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What Bathers Put Into a Pool: A Critical Review of Body Fluids and a Body Fluid Analog

Wesley Lamont Bradford
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Bathers add inorganic and organic materials to pool water primarily via sweat and urine but also via sunscreens and cosmetics. The organic nitrogen (organic-N) compounds react with chlorine to form organic chloramines that have no biocidal effectiveness, volatile inorganic chloramines, and other oxidation products that create high combined chlorine measurements and chlorinous odors. Recent research on the reactions of free available chlorine (FAC) with organic-N components of body fluids and models of other organic-N compounds likely to be present in pool water is reviewed. One recipe for a body fluid analog (BFA) was found in model pool studies to reproduce a field-observed median chlorine demand of 5.5 g/standard bather and to contain a reduced nitrogen mass per average bather within the ranges of published estimates. Guidelines for the combined chlorine measurement are routinely exceeded in operating pools and in model pool studies even at modest bather loads simulated using the BFA recipe.

Keywords: swimming pools, body fluids, body fluid analog, chloramines, organic chloramines, nitrogen trichloride, chlorinous odors, organic nitrogen, combined chlorine

It is broadly recognized that bathers add salts (inorganic materials) and organic materials to pool water as sweat, urine, saliva, lotions, and residue from the skin and hair. The chemistry of the pool water is transformed by these materials, collectively called “body fluids.” The total dissolved solids (TDS; generally the inorganic salts) total organic carbon (TOC), inorganic nitrogen (ammonia nitrogen— $\text{NH}_3\text{-N}$), and organic nitrogen (organic-N) concentrations increase, and the disinfectant dosing (usually as chlorine) requirement to maintain an acceptable free available chlorine (FAC) and/or total chlorine (TC) concentration for public safety purposes increases.

Most pool operators also know that as the number of bathers using the pool in a day increases, the occurrence of chlorinous odors in the water and in the air above the pool increases as well. The chlorinous odors are the result of reactions

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between FAC and inorganic ($\text{NH}_3\text{-N}$) and organic nitrogen (organic-N) to form volatile chloramines, primarily dichloramine (NHCl_2) and trichloramine (aka nitrogen trichloride [NCl_3]). These compounds will be discussed in this paper in relation to specific known components of human body fluids and the expected and observed formation of inorganic and organic chloramines or decomposition products by their reactions with FAC.

Another issue with which pool operators must deal is the combined chlorine (CC) measurement,¹ the difference between the TC and FAC measurements ($\text{CC} = \text{TC} - \text{FAC}$). The TC and FAC measurements are usually performed using test kits that are adaptations of the DPD colorimetric method or the DPD-FAS titration method adapted from the American Public Health Association, American Water Works Association, and Water Environment Federation, (2005; hereafter Standard Methods, 2005) method numbers 4500-Cl G and 4500-Cl F, respectively. Because the chloramines (both inorganic and organic) are weaker disinfectants than FAC and are often associated with chlorinous odors in the pool, for both health and aesthetic reasons, public health departments having inspection or regulatory authority over public swimming pools place limits on the TC and CC measurements. Guidelines or enforceable regulations vary by state and locality. The National Swimming Pool Foundation (NSPF; 2009) guidelines on the CC measurement are 0.2 mg/L for pools and 0.5 mg/L for spas. These guidelines are routinely exceeded in operating pools, spas (see for example Weaver, Li, Wen, Johnston, Blatchley, & Blatchley III, 2009) and in model pool studies even at low simulated bather loads (Judd & Bullock, 2003).

For the purposes of modeling the chemistry of pool water to improve methods for managing the quality of the water and the air, and to recognize quantitatively the requirements for disinfectant dosing (i.e., satisfying the chlorine or oxidant demand) as a function of the numbers of bathers per unit time, it is necessary to have a recipe of chemicals that mimics the composition and average volume rate of input of body fluids into a pool by bathers.

The purpose of this paper is to critically review the published literature and guidelines on the composition and volume rate of input of body fluids by bathers and the relationship between body fluid components and the formation of inorganic and organic chloramines, and products from the decomposition reactions between FAC and individual body fluid components.

A Body Fluid Analog

One recipe that mimics the composition of fluids in sweat and urine—the liquids exuded from bathers into a swimming pool—is given in Table 1 (Judd & Black, 2000). This body fluid analog (BFA) as presented is a concentrated solution; 25 mL represents one adult bather doing normal activities (playing, lap swimming) for one hour. The masses of each component and the TOC and reduced nitrogen added by one bather are calculated.² This recipe had been developed earlier and was used by Judd and Black (2000) for studies in model pools. The components consist of both inorganic salts that add to the TDS of the pool water, and several organic compounds of metabolic origin, some of which are amino acids as well as metabolic products containing nitrogen.

Table 1 Components of the BFA and Masses Exuded by One Average Bather

BFA Component	BFA Concentration	Mass/Average Bather	Total Organic Carbon (TOC)	Reduced Nitrogen (N)
	g/L	mg	mg	mg
NaCl	17.14	429	0	0
Na ₂ HPO ₄	8.62	216	0	0
Na ₂ SO ₄	6.14	154	0	0
NaHCO ₃	2.24	56.0	0	0
KCl	9.26	232	0	0
CaCl ₂	1.32	33.0	0	0
MgCl ₂	1.77	44.3	0	0
Ammonia (NH ₃)	4.08	102.0	0	84.0
Urea	29.6	740.0	148.0	345.2
Creatinine	3.62	90.5	38.4	33.6
Histidine	2.42	60.5	28.1	16.4
Hippuric acid	3.42	85.5	51.6	6.69
Uric acid	0.98	24.5	8.75	8.17
Citric acid	1.24	31.0	11.6	0
Totals			286.5	494.1

BFA recipe from Judd & Bullock (2003); calculations by the author.

By this recipe, one bather in one hour of normal swimming exudes **0.494 g** of reduced nitrogen (i.e., NH₃-N and organic-N compounds): 0.410 g of organic-N, mostly (0.345 g) as urea and (0.084 g) NH₃-N. One bather also adds 0.287 g organic carbon in one hour of normal swimming. The baseline of normal swimming is taken to be leisurely lap swimming. Experiments by Keuten, Peters, Daanen, de Kreuk, Rietveld, & van Dijk (2014) indicate that the nonpurgeable carbon (effectively the TOC) is much higher, however, up to 500 mg per standard bather due to previously unnoticed loss of lipids (sebum) from the skin.

Estimates of inputs of reduced nitrogen and urea vary. Weaver et al. (2008) cite World Health Organization (WHO) guidelines that are in general agreement with this recipe in that the major component containing organic nitrogen in both sweat and urine is urea; creatinine and other amino acids also are present but in smaller amounts and supply smaller amounts of organic-N. De Laat, Feng, Freyfer and Dossier-Berne (2011) cite earlier work indicating that a single bather exudes about **0.85 g** organic-N suggesting that the recipe in Table 1 may be deficient in -N-. De Laat et al. (2011) also cite WHO guidelines (dated 2006) stating the mass of urea added is 0.8–1.5 g/bather; the recipe in Table 1 adds 0.74 g urea/bather, lower than the range of the WHO guidelines. Weng and Blatchley (2011) estimated urea

inputs during a swimming competition to range 0.56–1.2 g/swimmer•day, lower than the WHO guidelines.

Judd and Bullock (2003) found the oxidant (chlorine) demand of one bather ranged 2.80–9.30 g (median of 5 measurements = 5.5 g/bather) using the recipe in Table 1 in the absence of added humic acid (which greatly increased the oxidant demand). The calculated theoretical oxidant demand of this recipe ranges 3.90–7.14 g/bather assuming oxidation of $-N-$ to N_2 only (ignoring the possible formation of NO_3^- which would increase the oxidant demand) plus either incomplete or complete mineralization of organic carbon to CO_2 . And in a survey of 11 indoor operating pools with records of chlorine usage and bather loads the median oxidant demand was found to be approximately 5.5 g/bather (Author, 2010, unpublished calculations, data and evaluation). The larger estimate of organic-N from De Laat et al. (2011) and the larger range for urea inputs per bather from the WHO guidelines would likely result in oxidant demands per bather that are outside the ranges observed by Judd and Bullock (2003) and supported by calculations and observations. Despite wide variations from various sources in the estimates of nitrogen and carbon added per bather, the recipe in Table 1 appears to be consistent with field and laboratory observations of oxidant demand per bather.

Goeres, Palys, Sandel, and Geiger (2004) used a recipe for body fluids similar to that in Table 1. It included NH_3-N (as NH_4Cl), urea, creatinine, and uric acid, but lactic acid rather than citric acid and albumin (egg white) for which a standard elemental chemical composition is unavailable (i.e., the contents of reduced nitrogen and carbon are difficult to assess without chemical analysis of the actual albumin used). Using their experimental description and normalizing the doses to $mass/m^3$ of pool volume/hours of operation, the Goeres et al. (2004) recipe adds $0.785 \mu g/m^3 \cdot hr$ of reduced nitrogen and $0.393 \mu g/m^3 \cdot hr$ of carbon compared with $15.5 mg/m^3 \cdot hr -N-$ and $9.0 mg/m^3 \cdot hr -C-$ using the recipe in Table 1 for the same experimental conditions. The lower loading rate of this recipe, being much lower than discussed in references cited above; appears to make it unrepresentative of fluids from bathers.

Regarding the volume of fluids exuded by one bather, De Laat et al. ((2011) cited earlier work indicating 25–77.5 mL of urine and 200–1000 mL of sweat and Weng and Blatchley (2011) also cited earlier work indicating 25–80 mL of urine and 200–1000 mL of sweat. Although the ranges for estimated fluid volumes exuded per bather are broad and are not well constrained for bather activity and temperature of the pool water, an appropriate and easily remembered rule-of-thumb is ~1 pint (~473 mL) of fluids/bather doing normal activities at a pool water temperature of 80–82°F. As temperature and activity levels rise, the volume would be expected to rise as well.

Each of the organic components of the BFA is discussed briefly below (discussions from Merck & Co., Inc. [1996], hereafter The Merck Index). Chemical structures of the organic components and reaction products discussed are shown in Figure 1. Structures of BFA organic components shown were obtained at <http://www.chemspider.com/Chemical-Structure.1906.html>. Simple structures of selected products of reaction with FAC were constructed by the author.

Urea is a product of protein metabolism and an abundant component of urine. The two $-NH_2-$ moieties can each accept two chlorine atoms in the +1 valence state (Cl(I)) which might be expected to be detected in the TC measurement. Li and

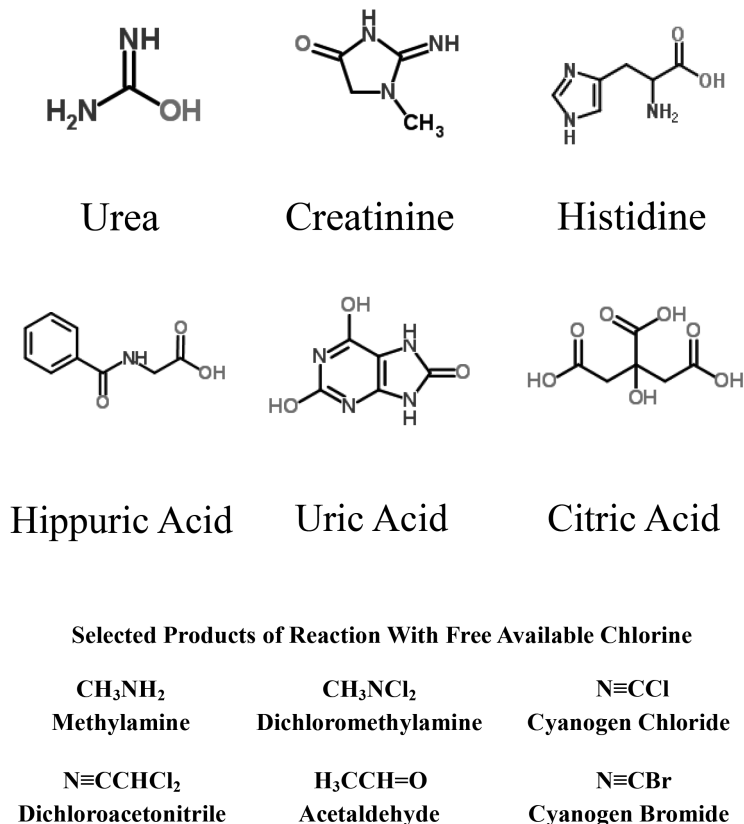


Figure 1 — Structures of organic components of the BFA and products of reaction with FAC.

Blatchley (2007) found that FAC reacted with urea to form NCl_3 . In comprehensive studies of reactions between FAC and urea, De Laat et al. (2011) found that urea consumed huge amounts of FAC (10 mols/mol) and decomposed slowly (1%/hour) in the presence of FAC to CO_2 , nitrogen gas (N_2) and nitrate (NO_3^-). Presumably due at least in part to slow degradation of urea, in 50 samples of 17 indoor pools in Poitiers, France, De Laat et al. (2011) found the mean urea concentration was $18 \pm 11.7 \mu\text{M}$ (normal range 10–50 μM —equivalent to 0.6–3 mg/L) but as high as 100 μM (6 mg/L).

Creatinine is the end product of creatine catabolism (metabolism of large protoplasmic molecules and tissues, with the liberation of energy). Creatinine is present in muscular tissues and is a normal constituent of urine (according to the Merck Index) and sweat (Tachikawa, Aburada, Tezuka, & Sawamura, 2005). Cl(I) substitution should occur at only the single $-\text{NH}_2-$ moiety with 2 Cl(I) atoms

being substituted and then detect as TC. Both NCl_3 and dichloromethylamine were formed in reactions with FAC (Li & Blatchley, 2007). Tachikawa et al. (2005) also noted the production of methylamine from chlorination of creatinine (and measured methylamine in samples of swimming pool water at concentrations up to 19 $\mu\text{g/L}$). They noted that it can form either mono- or dichloromethylamine, both of which measure as TC, specifically as dichloramine in the DPD-FAS titration. Judd and Bullock (2003) found that the addition of creatinine to the BFA in their model pool experiments significantly increased the NHCl_2 measurement (**up to 5 mg/L as chlorine**). Tachikawa et al. (2005) also found that the reaction between FAC and creatinine produces much more NHCl_2 than NH_2Cl (their DPD-FAS titration could not distinguish NCl_3 so it was probably included in the NHCl_2 measurement).

Histidine is an essential amino acid for human development. Li and Blatchley (2007) claim (without attribution) that histidine is a common constituent of human sweat. Cl(I) substitution should occur at the single $-\text{NH}_2-$ moiety (2 Cl(I)s) and be detected as TC and at the single $-\text{NH}$ moiety (one Cl(I)) on the unsaturated ring which might be detected as FAC in either the DPD colorimetric analysis or the DPD-FAS titration analysis, consistent with the behavior of the Cl(I)s attached to cyanurates. Li and Blatchley (2007) found that NCl_3 , cyanogen chloride, and dichloroacetonitrile were formed in reactions of FAC with histidine. Schmalz, Frimmel, and Zwiener (2011) confirmed formation of NCl_3 upon chlorination of histidine. Weaver et al. (2008) found that dichloroacetonitrile accumulates in the reaction as an intermediate to the formation of cyanogen chloride, cyanogen bromide (when Br is present as it often is in swimming pools) and conventional trihalomethanes.

Hippuric acid is present in the urine of herbivorous animals (discovered in horse urine, hence the name) and also in smaller amounts in human urine. One Cl(I) substitution should occur only at the $-\text{NH}$ moiety and may detect as FAC but certainly as TC. No studies of the chlorination degradation of hippuric acid have been found in the literature.

Uric acid is present in the urine of all carnivorous animals. It is the chief end product of the nitrogenous metabolism of birds and scaly reptiles and is found in their excrement. Uric acid is a metabolic breakdown product and high concentrations in blood lead to gout. It is associated with diabetes and kidney stones. One Cl(I) substitution should occur at each of the $-\text{NH}$ moieties on the unsaturated ring and detect as TC or FAC. Uric acid has some functional group similarity with creatinine having two imidazol groups which are polarized by carboxyl and hydroxyl groups. In the first known study of the reactions between FAC and uric acid, Lian, E, Li, & Blatchley (2014) found that uric acid was an efficient precursor of cyanogen chloride and NCl_3 , consistent with expectations based on structure.

Citric acid is widely distributed in plants and in animal tissues and fluids. Citric acid is widely used to provide acidity to beverages, confections, and to adjust the pH of foods and as an antioxidant. Citric acid is the only component of the BFA that contains no $-\text{N}-$ moieties and, thus, would not react with chlorine in the same way as the organic-N compounds. No studies of the chlorination degradation of citric acid have been found in the literature. However, as a highly-oxygenated organic acid (three carboxylic acid groups on a three-carbon backbone) it is likely to be easily oxidized by FAC.

Other Compounds Potentially Introduced Into Swimming Pools

Among the other organic-N compounds that could be introduced into swimming pools, the amino acids—building blocks of proteins and products of protein metabolism—are most prominent. Among early work on the reactions of amino acids with FAC, Scully, Yang, Mazina, and Daniel (1984) found that glycine $\text{NH}_2\text{CH}_2\text{COOH}$ —the simplest of the amino acids—decomposed at FAC doses to N concentration (i.e., $\text{Cl}/\text{N} > 3.0$ (Molar), similar to the chlorination behavior of $\text{NH}_3\text{-N}$.

Scully, Howell, Penn, and Mazina (1988) found that organic amines in general react 8.5 times faster with chlorine than does $\text{NH}_3\text{-N}$, forming 1 or 2-N organic chloramines *that are not bactericidal*. That is when organic amines are present in the water, the FAC dose is rapidly consumed in the formation of organic chloramines and all disinfection benefit of the FAC dose is lost.

Aoki (1989) argued that glycine and several other amino acids all had similar chlorination behaviors: at $\text{Cl}/\text{N} > 2.0$ (Molar) $\text{NH}_3\text{-N}$ is produced and forms NH_2Cl and NHCl_2 ; further decomposition products were acetaldehyde and CO_2 . Shang, Gong, and Blatchley (2000), however, found no evidence for acetaldehyde as a decomposition product of these amino acids (they were not looking for CO_2 ; however, it is likely that CO_2 is an ultimate decomposition product).

Models of Other Organic Amines (Organic-N)

Growing interest and concern over the formation of volatile inorganic chloramines—primarily NCl_3 —in swimming pool water and their health effects on swimmers prompted Schmalz et al. (2011) to study the formation of NCl_3 in reactions between FAC and 17 model organic-N compounds. NCl_3 was formed by 14 of the model compounds in reactions with FAC.

Not all of the model compounds studied by Schmalz et al. (2011) are known to be present in human body fluids but most are found in at least small concentrations in natural waters. Moreover, many of the functional groups represented by the model compounds are known to be present in the formulations of lotions, sunscreens, and other personal care products which are popular among swimmers and, thus, may be present in swimming pool water. Many of the functional groups are present in pharmaceuticals and, thus, are present in urine and feces of bathers using the medications and in treated wastewater discharged to receiving streams. Since 17% of bathers admit to urinating in pools (Wiant, 2011), the presence of many organic-N compounds containing these functional groups may be anticipated even though they have not been included in the BFA.

The three groups of the model compounds studied that are most relevant to swimming pools are discussed briefly below. All of these compounds produced NCl_3 upon chlorination.

Acid Amide Functional Group Compounds

This functional group is a carboxylic acid ($-\text{COOH}$) with $-\text{NH}_2$ substituted for the $-\text{OH}$ as illustrated by urea. Of the acid amide functional group models studied—urea, formamide and acetamide—only urea is known to be a component of body fluids.

Guanidine Functional Group Compounds

Creatinine is as an example of the guanidine functional group. Creatinine and its reactions with FAC were discussed in detail above.

α -Amino Acid Functional Group Compounds

The α -amino acid functional group is characterized by the amine ($-\text{NH}_2$) group being attached to the carbon atom immediately adjacent to the carboxylic acid ($-\text{COOH}$) group (i.e., in the α position). Schmalz et al. (2011) studied 10 model compounds containing this functional group, only one of which—histidine—is in the BFA recipe and none of the other nine α -amino acids is currently known to be a component of urine or sweat.

Within this functional group, glycine, aspartic acid, glutamic acid, and serine represent the major amino acids found in surface waters. Berger, Leitner, Dore, and Legube (1999) found that organic-N compounds in natural surface waters originate mainly from humic acids and that amino acids can reach concentrations of several micrograms/liter.

Glycine is of particular interest as a possible amino acid component of swimming pool water. It is considered nonessential for human development, but is common in cellular materials. Annual industrial production worldwide is $\sim 15,000$ tons (Wikipedia). It is used in cosmetics and toiletries, pharmaceuticals, as a dietary supplement, and in many other consumer products. Thus, although glycine is not commonly known to be a component of body fluids, its wide use in pharmaceuticals and personal care products presents opportunity for it to be present in human urine and on the skin of bathers. Lian et al. (2014) in their supplementary information cite a 1972 paper that reported glycine in urine in low concentrations compared to other organic-N compounds. Na and Olson (2006) found that glycine in molar excess of FAC forms monochloroglycine which is stable for 45 hr and then decomposes to NH_3 and formaldehyde ($\text{H}_2\text{C} = \text{O}$). But FAC in molar excess of glycine (usual in pools) forms *N,N*-dichloroglycine which decomposes to cyanide (CN^-) which, in turn, is rapidly chlorinated to cyanogen chloride which decomposes in excess FAC. Both monochloro- and dichloroglycine would detect as TC in the DPD colorimetric or DPD-FAS titration analyses.

Earlier experiments by Shang et al. (2000) with glycine, cysteine, and asparagine found that initial reaction with FAC produced 1 or 2-*N* chlorinated amino acids that detected as NH_2Cl and NHCl_2 (or NCl_3) in the DPD-FAS titration. Chlorinated glycine appeared stable for 30 min at dosed FAC/glycine molar ratios up to 1.2 but at higher dosed molar ratios decomposition within 30 min occurred. Cyanogen chloride was the main decomposition product of all three of these amino acids.³

Other Inorganic Compounds Potentially Introduced

Bodily fluids, even as represented by the BFA which necessarily excludes elements and compounds at lower concentrations (trace elements), naturally are not the only source of contaminants in swimming pool water. From experience, for example, it is known that the chemicals used for disinfection (bleach, calcium hypochlorite ($\text{Ca}(\text{OCl})_2$), on-site generated disinfecting solutions) and the makeup water itself often contain small amounts of various elements and compounds, such as iron (Fe), manganese (Mn), bromide (Br), and iodide (I). These have either been shown

already, or have the capability in theory, to affect the chemistry of pool water, the measurements used to make decisions in pool management and, possibly, even the operation of disinfectant dosing equipment as will be argued below.

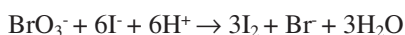
The effects of iron and manganese present as the oxides, that is Fe(III) and Mn(IV) as well as the effects of bromate (BrO_3^-) and iodate (IO_3^-)—higher valence states of Br and I—on the FAC and TC measurement are documented in the method descriptions for the DPD colorimetric and DPD-FAS titration methods (Standard Methods, 2005; Gordon, Cooper, Rice, & Pacey, 1992).

Bromate (BrO_3^-)

Bromate is present in bleaches and on-site generated disinfecting solutions (Snyder, Stanford, Pisarenko, Gordon, & Asami, 2009) and can accumulate in a pool with continuous disinfectant dosing. Bromate is known to produce a very small positive bias in the FAC measurement at near-neutral pH; Gordon et al. (1992) cite a 0.1% positive bias for both BrO_3^- and iodate (IO_3^-) in the presence of iodide (I^-) in distilled water. By contrast, IO_3^- is known to rapidly oxidize I^- to I_2 in mildly acidic solution (pH ~4; Standard Methods, 2005) and the chlorine oxide analog, chlorate (ClO_3^-), becomes a strong reacting oxidant only at much lower pH (pH ~1); this effect is the basis for one of the processes for generating ClO_2 using ClO_3^- (Black & Veatch Corporation, 2010).

Possible Effects on the TC Measurement

The possibility of any significant positive bias in the TC measurement (which is made at pH ~4 with I^- present) by the presence of BrO_3^- apparently has not been investigated, possibly because BrO_3^- , typically, is present in potable water at very low concentrations, too low for any bias to be significant (to wit, the U.S. EPA Maximum Contaminant Level [MCL] for BrO_3^- is 0.01 mg/L). Bromate is known to be reduced by mild reducing agents (ascorbic acid, sulfite, and thiosulfate) in mildly acidic solution (Snyder et al., 2009, p. 26). Cotruvo, Keith, Bull, Pacey, & Gordon (2010) demonstrated BrO_3^- (at 0.2 mg/L) oxidation of I^- to I_2 at low pH (pH ~0.7) even in the absence of other reducing agents. The rate of reaction (expressed as the half-life ($t_{1/2}$) of BrO_3^- in solution) decreased with increasing I^- concentration. The regression model developed from the experimental data predicts that a $t_{1/2}$ of 3 min (the time specified for completion of reaction in the TC measurement) would be achieved at I^- concentration of only 73 mg/L, a concentration likely to be present or even exceeded in the TC measurement. Therefore, BrO_3^- might be expected to cause a positive bias in the TC measurement through oxidation of I^- to I_2 (which forms the characteristic magenta color in reaction with DPD) in mildly acidic solution by the reaction:



This possibility cannot be discounted without experimentation. The positive bias in the TC measurement would be 1.7 mg TC/mg BrO_3^- . Thus, a BrO_3^- concentration of only 0.2 mg/L in pool water could alone produce a TC measurement of ~0.3 mg/L. Concentrations of BrO_3^- of 0.2–0.5 mg/L have been measured in waters of pools that had not been drained for several weeks (Author, 2013, unpublished data).

A Possible Mechanism for Loss of Oxidation-Reduction Potential Control

An Oxidation-Reduction Potential (ORP) dose controller, popular among pool operators, functions by measuring the ORP of the water, comparing it to a set point (which is maintained manually), and adding disinfectant if the measured ORP falls below the set point. The ORP set point is adjusted so that the DPD-measured FAC in the pool is maintained at a desired level. For proper functioning, the ORP measurement must respond to the FAC concentration (i.e., it must sense the potential of the reversible $\text{HOCl}/\text{OCl}^- \leftrightarrow \text{Cl}^-$ reaction couple). If a different reaction couple dominates the ORP of the water, the ORP measurement will be of that reaction couple and the controller will cease to control the FAC concentration. The effects of individual components and major ion composition on the ORP measurement are both expected from theory and observed in practice.⁴ Operators need to be aware of possible effects from pool composition.

Conventional wisdom is that both Br^- and BrO_3^- are conservative, similar to their chlorine analogs Cl^- and ClO_3^- ; i.e., not engaging in reactions that would lead to net losses from the water. It is noteworthy, therefore, that the concentrations of both Br^- and BrO_3^- in pool waters often do not track those of the known conservative constituents Cl^- , ClO_3^- , and ClO_4^- (Author, 2013, unpublished data). This observation strongly suggests that BrO_3^- is not conservative (i.e., it engages in reactions in the pool water leading to net losses [being reduced to Br^-] which at least partially removes the BrO_3^-).

Moreover, the ability of BrO_3^- to be reduced in pool water suggests that a reversible reaction couple is present. An analogous reaction couple involving ClO_3^- is unlikely because ClO_3^- is unreactive at near-neutral pH. Thus at some BrO_3^- concentration, the measured ORP may respond to a different reaction couple such as the $\text{BrO}_3^- \rightarrow \text{OBr}^-$ or $\text{BrO}_3^- \leftrightarrow \text{Br}^-$ couple. This mechanism, while to the author's knowledge has not been demonstrated in laboratory, may account for the occasional observations by pool operators that the ORP controller ceases to function in controlling the FAC.

Iodate (IO_3^-)

Iodate is an obvious candidate for a constituent that could cause a positive bias in the TC measurement; IO_3^- is a primary standard for calibration of the iodometric method (Standard Methods, 2005) for determining both FAC and TC. It reacts rapidly with I^- in mildly acidic solution to form I_2 with production of 1.22 mg equivalent chlorine per mg IO_3^- . Moreover, IO_3^- will be produced from I^- by reaction with FAC in the pool. Thus, I^- present in the pool water from any source will be converted to IO_3^- as long as FAC is present but will be detected *only* as TC.

Iodate has not been considered nor studied to date because it was thought to be present in extremely low concentrations and a convenient and inexpensive analytical method has not been available. Some commercial laboratories have been adapting a method based on ion chromatography (IC) because of findings of iodated forms of trihalomethanes (Bichsel & von Gunten, 2000; Richardson et al., 2008) and the possible pathway in their formation being through IO_3^- . Although no studies have been performed in this regard, because I^- is a critical nutrient for proper thyroid

function, it could be expected that I^- would be a component of body fluids which could, therefore, be a source of I^- in pool water in addition to being present in small amounts in the disinfectants. It might be expected to accumulate in the pool water.

Conclusions

- One recipe to mimic the composition of human body fluids (a BFA) and the masses of TOC and reduced nitrogen added by one bather is consistent with both the theoretical and observed median oxidant (chlorine) demand as a function of numbers of bathers—5.5 g FAC per bather (one bather doing normal activities for one hour).
- The ammonia (NH_3) and organic-N components of the BFA in reaction with FAC form inorganic and organic chloramines which detect as TC in the DPD colorimetric or DPD-FAS titration measurements of FAC and TC. The organic chloramines cause the CC measurement to be not reflective of the inorganic chloramines alone. Guidelines on the CC measurement are routinely exceeded in operating pools and in model pool studies where the CC measurement at modest bather loads was as high as 5 mg/L.
- The organic-N containing components of the BFA—and most of the 17 model amino acids and amine compounds studied—form NCl_3 in reactions with FAC. Other reaction products include cyanogen chloride, dichloromethylamine, dichloroacetonitrile, and acetaldehyde. Ultimate oxidation products are CO_2 , N_2 and NO_3^- .
- Chlorinous odors in pools are caused by volatile inorganic chloramines— NCl_3 and $NHCl_2$. The volatile organic decomposition products of organic-N components of the BFA—cyanogen chloride and dichloromethylamine—may also contribute to chlorinous odors and eye-tearing among swimmers.
- In terms of the chemistry of pool water, the benefits of requirements for bathers to shower before entering the pool and to avoid urinating in the pool are obvious: showering would be expected to remove sweat and sweat residues, cosmetics and lotions containing FAC-reactive components, and soil containing humic acid, thus preventing a huge source of chlorine demand from entering the pool; and avoiding urinating reduces the urea insult, reduces the resulting formation of chlorinous odors from NCl_3 and reduces the chlorine demand.

Notes

1. Combined chlorine is defined as the chlorine that is combined with ammonia to form the inorganic chloramines, monochloramine (NH_2Cl), dichloramine ($NHCl_2$), and trichloramine (NCl_3), and the nitrogen moieties of organic-N compounds forming organic chloramines. The combined forms of chlorine are distinguished from FAC which is the sum of three forms of free chlorine that may be present— Cl_2 gas, hypochlorous acid ($HOCl$), and hypochlorite anion (OCl^-). The most convenient and most used methods of routine measurement in pool water are barely capable of distinguishing between the three species of inorganic chloramines and usually cannot distinguish between $NHCl_2$ and NCl_3 . Moreover, chlorine attached to organic-N molecules, forming

organic chloramines, generally detects as TC and is, therefore, often considered to be a positive bias in the TC measurement. Thus the CC measurement, which is conventionally considered to represent the volatile inorganic chloramines only (which are largely responsible for chlorinous odors) can be thought of as being biased high by the presence of organic-N.

2. Reduced nitrogen is nitrogen with valence -3 as occurs in most organic compounds containing nitrogen. The nitrogen in ammonia ($\text{NH}_3\text{-N}$) is also valence -3. The nitrogen in nitrate (NO_3^-) has valence +5 and is not reduced nitrogen, for example.

3. According to the chemical agent literature, cyanogen chloride is so irritating to mucous membranes and lachrymatory that odor cannot be noticed. The Merck Index lists no odor from cyanogen chloride. However, cyanogen chloride is rapidly decomposed by FAC; thus, in swimming pools having substantial and measurable FAC concentrations ($> 1.0 \text{ mg/L}$), cyanogen chloride should be short-lived. Weaver et al. (2008) found cyanogen chloride in 11 pools sampled at concentrations of at most 0.1 mg/L .

4. The measured ORP is known to be influenced by the major ion composition of the water (the effect of Cl^- is predicted theoretically, for example, as a 30 mV decrease per decade increase in Cl^- concentration and the ORP is observed to decrease as the TDS concentration increases) and dramatically influenced by the presence of both inorganic and organic chloramines. A commonly observed effect of organic-N compounds is that the ORP at a given measured FAC drops by several 10s of millivolts when cyanuric acid is added to the water to a concentration of a few 10s mg/L .

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