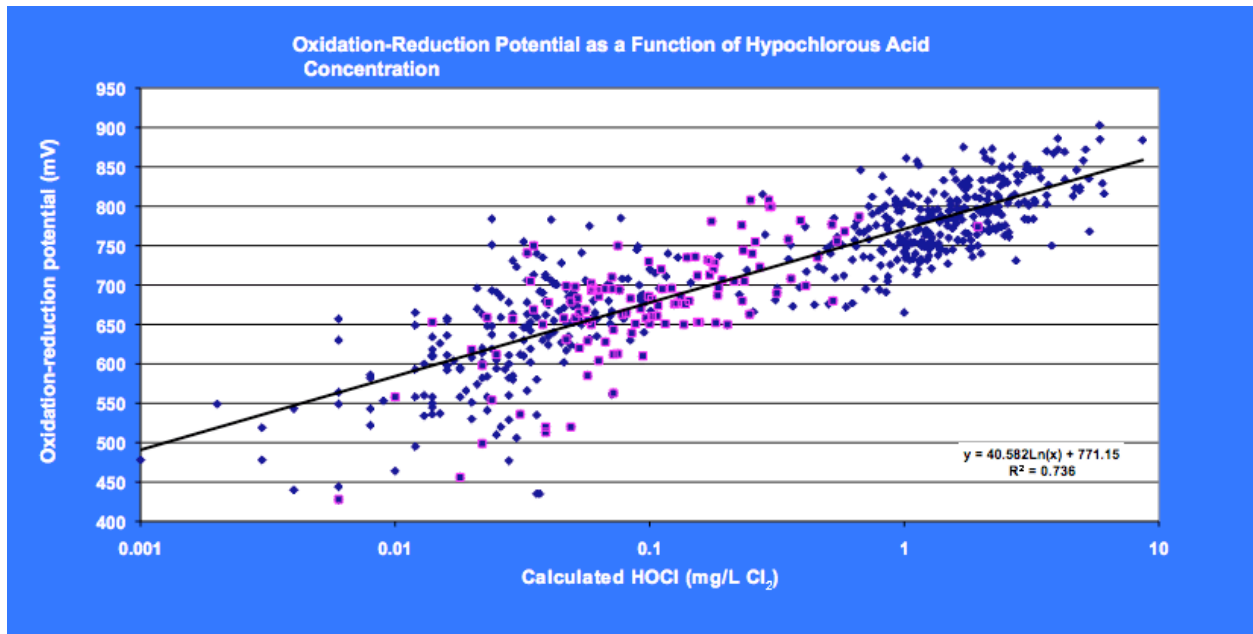
Count	HOCl	HPC	TCOLI	FCOLI	NCOLI	PSEUD	TSTAPH	FSTREP
58	< 0.001	43.10%	31.03%	17.24%	51.72%	5.17%	5.17%	1.72%
10	0.001-0.0019	30.00%	20.00%	20.00%	50.00%	0.00%	10.00%	0.00%
22	0.002-0.0039	9.09%	4.55%	4.55%	9.09%	0.00%	13.64%	0.00%
44	0.004-0.0079	2.27%	13.64%	6.82%	13.64%	4.55%	9.09%	0.00%
92	0.008-0.0159	7.61%	6.52%	3.26%	9.78%	0.00%	2.17%	0.00%
94	0.016-0.0319	4.26%	5.32%	2.13%	12.77%	0.00%	6.38%	1.06%
55	0.032-0.0639	3.64%	3.64%	3.64%	3.64%	0.00%	0.00%	0.00%
28	0.064-0.1279	0.00%	0.00%	0.00%	7.14%	0.00%	0.00%	0.00%
83	>0.128	4.82%	8.43%	6.02%	10.84%	1.20%	9.64%	0.00%
486	Overall	9.88%	9.67%	5.76%	15.84%	1.23%	5.56%	0.41%

Here you can see an even steeper S-curve effect at a very low chlorine level of around 0.002 ppm HOCl which at a pH near 7.5 is an FC of 0.004 ppm with no CYA. Basically, what appears to be going on is that it takes an incredibly low chlorine level to kill most bacteria faster than they can grow so one cannot really conclude that FC is the most influential variable since one could just as readily conclude that it is HOCl instead. Most heterotrophic bacteria have a CT value (chlorine concentration in ppm times time in minutes) for a 99% (2-log) kill of around 0.08 and this is equivalent to a 50% kill CT value of  $\log_{10}(1/0.5) * 0.08 / 2 = 0.012$ . Bacterial generation time (the time it takes to double in population) is from 15 to 60 minutes so using 15 minutes this means it would take only  $0.012 / 15 = 0.0008$  ppm FC to kill bacteria faster than they can reproduce. Since real pool water has slower kill times than lab conditions, the study results are not surprising and the main point is still the same – most of the common bacteria are incredibly easy to kill (in general) so the study results in reality were inconclusive with respect to FC vs. calculated HOCl (or even FC/CYA which they also didn't look at).

### Oxidation-Reduction Potential (ORP)

The graphs below were taken from 620 samples from 194 commercial/public pools and spas with the data collected by Jeff Luedeman in Bloomington and Richfield, Minnesota. There's a lot of scatter and outliers (a small amount of variation is from the different pH), but the basic trend is pretty obvious. In the lower graph, the diamonds to the upper right are unstabilized pools, the diamonds to the lower left are stabilized pools, and the squares with the red borders are stabilized pools with CYA < 30 so 15 ppm was used in the calculations. (The first graph says "DPD" for the Free Chlorine axis, but in fact a FAS-DPD test from the Taylor K-2006C kit was used).





It should be pretty obvious that ORP is more highly correlated with hypochlorous acid concentration than with Free Chlorine (FC) alone.

### Side Effects of Chlorine Sources

Cyanuric Acid (CYA) is a double-edged sword. On the one hand, it protects chlorine from rapid breakdown in sunlight and it also moderates chlorine's strength, but on the other hand too much CYA can moderate that strength to lower kill rates and oxidation to an unacceptable level, especially for preventing algae growth. The use of stabilized chlorine can build up CYA fairly rapidly. The following are chemical facts that are indisputable and based on the core chemistry where chlorine measurements are in units of ppm  $\text{Cl}_2$ .

For every 10 ppm Free Chlorine (FC) added by Trichlor, it also increases Cyanuric Acid (CYA) by 6.1 ppm.

For every 10 ppm FC added by Dichlor, it also increases CYA by 9.1 ppm.

For every 10 ppm FC added by Cal-Hypo, it also increases Calcium Hardness (CH) by at least 7.1 ppm.

For every 10 ppm FC, all sources of chlorine add 8.2 ppm salt as the chlorine converts to chloride when it gets used up (oxidizing organics, killing pathogens, breaking down from sunlight). Chlorinating liquid, bleach and lithium hypochlorite add an additional 8.2 ppm salt while Cal-Hypo adds around 2 ppm additional salt.

A simple calculation shows that even at a low 1 ppm FC per day chlorine usage, continued use of Trichlor will increase CYA by over 100 ppm in 6 months if there is no water dilution. Using Cal-Hypo will increase CH by nearly 130 ppm in 6 months. All sources of chlorine will increase salt levels by at least 150 ppm in 6 months with chlorinating liquid, bleach and lithium hypochlorite increasing salt at double this rate. Most outdoor residential pools

without pool covers have chlorine usage closer to 2 ppm FC per day and even weekly backwashing of sand filters is not enough to dilute the water except in the smallest of pools.

There is no product labeling nor documentation of the above chemical facts and such information is not taught in NSPF CPO nor APSP TECH courses other than a vague qualitative description of how stabilized chlorine can lead to a buildup of CYA and that Cal-Hypo increases CH. The issue is not so much having to do with safety (except, perhaps, for person-to-person transmission risk) since it has already been shown how easy it is to kill most bacteria with very low levels of chlorine (that is, low FC/CYA ratios), but algae is much harder to kill so continued use of stabilized chlorine without supplemental algaecides or phosphate removers can lead initially to nascent non-visible algae growth that appears as a mysterious chlorine demand before eventually showing as an algae bloom.

The swimming pool industry only talks about how CYA protects chlorine from sunlight so does not consider its positive and negative effects as a chlorine buffer moderating chlorine's strength. The general recommendation of not using any CYA at all in indoor pools or spas leads to inconsistent sanitation with active chlorine (hypochlorous acid) concentrations in indoor pools and spas being 5-20 times or more higher than in most pools using CYA. This has implications for oxidation of swimsuits, skin and hair, corrosion rates, and for production of nitrogen trichloride as described below.

### Breakpoint Chlorination Models and Cyanuric Acid Effects on Nitrogen Trichloride

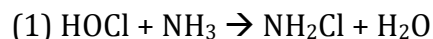
The basic breakpoint reaction was described by Griffin (1939), but the first reasonable detailed model was proposed by Wei & Morris (1974 -- in Chapter 13 in the same "Chemistry of Water Supply, Treatment and Distribution" book that has the O'Brien paper on the chlorine/CYA equilibrium constants). Subsequent improvements were made to the model by Saunier & Selleck (1976) and most recently by Jafvert & Valentine (1992) which should be considered to be the best model to-date. The following is the following paper

Chad T. Jafvert and Richard L. Valentine, "Reaction Scheme for the Chlorination of Ammoniacal Water", Environ. Sci. Technol., Vol. 26, No. 3, 1992, pp. 577-585.

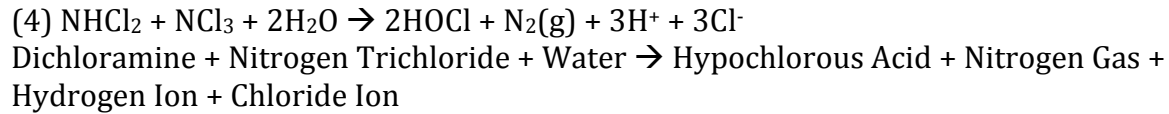
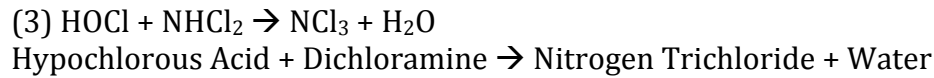
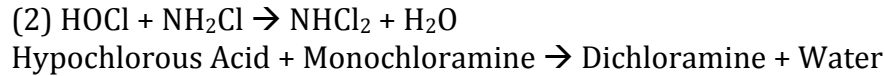
A link to be able to purchase this paper is the following:

<http://pubs.acs.org/doi/abs/10.1021/es00027a022>

Though the model lists 14 reactions, including both forward and reverse reaction rates, the dominant reactions are the following:



Hypochlorous Acid + Ammonia  $\rightarrow$  Monochloramine + Water



The first reaction producing monochloramine is by far the fastest. It is over 95% complete in one minute when the FC is around 10% of the CYA and the ammonia is much less than the chlorine so that the chlorine level remains fairly constant. With no CYA, the reaction is mostly complete in a couple of seconds. The subsequent reactions are far slower.

You can then see that hypochlorous acid participates in two reactions (after initially producing monochloramine), one producing dichloramine and another producing nitrogen trichloride. So the net reaction going from monochloramine to nitrogen trichloride takes two hypochlorous acid and this net reaction rate varies as the square of the hypochlorous acid concentration. You can see that nitrogen trichloride is broken down by dichloramine and the latter is produced with a reaction rate that varies linearly with hypochlorous acid concentration. So in the steady state, the amount of nitrogen trichloride is linearly dependent on the hypochlorous acid concentration. This can also be seen by the following rate reaction balance at steady state.

$$k_3[\text{HOCl}][\text{NHCl}_2] = k_4[\text{NHCl}_2][\text{NCl}_3]$$

Rate of formation of Nitrogen Trichloride = Rate of destruction of Nitrogen Trichloride

so,  $k_3[\text{HOCl}] = k_4[\text{NCl}_3]$

**The nitrogen trichloride concentration in the steady state is linearly proportional to the hypochlorous acid concentration.** Since nitrogen trichloride is very volatile, this implies that the rate of outgassing of nitrogen trichloride may be proportional to the hypochlorous acid concentration since the outgassing rate is likely to be proportional to its concentration in the water.

A similar rate reaction balance for dichloramine gives the following.

$$k_2[\text{HOCl}][\text{NH}_2\text{Cl}] = k_3[\text{HOCl}][\text{NHCl}_2] + k_4[\text{NHCl}_2][\text{NCl}_3]$$

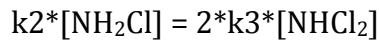
Rate of formation of Dichloramine = Rate of destruction of Dichloramine

and substituting the earlier steady-state equation we have

$$k_2[\text{HOCl}][\text{NH}_2\text{Cl}] = k_3[\text{HOCl}][\text{NHCl}_2] + k_3[\text{HOCl}][\text{NHCl}_2]$$

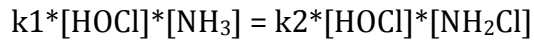
which reduces to





So **the ratio of monochloramine to dichloramine is constant and independent of hypochlorous acid concentration.**

We can look at the steady-state for monochloramine assuming a constant introduction of ammonia into the water.



Rate of formation of Monochloramine = Rate of destruction of Monochloramine

so **the ratio of ammonia to monochloramine is constant and independent of hypochlorous acid concentration.** Finally, we can look at the steady-state for ammonia.



Rate of formation of Ammonia = Rate of destruction of Ammonia

which says that for a constant rate of introduction of ammonia, **the amount of ammonia, and therefore monochloramine and dichloramine (from above), are inversely proportional to the hypochlorous acid concentration.**

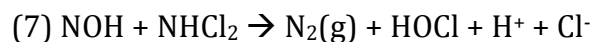
Earlier models had reactions forming an intermediate, and the Jafvert & Valentine model has this as well, but it is not the dominant reaction in that model. The following shows the intermediate reactions such as found with Wei & Morris.



Dichloramine + Water  $\rightarrow$  Intermediate + Hydrogen Ion + Chloride Ion



Intermediate + Monochloramine  $\rightarrow$  Nitrogen Gas + Water + Hydrogen Ion + Chloride Ion



Intermediate + Dichloramine  $\rightarrow$  Nitrogen Gas + Hypochlorous Acid + Hydrogen Ion + Chloride Ion

In the Wei & Morris model, there is no destruction of nitrogen trichloride, so its rate of production is the product of the hypochlorous acid concentration and the dichloramine concentration. In the above, reaction (7) is more dominant than reaction (6). The formation of the intermediate NOH is a rate limiting step so dichloramine is built up and therefore the rate of production of nitrogen trichloride is linearly dependent on the hypochlorous acid concentration.

For a realistic example, consider a pool with 3 ppm FC and no CYA vs. a pool with 3 ppm FC and 30 ppm CYA. Both are at a pH of 7.5 (there is far more nitrogen trichloride produced at lower pH) and the temperature is 77F. If it is assumed that the chlorine level is maintained

at a constant level and that there is a constant introduction of ammonia in the water at a rate of 0.1 ppm N per hour, then we have the following steady state amount using Jafvert & Valentine in a spreadsheet I made in the following link

<http://richardfalk.home.comcast.net/~richardfalk/pool/Breakpoint.xls>

#### OXIDATION OF AMMONIA

SPECIES	NO CYA	30 ppm CYA
Monochloramine	0.02 ppm	0.70 ppm
Dichloramine	2.97 ppb	85.42 ppb
Nitrogen Trichloride	70.96 ppb	2.35 ppb

You can see from the above that **with no CYA in the water, there is less monochloramine and dichloramine but more nitrogen trichloride compared to having CYA in the water.** The differences are roughly a factor of the CYA level because that is roughly the difference in the hypochlorous acid concentration (the breakpoint chlorination spreadsheet assumes 3 ppm FC with 30 ppm CYA results in about 0.05 ppm hypochlorous acid at pH 7.5 -- the actual amount is closer to 0.042 ppm). Nitrogen trichloride is the most volatile and irritating. The monochloramine odor threshold is 0.65 ppm (650 ppb); for dichloramine it is 100 ppb; for nitrogen trichloride it is 20 ppb. The equilibrium concentrations in air for monochloramine and dichloramine are somewhat lower than that in water, but nitrogen trichloride is extremely volatile so will not saturate the air before becoming extremely noticeable and irritating.

The above is just for breakpoint chlorination of ammonia. As seen in Table 4.1 on document page 62 (PDF page 85) of the following link

[http://www.who.int/entity/water\\_sanitation\\_health/bathing/srwe2full.pdf](http://www.who.int/entity/water_sanitation_health/bathing/srwe2full.pdf)

urea has 68% of the nitrogen in sweat compared to 18% for ammonia while in urine it's 84% vs. 5%. There is no definitive model for oxidation of urea by chlorine, though some mechanisms have been proposed (by Wojtowicz) including the slow formation of a quad-chloro urea followed by rapid breakdown to dichloramine and nitrogen trichloride. If I repeat the above analysis using an 80%/20% split of urea to ammonia and assume a steady state buildup, then I get the following results.

#### OXIDATION OF UREA & AMMONIA

SPECIES	NO CYA	30 ppm CYA
Monochloramine	0.01 ppm	0.28 ppm
Dichloramine	1.19 ppb	34.17 ppb
Nitrogen Trichloride	70.84 ppb	2.35 ppb

You can see that the resulting nitrogen trichloride is the same as before, but that there is lower monochloramine and dichloramine by a factor of 2.5.

The rate of ammonia/urea introduction of 0.1 ppm N per hour is for heavy bather loads since it represents a chlorine usage of nearly 1 ppm FC per hour. One swimmer may produce around 0.1 ppm N per hour in 1000 gallons so only a pool with many people being active would have this sort of usage. Of course, having children in the water that urinate would provide a very high load. If a child urinates 100 ml (3.4 fluid ounces), then in 1000 gallons this is about 0.3 ppm N.

Since the UV in sunlight breaks down nitrogen trichloride fairly quickly and since air circulation is also good outdoors, the current recommendations for FC as a % of CYA are reasonable for outdoor pools. The slower breakpoint is not generally a problem unless the bather load is high. For commercial/public pools with higher bather loads, an FC that is 20% of the CYA level may be more appropriate. For indoor pools, the slower breakpoint might be more of an issue so perhaps an FC that is 20% of the CYA level may be better even when there is not high bather load in such pools. From the models, **not using any CYA at all in any pool (indoor or outdoor) can result in far higher irritating nitrogen trichloride concentrations and also has the chlorine level be too strong for outgassing of chlorine (mostly hypochlorous acid), corrosion of immersed metal and oxidizing of swimsuits, skin and hair.** Since it is not practical to maintain 0.2 ppm FC everywhere in an indoor pool due to local usage and imperfect circulation, using a small amount (20 ppm) of CYA as a hypochlorous acid buffer makes sense, but should not be overdone. To ensure sufficient oxidation rates, an FC of 4 ppm with 20 ppm CYA, which is equivalent to 0.2 ppm FC with no CYA, could be a reasonable balance between oxidation rates and a balance between monochloramine, dichloramine and nitrogen trichloride while still providing plenty of chlorine to not run out locally under bather load.

### Next Steps

Clearly, investigations on volatile chlorine disinfection by-products, including monochloramine, dichloramine and nitrogen trichloride, should include analysis of water (both in the lab and in real pools) using Cyanuric Acid (CYA) as well as those without. Unfortunately, all studies I have seen that have been done and that are currently in progress are not looking at CYA at all.

The EPA Swimming Pool Water Disinfectants standard, DIS/TSS-12, needs to be revised to reflect the effect of CYA. The current laboratory standard measures kill rates without any initial CYA in the water. Also, the EPA maximum limit of 4 ppm FC for swimming pools, which is based on drinking water standards, needs to be re-evaluated in light of CYA's moderation of chlorine's strength and the minimal skin absorption of CYA and, by extension, the chlorinated cyanurates as described in the following link:

<http://www.informapharmascience.com/doi/ref/10.3109/15569529309036260>

For ingestion, it is FC that matters independent of CYA, but the 4 ppm FC standard was based on drinking quarts of water every day and the amount of swimming pool water that is normally swallowed is a far smaller amount.