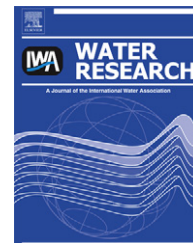


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Trichloramine in swimming pools – Formation and mass transfer

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ABSTRACT

Trichloramine is a volatile, irritant compound of penetrating odor, which is found as a disinfection by-product in the air of chlorinated indoor swimming pools from reactions of nitrogenous compounds with chlorine. Acid amides, especially urea, ammonium ions and α -amino acids have been found as most efficient trichloramine precursors at acidic and neutral pH. For urea a relative NCl_3 formation of 96% at pH 2.5 and 76% at pH 7.1 was determined. Even under sub-stoichiometric molar ratios of Cl/N the formation of NCl_3 is favored over mono and dichlorinated products. However, the reaction kinetics of urea with chlorine is slow under conditions relevant for swimming pools. Also the mass transfer of NCl_3 from water to the gas phase which was calculated by the Deacon's boundary layer model could be shown as a relatively slow process. Mass transfer would take 20 h or 5.8 d for a rough or a quiescent surface of the water, respectively. This is much more than a typical turnover rate of 6–8 h of a treatment cycle of a 25 m swimming pool. Therefore processes to remove NCl_3 and its precursors can help to minimize the exposure of bathers.

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1. Introduction

For hygienic safety and protection of bathers against infectious diseases the disinfection of swimming pool water (SPW) is absolutely essential. Chlorine dosed in gaseous form or as sodium hypochlorite is the most common method for disinfection of SPW. To achieve a sufficient disinfection capacity the concentration of free chlorine should be kept in the range between 0.3 and 0.6 mg/L according to the [German Pool Water Standard DIN 19643](#). In the United States, Australia and many other European countries concentrations up to 3 mg/L of free chlorine are recommended.

Under operating conditions SPW is continuously loaded with organic carbon and particularly with nitrogen compounds. Each bather contributes with considerable amounts of body

fluids, hair, skin particles, microorganisms and cosmetics. Components of the bather load are only partly removed in the treatment and therefore cycle many times in the system “pool water – treatment – pool water”. In each passage through the treatment the water is subsequently dosed with chlorine, which can react with water constituents. Thus the compounds are partly degraded and transformed to disinfection by-products (DBPs). The reaction between components of the bathers load and the dosed chlorine to toxic DBPs cannot be completely avoided but has to be minimized. Besides trihalomethanes (THM) – the best known DBPs – many other chlorinated DBPs have been analyzed in SPW and drinking water, for example halogenated acetic acids, aldehydes or acetonitriles ([Zwiener et al., 2007](#); [Richardson et al., 2007](#)). Chlorinated nitrogenous reaction products are generally less known and are routinely

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monitored only by the not well defined sum parameter combined chlorine.

Recently published epidemiological studies on respiratory functions and asthma give evidence for adverse health effects from attending chlorinated swimming pools. Reports show an increase in lung epithelium permeability (Bernard et al., 2003), respiratory complaints (Levesque et al., 2006) or developing asthma (Nickmilder and Bernard, 2007). Mostly trichloramine is suggested to cause eye and upper respiratory tract irritation (Massin et al., 1998), biomarker changes in the lung and development of asthma (Bernard et al., 2006). Hery et al. (1995) and Gagnaire et al. (1994) reported on irritating complaints of eye and throat among pool attendants and irritating effects on mice at trichloramine concentration levels higher than 0.5 mg/m^3 in the air. The proposed INRS (French Institute for Occupational Health and Safety) guideline value of 0.5 mg/m^3 for NCl_3 for indoor pool air is based on these investigations.

Trichloramine itself is an irritant and in higher concentrations an explosive compound of penetrating odor. It is slightly soluble in water (0.025 mol/L , 25°C , pH 1–10) and its octanol-water partition coefficient log D is 2.64 (25°C , pH 1–10) (SciFinder Scholar, 2006). It is four times more volatile than chloroform and partitions to the air of swimming pools (Henry coefficient, NCl_3 10 atm L mol^{-1} (25°C); Holzwarth et al., 1984; Sander, 1999).

Air measurements of NCl_3 in indoor pool settings reveal concentrations between 0.1 and 18.8 mg/m^3 (Hery et al., 1995; Stottmeister and Voigt, 2006). Air concentrations of trichloramine strongly depend on air circulation and on water agitation by bathers and attractions (Zirbs, 2008). However, they are not correlated with the concentration of the indicator parameter combined chlorine in the SPW (Stottmeister and Voigt, 2006), since air ventilation is the predominant parameter. Furthermore, the contribution of NCl_3 and dichloramine to the total combined chlorine is low and typically in the range between 15 and 20% (Weaver et al., 2009). Further monitoring programs for trichloramine concentrations in air of different pool settings have been started meanwhile in Germany by Bavarian and Federal Consumer and Occupational Health and Safety Agencies (LGL-Bayern, BGIA).

Up to now no systematic data are available which show the relation between the occurrence of precursor substances, the reaction conditions and the resulting trichloramine exposure in water and air of swimming pool settings. N-chlorination reactions are described by an initial electrophilic attack of HOCl to the nucleophilic nitrogen. For ammonium ions decreasing chlorine reactivity with increasing numbers of substituted chlorine atoms were reported. At pH 7 second order reaction rates of ammonium ions with HOCl of $1.3 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ and monochloramine with HOCl of $2.7 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$ were given by Deborde and von Gunten (2008) (calculated from data of Qiang and Adams, 2004; Morris and Isaac, 1983). The reaction kinetics of trichloramine formation is more complex. Here a general base catalyzed mechanism with third order rate constants was proposed (Hand and Margerum, 1983).

In water the two species of ammonia (NH_3 and NH_4^+) are present, but chlorine reactivity of NH_4^+ species was reported to be negligible (Qiang and Adams, 2004). Under acidic conditions ammonium ions are the prevailing species, here

the first chlorination step is slowed down by a factor of 10^6 compared to the uncharged ammonia molecule (Saguinsin and Morris, 1975). Ammonium ions, urea and to some extent creatinine and amino acids have been described as precursors for trichloramine formation in chlorination processes (Li and Blatchley, 2007; Shang and Blatchley, 1999; Na and Olson, 2004; Blatchley and Cheng, 2010). The kinetics of chlorine degradation in the presence of urea at neutral and alkaline pH conditions have been first described by Fuchs (1962). Due to the slow reaction he also showed a continuous increase of the urea concentration in the water within a period of three months up to a concentration of 24 mg/L for a swimming pool where only water was added to balance evaporation (sand filtration, $0.1\text{--}0.3 \text{ mg/L Cl}_2$, pH 8–10).

The objective of this study was to determine the major reactions and processes involved in the formation of trichloramine in swimming pools and the resulting exposure of bathers. For that purpose different nitrogenous compounds and the major components of urine and sweat have been tested for their relative NCl_3 formation. Reaction parameters, reaction kinetics and the mass transfer of NCl_3 from water to air were considered. The results should set a sound basis to apply suitable measures to minimize the exposure of the bathers and bath attendants by NCl_3 .

2. Materials and methods

2.1. Experimental procedures

All chemicals, phosphate salts and nitrogen compounds used in this study were p.a. reagent grade and mostly obtained from Merck (Darmstadt, Germany), except sodium hypochlorite solution ($\sim 90 \text{ g/L Cl}_2$, daily controlled by DPD method) was from Roth (Karlsruhe, Germany). Lysine, arginine, acetamide, glutamic acid and β -alanine were from Sigma–Aldrich (Steinheim, Germany). Free and combined chlorine were analyzed with the photometric DPD method (Spectroquant® chlorine cell test, according to EN ISO 7393-2:2000), urea with the enzymatic and colorimetric indophenol blue method (Microquant® urea-test; both from Merck, Darmstadt, Germany). UV-spectra were recorded on a Cary 50 spectra-photometer (Varian, Darmstadt, Germany). GC-MS instruments and operating parameters are described in the supporting information (Figure S6).

All chlorination experiments were performed in glassware, which was soaked before use in sodium hypochlorite solution for 24 h to remove the chlorine demand.

NCl_3 formation experiments were carried out in aqueous phosphate buffer solutions (pH 2.5–7.7) with $1.0 \times 10^{-2} \text{ mol/L}$ nitrogen compound (as N). Sodium hypochlorite solutions were added at molar chlorine to nitrogen ratios between 0.15 and 5. The phosphate buffer concentration in the reaction mixture was 0.25 mol/L . The pH varied at maximum by ± 0.2 at pH 5.9, pH 6.3, pH 7.1 and pH 7.7, by ± 0.3 at pH 2.5 and by ± 0.5 at pH 4.0. The reaction time was 30 min to compare the reactivity of all N-compounds under the same conditions. After 30 min reaction was assumed to be completed for all compounds studied at the concentrations applied. Reaction products were analyzed by UV-spectroscopy ($\lambda = 190\text{--}500 \text{ nm}$) after extraction to hexane. To check the effects of the hexane

extraction on the yield of NCl_3 formation, comparative measurements were done with urea chlorine mixtures. NCl_3 yields were measured after extraction with hexane and directly in the aqueous phase. Similar results were achieved with both methods (detailed information is given in Supporting information paragraph 3). Additionally, the hexane phases were analyzed after washing steps with deionized water by UV-spectroscopy and GC-MS. UV-spectra formed by overlaid spectra of further chlorination products were deconvoluted with Gaussian functions for each compound (paragraph 1 Supporting information; Figures S1–S4). Quantitative data were calculated from the measured and deconvoluted UV-spectra with the UV-absorption coefficients given in the Supporting information in Table S1. The absorption coefficients of NCl_3 solutions in hexane were obtained from measurements of the nitrogen content (N-Analyzer, chemiluminescence of NO with O_3 , TN 05, Abimed, Langenfeld, Germany) and of the chloride content after reduction of NCl_3 with As_2O_3 in a sodium carbonate solution (Hery et al., 1995). The chloride concentration was analyzed after cation exchange (Dowex 50 WX 8) with ion chromatography (IC 790, Metrohm, Herisau, Switzerland; column: Metrosep Anion Dual 2, 75 mm \times 4.6 mm, 6 μm particles; eluent 5 mM phthalic acid with 2% acetonitrile at pH 4.5).

Chlorination experiments with initial urea concentrations of 3.33×10^{-5} mol/L (nitrogen concentration $c(\text{N}) = 6.67 \times 10^{-5}$ mol/L) and 3.33×10^{-4} mol/L were performed in stirred volumetric flasks. The products were extracted with 5 mL and 10 mL hexane to achieve concentration factors of 10–100. The hexane phases were analyzed after reaction times of 1 h, 3 h, 24 h, 48 h, 72 h and 96 h by UV-spectroscopy. Maximum total NCl_3 yields for experiments with urea concentrations of 3.33×10^{-4} mol/L were achieved after 24 h and with urea concentrations of 3.33×10^{-5} mol/L after up to 72 h.

The experiments for the reaction kinetics were performed in stirred 2 L-Erlenmeyer flasks, which were wrapped in aluminum foil to exclude light. The temperature was controlled by an Ikatron ETS D-4 fuzzy system (IKA-Works, Staufen, Germany). The initial chlorine concentration was 1.13×10^{-5} mol/L and the urea concentration was 3.33×10^{-5} mol/L (molar Cl/N ratio = 0.17). A pH of 6.9 ± 0.1 was adjusted with phosphate buffer ($c = 1.7 \times 10^{-4}$ mol/L). Chlorine was measured with the DPD method and urea with the enzymatic and colorimetric indophenol blue method.

2.2. Calculation of trichloramine concentrations in air

The air concentrations of NCl_3 were modeled for an indoor pool with a water volume $V_w = 960 \text{ m}^3$, a water temperature $T = 28 \text{ }^\circ\text{C}$, a water surface area $A = 312.5 \text{ m}^2$ and an air volume of the pool hall $V_a = 5760 \text{ m}^3$.

The general Fick's first law to describe mass fluxes (Eq. (1)) of volatile compounds $F_{\text{ia/w}}$ from the water to gas phase was reduced under assumption of a low NCl_3 partial pressure ($P_{\text{NCl}_3\text{a}}$) in the air above the water surface compared to the concentration in the water. The total mass transfer coefficient ($v_{\text{ia/w}}$) (Eq. (2)) considers both phases of the boundary – air and water phase. For substances with Henry coefficients much higher than $0.025 \text{ L bar mol}^{-1}$ which is given for NCl_3 with $K_{\text{H,NCl}_3} = 11.6 \text{ L bar mol}^{-1}$ ($T = 301 \text{ K}$) the mass transfer is

controlled by the aqueous phase (Schwarzenbach et al., 2003). So the gas phase regime could be neglected and the flux of NCl_3 to the air was described by a one film model with liquid mass transfer coefficients ($v_{\text{NCl}_3\text{w}}$) according to (Eq. (3)) (Schwarzenbach et al., 1979). To calculate the liquid mass transfer coefficient for NCl_3 ($v_{\text{NCl}_3\text{w}}$) the Deacon's boundary layer model (Deacon, 1977; Schwarzenbach et al., 2003) was used. Different water surface characteristics were considered on the basis of a direct linear correlation (Mackay and Yeun, 1983) with water evaporation rates for unused swimmer pools, used swimmer pools and whirl pools given in the German Guideline VDI 2089-1. Additional information is given in the paragraph 6 supporting information.

$$F_{\text{ia/w}} = v_{\text{ia/w}} \left(c_{\text{iw}} - \frac{P_{\text{ia}}}{K_{\text{Hi}}} \right) \quad (1)$$

$$\frac{1}{v_{\text{ia/w}}} = \frac{1}{v_{\text{iw}}} + \frac{1}{v_{\text{ia}} K_{\text{ia/w}}} \quad (2)$$

$$F_{\text{NCl}_3\text{w}} = v_{\text{NCl}_3\text{w}} c_{\text{NCl}_3\text{w}} \quad (3)$$

c_{iw} = concentration of the substance i in the water (mol L^{-1})

P_{ia} = partial pressure for the substance i in the air above (bar)

v_{iw} = liquid phase mass transfer coefficient for substance i (cm s^{-1})

v_{ia} = air phase mass transfer coefficient for substance i (cm s^{-1})

$K_{\text{ia/w}}$ = dimensionless Henry coefficient; $K_{\text{ia/w}} = K_{\text{Hi}}/RT$;
 K_{Hi} = Henry coefficient in L bar mol^{-1} ; $R = 0,08314 \text{ L bar K}^{-1} \text{ mol}^{-1}$;
 T = temperature in Kelvin

The Henry constant for NCl_3 at the temperature of $28 \text{ }^\circ\text{C}$ was calculated according to Sander (1999) with the enthalpy of solution $\Delta_{\text{soln}}H/R = 4100 \text{ K}$.

2.2.1. Safety advice

NCl_3 is an explosive, unstable compound that can explode in form of its pure liquid above its boiling point of $71 \text{ }^\circ\text{C}$ or in concentrated solutions when catalyzed by light or other catalysts. Concentrations higher than 2 g/L in water (Savickas et al., 1989; Schlessinger, 1966) or isolation of the pure compound have to be imperatively avoided. Never isolate or concentrate NCl_3 . Only handle diluted gas streams or solutions of NCl_3 behind a shield and in a well-ventilated hood.

3. Results and discussion

3.1. Screening for NCl_3 precursor compounds

Organic precursor compounds with different functional nitrogen containing groups and different forms of bound nitrogen have been investigated for their potential to form trichloramine. The precursors were chosen with the aim to include the major components of urine and sweat and to get a systematic structural variation of relevant nitrogenous compounds (Fig. 1). Urea is considered as the most important N-compound followed by ammonia and creatinine. The functional groups selected were acid amides, amino acids and alkyl

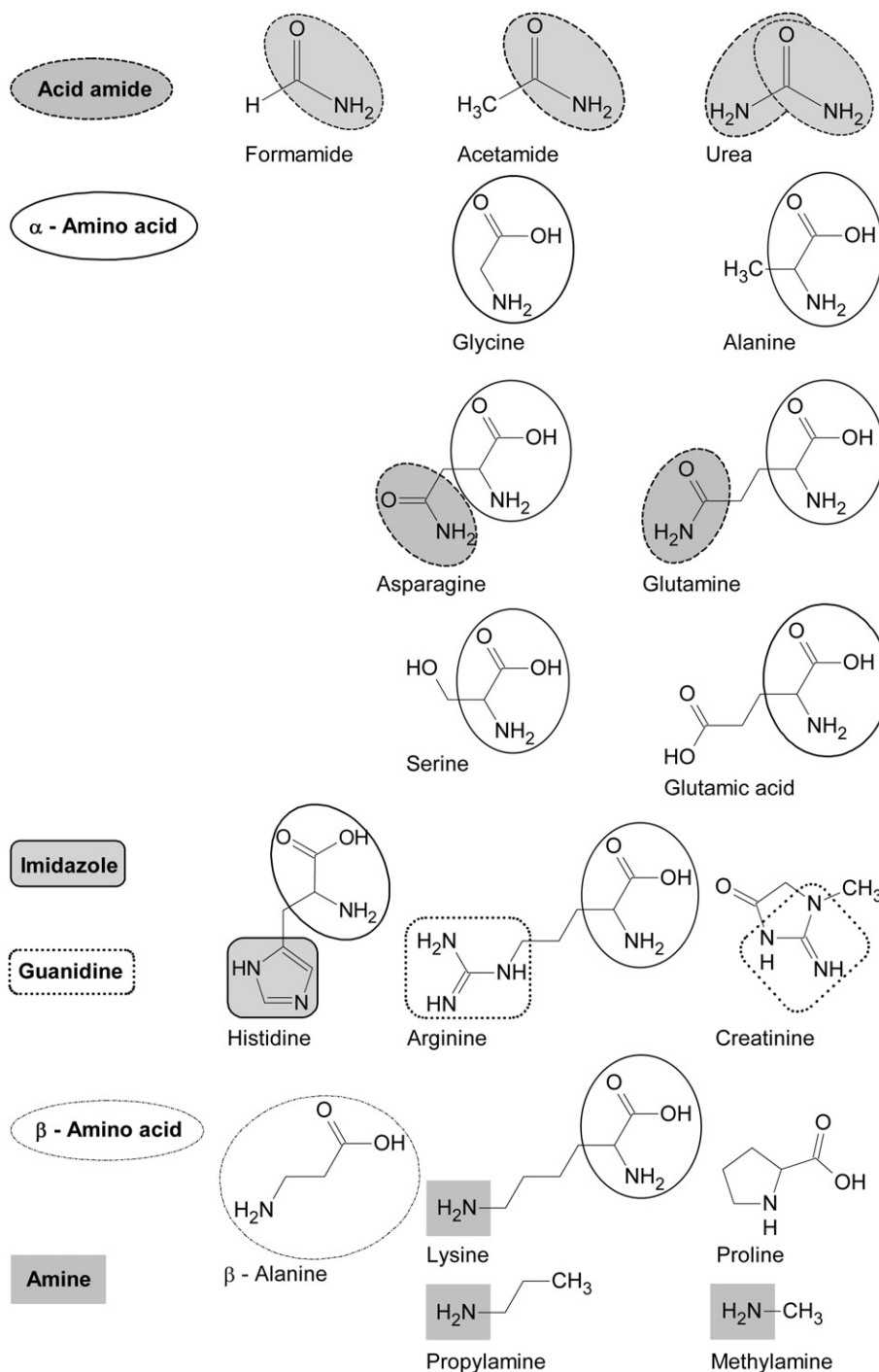


Fig. 1 – Nitrogenous compounds with different functional groups and different forms of bound nitrogen.

amines as well as compounds with guanidine type structures (arginine, creatinine). The results of the relative trichloramine formation after chlorination at a molar Cl/N ratio of 5 at varied pH are shown in Table 1. The compounds were arranged according to decreasing NCl_3 formation at pH 7.1.

Generally, increasing NCl_3 yields were found with decreasing pH values. This pH effect can be rationalized on the basis of the pH dependent equilibrium reaction of both free chlorine and the nitrogen compound. HOCl is the main reactive chlorine species in aqueous solution. As expected

considerable lower NCl_3 yields were found at pH 7.7 where OCl^- are the main species. The other effect is that low pH values result in protonation of the bound nitrogen, which slows down the reaction of the first chlorine attack and thus favors the reaction of the second and third chlorine attack. Data for the apparent rate constants k_{app} of chlorination reactions can be deduced from the literature (Deborde and von Gunten, 2008). k_{app} for NH_3 at pH 7 is $1.3 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ and much lower at pH 4 ($1.2 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$). Whereas for monochloramine k_{app} is $1.2 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$ at pH 7 and

Table 1 – Relative NCl₃ formation of different nitrogenous substances. Reaction of 10 mmol/L nitrogenous compound (calculated as N) with chlorine at a molar Cl/N ratio of 5 in buffered solution. Names and numbers in italics indicate that the spectra had to be deconvoluted by Gaussian functions (cf. to Supporting information Figures S1–S4) (n.d. = not detectable < 0.1%).

	pH value						
	2.5 ± 0.3	4.0 ± 0.5	5.9 ± 0.2	6.3 ± 0.1	6.7 ± 0.1	7.1 ± 0.1	7.7 ± 0.2
	Relative NCl ₃ -formation Molar ratio c(NCl ₃)/c(N) × 100 (%) (± standard deviation)						
Urea	96.0 ± 5.4	–	94.7 ± 3.2	90.2 ± 1.3	86.1 ± 0.2	75.8 ± 4.3	23.9 ± 0.3
Ammoniumchloride	98.6 ± 5.6	89.3 ± 1.3	64.5 ± 3.7	60.0 ± 1.4	55.0 ± 2.4	37.4 ± 2.0	20.4 ± 1.8
Formamide	91.3 ± 0.6	36.2 ± 1.8	52.5 ± 1.1	62.0 ± 0.2	59.3 ± 3.6	36.8 ± 2.0	18.0 ± 2.8
Glycine	22.0 ± 2.1	49.3 ± 2.0	48.0 ± 1.8	34.5 ± 0.3	30.8 ± 2.9	31.9 ± 0.2	18.4 ± 2.6
Histidine	31.6 ± 0.7	38.8 ± 1.6	34.9 ± 0.8	35.4 ± 0.5	32.8 ± 2.0	26.2 ± 1.1	13.6 ± 0.4
Asparagine	62.5 ± 0.8	51.3 ± 3.3	42.1 ± 1.9	39.6 ± 1.4	30.4 ± 5.0	22.7 ± 0.3	10.0 ± 1.6
Acetamide	64.7 ± 5.0	77.4 ± 0.3	39.4 ± 0.2	32.2 ± 3.5	27.8 ± 3.2	22.5 ± 1.0	12.5 ± 2.1
Serine	73.5 ± 4.7	61.0 ± 3.4	15.1 ± 0.4	16.3 ± 0.3	17.7 ± 0.7	19.1 ± 0.4	11.5 ± 0.3
Creatinine	4.9	14.2	34.6	26.1	17.3	10.6	3.1
Glutamine	51.6 ± 0.2	43.8 ± 2.5	13.3 ± 1.0	13.6 ± 0.6	12.2 ± 0.7	10.1 ± 0.2	10.5 ± 0.2
Arginine	28.5	28.5	15.7	16.6	11.4	6.6	3.3
Glutamic acid	44.3 ± 3.1	30.0 ± 2.3	19.3 ± 0.5	13.2 ± 2.2	9.2 ± 0.4	4.6 ± 0.6	0.6 ± 0.2
Alanine	79.8 ± 2.8	51.0 ± 3.1	5.4 ± 0.2	4.6 ± 0.2	3.7 ± 0.4	2.9 ± 0.1	2.6 ± 0.1
β-Alanine	6.2 ± 0.5	0.8 ± 0.1	0.8 ± 0.1	0.9 ± 0.1	0.9 ± 0.2	0.8 ± 0.1	0.7 ± 0.1
Lysine	32.6	–	n.d.	n.d.	n.d.	n.d.	n.d.
Proline	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Propylamine	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Methylamine	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

$1.5 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$ at pH 4. Also the decomposition of NCl₃ is described by a base catalyzed reaction or by a reaction with NHCl₂. However, NHCl₂ played only a minor role in our experiments and was not considered in detail. Therefore, increasing pH values result in increasing NCl₃ decay (Kumar et al., 1987). Decay products are nitrogen and at basic conditions nitrate (Jafvert and Valentine, 1992).

Maximum NCl₃ yields were found for glycine, histidine and acetamide at pH 4 and for creatinine at pH 5.9. Ammonia, urea, formamide and the α-amino acids α-alanine and serine revealed as the most efficient NCl₃ precursors at pH 2.5. However, at pH 7.1 the ranking with decreasing NCl₃ formation is urea, ammonia, formamide, glycine, and histidine. Important prerequisites for an efficient NCl₃ formation seem to be both the amine or amide function, which guarantees efficient chlorination, and the polarization of the C–N bond for facilitated cleavage of the chlorinated nitrogen moieties.

This can be demonstrated nicely by the drop of the NCl₃ formation yield going from an α-amino acid (α-alanine) to a β-amino acid (β-alanine). Asparagine and glutamine having both α-amino acid and acid amide functions also showed high NCl₃ yields. Nitrogen bound in other forms like imidazole or guanidine like structures does not seem to contribute considerably to the NCl₃ formation like the data reveal for histidine, arginine or creatinine at pH 2.5. The NCl₃ yield found for histidine and arginine can be attributed mostly to the α-amino acid function. However, at increased pH the guanidine structure can also contribute to the NCl₃ formation as the data show for creatinine at pH 5.9 (34.6%) and pH 6.3 (26.1%). For compounds with a single amine group without further polarization of the C–N bond no NCl₃ formation could be observed. Methylamine, propylamine (pH 2.5–7.7) and the side chain of lysine (pH 5.9–7.7) almost quantitatively react to

N,N-dichlorination products which was shown by the shift in UV absorption to 309 nm and confirmed by GC-MS data (Figure S6a–c). Also for the amino acid proline no NCl₃ formation could be observed. But again the UV absorbance band with a maximum at 309 nm was a typical hint for N,N-dichlorinated products.

3.2. NCl₃ formation for different chlorine to nitrogen ratios

Urea and ammonia as major precursors and glycine as an example for an amino acid of medium NCl₃ formation potential were selected to investigate the effect of different molar chlorine to nitrogen ratios on the NCl₃ formation (Cl/N = 0.5 to 5). The results in Fig. 2 are given in % of the stoichiometric theoretical yield. The theoretical yield is defined as the complete conversion of the whole initial nitrogen or chlorine to NCl₃.

The NCl₃ formation from ammonium ions and urea at sub-stoichiometric Cl/N ratios (e.g. 1) at pH 2.5 revealed the preference of the formation of trichloramine compared to mono and dichlorinated products (Fig. 2a). If this would be not the case no NCl₃ would be formed at Cl/N ratios of 2 and below. This is in accordance with the nearly quantitative transformation reactions of monochloramine (Eq. (4)) and dichloramine (Eq. (5)) at pH < 3 (Corbett et al., 1953).



Urea revealed a considerably high NCl₃ formation potential at neutral pH (Fig. 2b). 38% and 27% of the theoretical NCl₃ yield could be achieved at the sub-stoichiometric ratios of Cl/N of 1 and

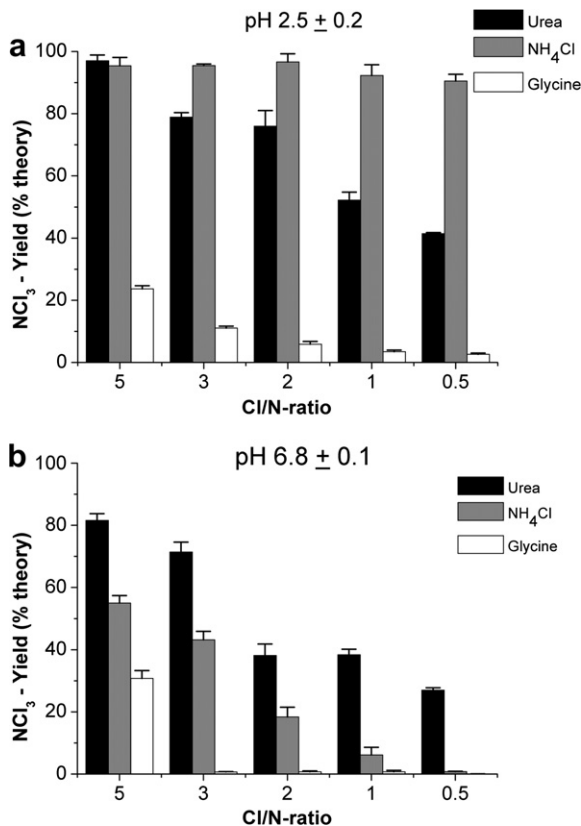


Fig. 2 – NCl_3 – yield in % of the stoichiometric theoretical yield for urea, ammonium chloride and glycine after chlorination at different molar chlorine to nitrogen ratios (Cl/N) - Reaction of 1.0×10^{-2} mol/L N-compound (as nitrogen) with chlorine, in buffered solutions at pH 2.5 ± 0.2 (2a) and pH 6.8 ± 0.1 (2b).

0.5 which means that 13% and 5% of the nitrogen in urea have been transformed to NCl_3 under this conditions (Cl/N = 1 and Cl/N = 0.5). As expected glycine revealed as a less efficient NCl_3 precursor under sub-stoichiometric conditions. At Cl/N ratio of 1 only 3.5% and 0.8% of the theoretical NCl_3 yield could be measured as reaction product of glycine with chlorine at acidic and neutral pH, respectively. This can be explained by the rapid conversion of glycine to N-mono- and N,N-dichloroglycine followed by the rate limiting decay to further products (Na and Olson, 2006).

3.3. Trichloramine formation from urea

Since urea revealed as the most important NCl_3 precursor, also at neutral pH, and is a main constituent of the bathers load, the formation of NCl_3 from urea was considered in more detail. Urea concentrations up to 2 mg/L could be measured in different swimming pools (Table S3). Initial urea concentrations of 2 mg/L (6.7×10^{-5} mol/L nitrogen) and 20 mg/L (6.7×10^{-4} mol/L nitrogen) were selected for chlorination experiments, and the data were compared to the already discussed results at higher concentrations. In Fig. 3 the NCl_3 yields at pH 6.8 are given for different molar Cl/N ratios.

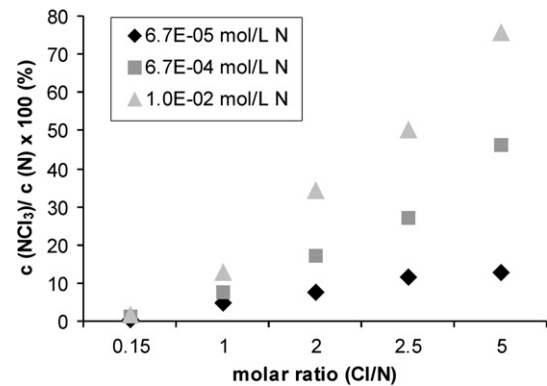


Fig. 3 – NCl_3 formation of urea at different initial concentrations (6.7×10^{-5} mol/L N; 6.7×10^{-4} mol/L N and 1.0×10^{-2} mol/L N) and varied molar Cl/N ratios in buffered solutions at pH 6.8 ± 0.1 .

Due to the slow reaction of urea with chlorine the required reaction time had to be increased with decreasing urea concentrations. For a nitrogen concentration of 1.0×10^{-2} mol/L 30 min were sufficient, whereas for a concentration of 6.7×10^{-5} mol/L up to 72 h were required to reach the maximum NCl_3 yields. Generally, decreasing initial urea concentrations resulted in decreasing NCl_3 yields independent of the Cl/N ratio. The lower NCl_3 yields at low urea concentrations can be explained by the increasing importance of the decomposition reaction of NCl_3 or other side reactions in aqueous solutions with increasing reaction time. Data on half-lives between 6 and 25 h of aqueous NCl_3 solutions at pH 7 were published by Saguinsin and Morris (1975) and Kumar et al. (1987), whereas the higher half-lives are consistent with the experiments at low concentrations. The results for a Cl/N ratio of 1 show that 13% of the urea nitrogen were transformed to NCl_3 for $c(\text{N})$ of 1.0×10^{-2} mol/L, and 7.5% and 4.7% of the urea nitrogen were transformed to NCl_3 for $c(\text{N})$ of 6.7×10^{-4} mol/L and $c(\text{N})$ of 6.7×10^{-5} mol/L. The results are in accordance to that of Blatchley and Cheng (2010) who found NCl_3 yields in the same order of magnitude. At typical conditions relevant for swimming pools with urea concentrations of 2 mg/L and chlorine concentrations of 0.6 mg/L (Cl/N = 0.15) up to 1% of the urea nitrogen can be transformed to NCl_3 despite the sub-stoichiometric Cl/N ratio.

3.4. Trichloramine in swimming pools – modeling the indoor pool situation and practical consequences

In swimming pools the air concentration of NCl_3 is governed by several, partly coupled processes:

- Formation and degradation of NCl_3 in water from the reaction of precursors and free chlorine.
- Partitioning of NCl_3 between the water and gas phase.
- Advective flow (air exchange) and degradation in the gas phase.

The kinetics of NCl_3 formation, degradation and the mass transfer from the water to the gas phase will be considered in

more detail. The understanding of the major drivers is important to take the best measures to minimize NCl_3 concentration in the water and in the gas phase of swimming pools, especially of indoor pools.

In the lab experiment only chlorine and urea are present as reaction partners. So a pseudo first order reaction rate constant of $4.58 \times 10^{-6} \text{ s}^{-1}$ for the reduction of chlorine concentration could be determined for reaction conditions typical for real SPW with concentrations of free chlorine of $1.13 \times 10^{-5} \text{ mol/L}$ and urea of $3.3 \times 10^{-5} \text{ mol/L}$ ($\text{Cl/N} = 0.17$; $\text{pH} 6.9$; $T = 30 \text{ }^\circ\text{C}$) (Fig. 4). Since urea is present in high excess compared to chlorine, only 4% of urea would be converted to NCl_3 , if chlorine is consumed completely. The initial urea concentration won't be decreased considerably.

NCl_3 is a known instable product in aqueous solutions with first order decay rate constants between $3.4 \times 10^{-5} \text{ s}^{-1}$ (20 °C, Saguinsin and Morris, 1975) and $7.5 \times 10^{-6} \text{ s}^{-1}$ (25 °C, Kumar et al., 1987) at pH 7. With this data the reaction of chlorine and urea was described as an irreversible consecutive reaction where NCl_3 is formed as an intermediate product (Eq. (7)). k_1 and k_2 are first order reaction rate constants.



The following time dependent modeled concentrations of free chlorine and NCl_3 shown in Fig. 4 were obtained from (Eq. (8)) and (Eq. (9)).

$$[\text{Chlorine}] = [\text{Chlorine}]_0 \times e^{-k_1 t} \quad (8)$$

$$[\text{NCl}_3] = k_1 / (k_2 - k_1) \times (e^{-k_1 t} - e^{-k_2 t}) \times [\text{Chlorine}]_0 \quad (9)$$

With the low decay constant from the literature of $7.5 \times 10^{-6} \text{ s}^{-1}$ a steady state level of $2.96 \times 10^{-6} \text{ mol/L}$ NCl_3 and

with the higher decay constant of $3.4 \times 10^{-5} \text{ s}^{-1}$ NCl_3 concentrations up to $1.03 \times 10^{-6} \text{ mol/L}$ were obtained. This results in a transformation between 1.5 and 4.4% of the nitrogen in urea to NCl_3 . In the next step the mass transfer of NCl_3 from the water to the air was considered. According to the Deacon's boundary layer model (in Schwarzenbach et al., 2003) the calculated liquid mass transfer coefficients were $v_{\text{NCl}_3, \text{w}} = 0.6 \times 10^{-3} \text{ cm/s}$ for quiescent (unused) pools, $v_{\text{NCl}_3, \text{w}} = 2.4 \times 10^{-3} \text{ cm/s}$ for rippled (normal used) pools and $v_{\text{NCl}_3, \text{w}} = 4.4 \times 10^{-3} \text{ cm/s}$ for rough surfaces (whirlpool) (paragraph 6 supporting information). The NCl_3 concentration in water $c_{\text{NCl}_3, \text{w}}$ of 0.08 mg/L is a very realistic assumption and would result from an urea concentration of 2 mg/L and a 1% conversion to NCl_3 (cf. long term NCl_3 formation at sub-stoichiometric Cl/N ratios in Fig. 3 and kinetic consideration as an irreversible consecutive reaction Fig. 4). The NCl_3 concentration of 0.08 mg/L is also in accordance to literature data for mean NCl_3 levels of 11 swimming pools between 0.02 and 0.19 mg/L (Weaver et al., 2009). Resulting fluxes for NCl_3 from water to air are then calculated to $1.8 \times 10^{-3} \text{ g h}^{-1} \text{ m}^{-2}$, $7.0 \times 10^{-3} \text{ g h}^{-1} \text{ m}^{-2}$ and $12.6 \times 10^{-3} \text{ g h}^{-1} \text{ m}^{-2}$ again for quiescent, rippled and rough water surfaces, respectively (Table 2). To transfer the NCl_3 fluxes to air concentrations of NCl_3 a typical indoor pool geometry (water surface 312.5 m², air volume 5760 m³) and two scenarios for air ventilation rates have been assumed. A minimum air ventilation rate of 0.5 per hour at a fresh air supply of 30% is recommended by the German standard (VDI 2089-1, 2008; DIN 4108, 2003). A typical ventilation rate is 2 air exchanges per hour at a fresh air supply of 50%. The resulting air concentrations of NCl_3 range from 0.10 mg/m³ for smooth water surface at a high ventilation rate to 4.5 mg/m³ for rough water surface at a low ventilation rate. The data clearly show that for a typical bather load NCl_3 concentrations in the air can be well above the

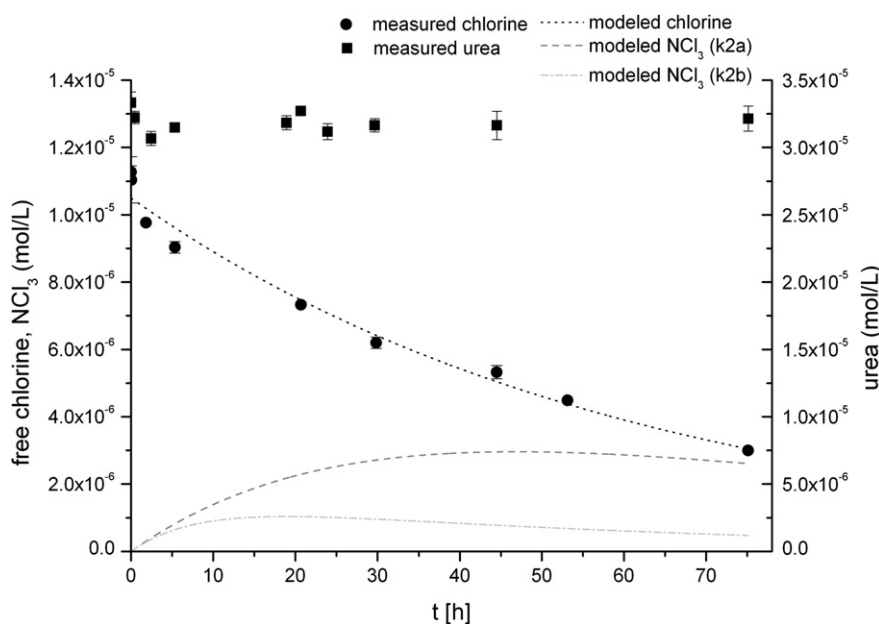


Fig. 4 – Measured and modeled reaction progress of chlorine with urea. - c_0 (free chlorine) = $1.13 \times 10^{-5} \text{ mol/L}$; c_0 (urea) $3.33 \times 10^{-5} \text{ mol/L}$, $\text{pH} 6.9 \pm 0.1$; $T = 30 \text{ }^\circ\text{C}$. (error bars 1 s ($n = 2$) for the measured values). Pseudo first order decay of free chlorine: $y = 1.05\text{E}-05e^{-4.58\text{E}-06x}$; $R^2 = 0.988$). Modeled NCl_3 concentrations from decay rate $k_{2a} = 7.5 \times 10^{-6} \text{ s}^{-1}$ (Kumar et al., 1987) (dashed line) and $k_{2b} = 3.4 \times 10^{-5} \text{ s}^{-1}$ (Saguinsin and Morris, 1975) (dotted-dashed line).

Table 2 – Calculated trichloramine concentrations in indoor pool air. - Modeling parameters: $c(\text{NCl}_3)$ (water): 0.08 mg/L; volume of water V_w : 960 m³; surface area of water A: 312.5 m²; volume of air V_a : 5760 m³, water temperature T: 28 °C.

	Quiescent surface (unused pool)		Rippled surface (used swimmer pool)		Rough surface (whirlpool)	
Input						
$v_{\text{NCl}_3\text{w}}$ (cm s ⁻¹)	0.6 × 10 ⁻³		2.4 × 10 ⁻³		4.4 × 10 ⁻³	
$c_{\text{NCl}_3\text{w}}$ (mg L ⁻¹)	0.08		0.08		0.08	
Output						
$F_{\text{NCl}_3\text{w}}$ (g h ⁻¹ m ⁻²)	1.8 × 10 ⁻³		7.0 × 10 ⁻³		12.6 × 10 ⁻³	
$R_{\text{NCl}_3\text{w}}$ (g h ⁻¹)	0.55		2.20		3.93	
$R_{\text{NCl}_3\text{w}}/V_{\text{air}}$ (mg m ⁻³ h ⁻¹)	0.10		0.38		0.68	
$c_{\text{NCl}_3\text{wair}}$ (mg m ⁻³)	low ventilation ^a	high ventilation ^b	low ventilation ^a	high ventilation ^b	low ventilation ^a	high ventilation ^b
	0.64	0.10	2.54	0.38	4.54	0.68

a air ventilation rate 0.5/h and fresh air percentage of 30%.

b air ventilation rate 2/h and fresh air percentage of 50% (typical).

proposed INRS guideline value of 0.5 mg/m³ of NCl₃ in air (Hery et al., 1995; Gagnaire et al., 1994) under low air exchange and high stripping conditions. The water-air exchange reveals as a slow process compared to the turnover rate of the pool water treatment and the decay rate of NCl₃ in water. The transfer of NCl₃ from water to air of a swimming pool would take 5.8 d or 20 h for smooth or rough water surface, respectively. Therefore a part of the dissolved NCl₃ can be removed in the treatment cycle.

Hence two means are possible to minimize the NCl₃ exposure of bathers: the reduction of urea due to its slow reaction kinetics of NCl₃ formation and the degradation of NCl₃ due to its slow mass transfer. Both processes are slower than a typical treatment cycle of a 25 m swimming pool which is between 6 and 8 h. Up to now urea is predominantly degraded by chlorine only. Ozonation is not very efficient due to the short contact time of often less than 1 min and due to the slow reaction rates of ozone with urea ($k = 0.05 \text{ L mol}^{-1} \text{ s}^{-1}$) (Eichelsdoerfer and von Harpe, 1970; Hoigné and Bader, 1983). The decomposition of NCl₃ in water can also be taken into consideration if sufficient reaction time is provided or for example UV irradiation was already used to control combined chlorine and NCl₃ (Cassan et al., 2006; De Laat and Berne, 2009). A more challenging task for the future is to develop a cost efficient and quantitative decomposition process for urea and other precursors in pool water treatment.

4. Conclusions

The formation of trichloramine in swimming pool water and the mass transfer from the aqueous to the gas phase was investigated. The results demonstrated that urea, ammonium ions, α -amino acids and creatinine from the bathers load can be considered as precursors for trichloramine formation in swimming pool water. Urea revealed as the most important trichloramine precursor. At neutral pH values NCl₃ yields of chlorination experiments at sub-stoichiometric chlorine to nitrogen ratios revealed the preference of the formation of trichloramine compared to mono- and dichlorinated products. The reaction kinetics of trichloramine formation and degradation was regarded in a simplified model as an

irreversible consecutive reaction with a slow formation and a faster degradation of trichloramine. Under real swimming pool water conditions, a conversion of 1% of the urea nitrogen to trichloramine was determined. Furthermore, the mass transfer of trichloramine from the water into the gas phase was calculated with the Deacon's boundary layer model. For typical NCl₃ concentrations in the water, air concentrations of NCl₃ varied over a wide range and strongly correlated with the characteristics of the air-water surface and the ventilation. However the mass transfer of NCl₃ from water to air is quite slow compared to a typical treatment cycle. Therefore the removal of precursor compounds and the disinfection by-product trichloramine in the pool water treatment would be an attractive possibility to improve the water and air quality of swimming pools.

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Appendix. Supporting information

Supplementary data related to this article can be found online at [doi:10.1016/j.watres.2011.02.024](https://doi.org/10.1016/j.watres.2011.02.024).

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