

NITROGEN-CONTAINING DISINFECTION BY-PRODUCTS IN INDOOR POOL SETTINGS – FORMATION AND EXPOSURE

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ABSTRACT

Disinfection of swimming pool water with chlorine is worldwide the most common method. However, a compromise has to be taken between the hygienic safety and the occurrence of toxic disinfection by-products (DBPs). Among the well-known trihalogenmethanes, numerous other DBPs of different chemical classes like chloramines, halogenated acetonitriles, halogenated nitro compounds and nitrosamines were analysed in swimming pool water (Zwiener et al., 2007). Many of them show cytotoxicity and genotoxicity (Richardson et al., 2007), some are volatile and therefore partition to the gas phase. Trichloramine is an irritant compound of penetrating odour and can be measured predominantly in the air of indoor swimming pools since it is four times more volatile than chloroform. Recent epidemiological studies correlate swimming pool attendance with respiratory complaints and the increased risk of developing asthma. Mostly trichloramine is suggested to cause eye, upper respiratory tract irritation (Massin et al., 1998) and biomarker changes in the lung (Bernard et al., 2006). A transdisciplinary approach is necessary to address current research questions on the formation, and minimization of DBPs, their toxicological relevance and their risk for humans. Recent and current joint research projects addresses these topics: „Integrated Risk Assessment for the New Generation of Disinfection By-Products“ and “Health Related Treatment Optimisation of Swimming Pool Water”.

In this presentation nitrogen-containing DBPs, especially NCl_3 , will be considered in more detail in indoor swimming pools. The major drivers of the partly coupled chemical processes of NCl_3 formation were elucidated in laboratory experiments. Nitrogen compounds of the bathers load like urea, ammonia and α -amino acids revealed as most efficient NCl_3 precursors. At neutral pH 76% of the nitrogen of urea could be transformed to NCl_3 . Even at substoichiometric molar ratios of chlorine to nitrogen the formation of NCl_3 was favored over the production of mono and dichlorinated products. However, the reaction kinetics of urea with chlorine is rather slow. Half lives for urea of more than 23 hours were determined under conditions relevant for swimming pools. The mass transfer of NCl_3 from water to the gas phase was estimated by a one-film model and revealed as a relatively slow process, too. A quantitative mass transfer of NCl_3 from water to air would take 19 h or 5.5 days for a rough (whirlpool) or a smooth surface (unused pool) of the water, respectively. This is much more than a typical turnover rate of 0.4 to 8 h of a treatment cycle of swimming pools. Therefore a great part of the produced NCl_3 in the swimming pool water is transferred to the SPW treatment. There the possibility of a removal, before it is transferred to the air, is given. Further measures will be necessary to reduce NCl_3 in indoor pools. Possibilities will be the degradation of the most important precursors and the reduction of the nitrogen input by the bathers with demands to behaviour measures like showering before going in to the pool.

Keywords	Chlorination reactions, trichloramine formation, mass transfer
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INTRODUCTION

Disinfection of swimming pool water with chlorine is worldwide the most common method. However, a compromise has to be taken between the hygienic safety and the occurrence of toxic disinfection by-products (DBPs). Among the well-known trihalogenmethanes, numerous other DBPs of different chemical classes like chloramines, halogenated acetonitriles, halogenated nitro compounds and nitrosamines were analysed in swimming pool waters (Zwiener et al., 2007). Many of them show cytotoxicity and genotoxicity (Richardson et al., 2007), some are volatile and therefore partition to the gas phase. Trichloramine is an irritant penetrating odour and can be measured predominantly in the air of indoor swimming pools since it is four times more volatile than chloroform. Recent epidemiological studies correlate swimming pool attendance with respiratory complaints and the increased risk of developing asthma. Mostly trichloramine is suggested to cause eye, upper respiratory tract irritation (Massin et al., 1998) and biomarker changes in the lung (Bernard et al., 2006). A transdisciplinary approach is necessary to address current research questions on the formation, and minimization of DBPs, their toxicological relevance and risk for humans. The recently started joint research project "Health Related Treatment Optimisation of Swimming Pool Water" address these topics. One focus is on nitrogen-containing DBPs, especially NCl_3 , which is addressed also in this presentation. In this context the major drivers of the partly coupled chemical processes of NCl_3 formation and partitioning were elucidated in laboratory experiments.

MATERIAL AND METHODS

Chlorination experiments were done with sodium hypochlorite solution and different nitrogen precursor compounds like ammonia, urea, amino acids and organic amines (Figure 1). The pH was adjusted with phosphate buffer. Experiments were done with chlorine to nitrogen ratios from 0.15 to 5, pH values between 2.5 and 8.0 and precursor concentrations from 6.7×10^{-5} mol/L to 1.0×10^{-2} mol/L. The reaction products were analysed by UV-spectroscopic and mass spectrometric methods. Free chlorine was determined with the DPD-method (Spectroquant® chlorine cell test, Merck).

To describe mass fluxes of NCl_3 from the water to the gas phase the general Fick's law was applied. The liquid mass transfer coefficient for NCl_3 was calculated according the Deacon's boundary layer model (Deacon, 1977; Schwarzenbach et al., 2003). 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 $T = 28^\circ\text{C}$, a water surface area $A = 312.5 \text{ m}^2$ and an air volume of the pool hall $V_a = 5760 \text{ m}^3$.

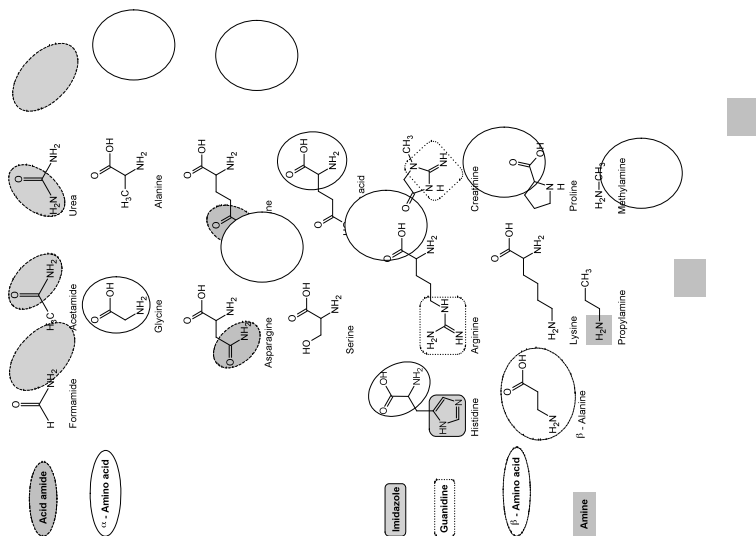


Figure 1 Nitrogenous compounds with different functional groups and different forms of bound nitrogen.

RESULTS AND DISCUSSION:

Nitrogen compounds of the bathers load like urea, ammonia and α -amino acids revealed as most efficient NCl_3 precursors compared to other compounds investigated (Table 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 and the pH dependent stability of NCl_3 . Urea showed a special NCl_3 formation. At neutral pH 76% of the nitrogen of urea could be transformed to NCl_3 . Even at substoichiometric molar ratios of chlorine to nitrogen the formation of NCl_3 was favored over the production of mono and dichlorinated products.

Table 1 Relative NCl_3 -formation of different nitrogenous substances. – Reaction of 10 mmol/L nitrogenous compound (calculated as N) with chlorine at a molar chlorine to nitrogen ratio of 5 in buffered solution. (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 $c(\text{NCl}_3) / c(\text{N}) \times 100 (\%) (\pm \text{standard deviation})$							
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
Glutaminc 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.

However, the reaction kinetics of urea with chlorine is rather slow. Half lives for urea of more than 23 hours were determined under conditions relevant for swimming pools. The mass transfer of NCl_3 from water to the gas phase was estimated by a one-film model and revealed as a relatively slow process, too. A quantitative mass transfer of NCl_3 from water to air would take 20 h or 5.8 days for a rippled surface like in a crowded pool or for a smooth surface like in an unused pool, respectively. This is much more than a typical turnover rate of 6 h to 8 h of a treatment cycle of swimming pools. Therefore a great part of the produced NCl_3 in the swimming pool water is transferred to the SPW treatment. There is the possibility of removal, before it is transferred to the air. Further measures will be necessary to reduce NCl_3 in indoor pools. This includes technical and behavioural means, like the removal of the most important precursors and the reduction of the nitrogen input by the bathers.

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