Trichloramine prevention remains better than cure

Recreation *is the first UK publication to feature new research from Germany that is relevant to anyone involved in managing, working in or using indoor swimming pools*

BEST PRACTICE REMAINS LARGELY UNCHANGED

This German research, published here for the first time in the UK, provides an important step forward in our understanding of the relationship between chlorine levels in pools and the production of trichloramines. Essentially, high combined chlorine levels do not automatically mean high trichloramine levels.

The key precursor for the formation of trichloramines (nitrogen trichloride) is urea from urine, sweat and skin cells. Best practice remains largely unchanged: that the concentration of urea in pool water must be minimised.

Keys to minimising urea concentration:

- Educate pool users: prevention is better than cure. Comprehensive pre-swim hygiene measures including using the toilet (elimination of the urine source) and washing thoroughly prior to pool use (the skin source) will help greatly.
- Remove urea by water treatment through ozone-activated carbon treatment or photo-oxidation.
- Reduce the urea concentration by dilution (adding 30 litres of fresh water per pool user).
- Provide good pool hall ventilation, ideally without re-circulation or at least 30 per cent fresh air.

1. Introduction

Trichloramine (nitrogen trichloride, NCl_3) is formed, along with other chlorine-nitrogen compounds, in the chlorination of swimming and bathing pool water. It belongs to the compounds that are subsumed under the chemical parameter 'combined chlorine'. Combined chlorine is defined as the sum of the following compounds [1]: derivatives of ammonia in which one, two or three hydrogen atoms have been replaced by chlorine atoms (monochloramine, NH2Cl; dichloramine, NHCl2; trichloramine, NCl3); and all chlorinated derivatives of urea and organic nitrogen compounds such as creatinine and amino acids.

A direct analysis method for combined chlorine does not exist. Its concentration has to be calculated from the difference between total chlorine and free chlorine. Unfortunately, however, the result does not indicate which individual substances it contains, and at what concentrations.

Trichloramine has an intense, pungent odour similar to that of chlorine – the typical indoor pool smell. It irritates the eyes and mucous membranes. Because of its high vapour pressure and poor water-

solubility, it readily escapes from swimming and bathing pool water and may consequently accumulate in the air of indoor pools and then lead to breathing problems and eye irritations. The irritating effects are similar to those of chlorine gas [2].

Belgian researchers hypothesised that the exposure of schoolchildren to trichloramine during visits to indoor chlorinated swimming pools adversely affected the lung epithelium permeability of the children and could lead to an increased risk of developing asthma [3]. English scientists reported asthma symptoms in lifeguards and swimming teachers caused by chloramines [4]. More recent studies corroborate the above hypothesis [5, 6].

In summer 1999, the German Federal Environmental Agency, as a precaution, started to measure trichloramine in the air of indoor pools as part of scientific investigations into the formation and minimisation of undesirable by-products of swimming and bathing pool water chlorination. The object was to obtain initial information as to whether and to what extent the air in German indoor swimming pools is contaminated by this compound. No such information was available for German indoor pools at the time.

The following is a report on the formation and properties of trichloramine and its analysis. First measurement results are presented and discussed.

2. Urea and formation of trichloramine in pool water

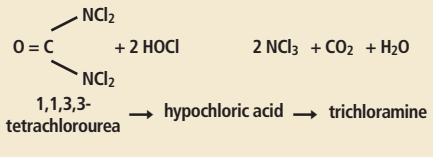
Considerable amounts of urea are introduced to swimming and bathing pool water by pool users.

UREA CONCENTRATION		
Urine	Sweat	Skin
21.9g/l	1.5g/l	8 µg/cm_

Table 1: Average concentration of urea in urine, sweat and the horny layer of the epidermis.

COMPOUND	H
Hypochloric acid	0.069
Monochloramine	0.45
Dichloramine	1.52
Trichloramine	435

Table 3: Henry's law constants (H).



The sources are the skin, urine and sweat. Urea is the main final product of the protein metabolism of humans. About 90 per cent is excreted via the kidneys (urine), the remainder via sweat and intestinal secretions. It also forms during skin hornification.

Urea is a chemical compound with the following formula: $H_2N\text{-}CO\text{-}NH_2$. In its pure form, it forms colourless and odourless crystals which are readily soluble in water. The presence of urea in chlorinated pool water leads to the formation of trichloramine.

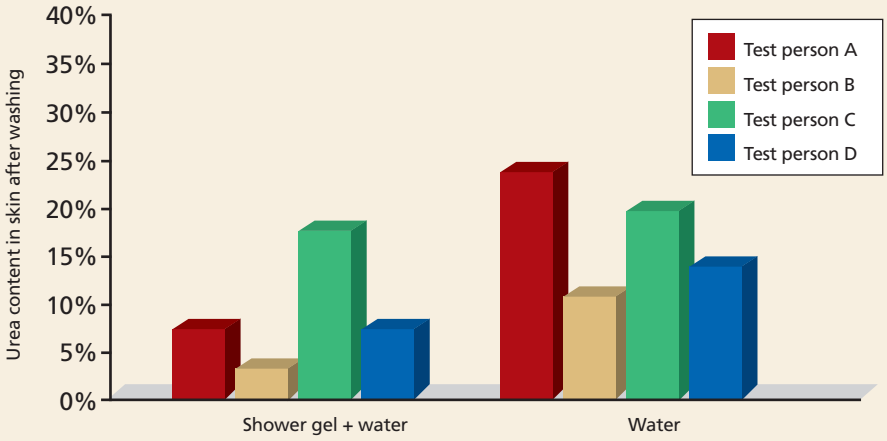


Figure 1: Influence of washing on the urea content in the stratum corneum, after (8).

	Free chlorine	Mono -chloramine	Dichloramine	Trichloramine
Mg/l				
No eye irritation in rabbits[1)]	0-8	0-2	No data	No data
Distinct eye irritation in rabbits[1)]	30	4	No data	No data
Odour and taste threshold[2)]	20	5	0.8	0.02

1) Eichelsdörfer et al. [16] ; 2) Spon [17]

Table 2: Properties of chlorine and chloramines.

Urea sources: skin, urine and sweat

The skin is the largest organ of the human body, with a surface area of approximately 1.5 to 2m^2. Urea is a product of the degradation of the amino acid arginine during skin hornification [7]. It belongs to the natural factors that keep the skin moist.

The urea content in the horny layer (stratum corneum) of healthy skin is about 8 µg per cm^2 of skin surface, for both men and women. 2m^2 of skin surface would thus contain about 0.16 g of urea. Pool water readily removes water-soluble organic and inorganic constituents including urea from the skin of pool users. Assuming that all urea in the stratum corneum is fully washed into pool water in this way, then 1,000 pool users would release about 160g of urea into pool water. Thorough washing and showering by pool users prior to pool use removes about 75 to 97 per cent of the urea contained in the stratum corneum and is thus a very effective way to prevent urea input into pool water (Figure 1). Substantial amounts of urea and other nitrogen compounds may also be introduced into pool water through urine and sweat. Table 1 lists average concentrations of urea in urine, sweat and the horny layer of the epidermis.

Different figures are given in the literature as regards urine and sweat input to pool water [9 – 13]. Assuming a urine input of 35 ml per pool user as determined by Gunkel and Jessen [9], the input of urea to pool water would be about 0.8g per pool user. The amount of sweat released to pool water per pool user depends on many factors, such as water temperature, air humidity, physical condition and activity of the pool user. The expert literature indicates that an active swimmer, for example, may excrete up to one litre of sweat per hour [14]. Urea input with one litre of sweat would amount to about 1.5g per pool user and hour.

Trichloramine formation mechanism

In the scientific literature, the mechanism of trichloramine formation from urea is discussed from three different directions:

- Enzymatic degradation of urea, by the enzyme urease which is contained in various bacteria, to ammonia or ammonium, and reaction of the latter with free chlorine to trichloramine. According to Jessen and Gunkel [13], this process does not occur in chlorinated pool water;
- Hydrolysis (cleavage by the action of water) of urea, with formation of ammonia or ammonium, and subsequent reaction with free chlorine to trichloramine. This occurs only at temperatures of more than 65C and is not, therefore, relevant to pool water;
- The decisive mechanism for the formation of trichloramine in pool water is the step-by-step

reaction of the urea introduced by pool users with free chlorine to 1,1,3,3-tetrachlorourea and finally to trichloramine, as described in the literature [15].

Properties of trichloramine

Trichloramine is an undesirable by-product of disinfection, which has a strong irritating effect on the eyes, nose, throat and bronchial tubes. Its odour is similar to that of chlorine. The odour and taste threshold in water is very low, at 0.02 mg/l. A threshold concentration for eye irritation caused by the presence of trichloramine in pool water has not been established to date.

Eichelsdörfer et al. [16] demonstrated for free chlorine and monochloramine that distinct eye irritation in rabbits does not start at a concentration lower than about 30 mg/l and 4 mg/l, respectively. The value for trichloramine ought to be markedly lower. Table 2 summarises the literature data.

Previously, it had long been assumed that trichloramine forms only at a pH less than or equal to 4.4. However, this view has had to be revised; trichloramine is also formed at higher pH values such as occur in pool water, and is rather stable under such conditions. Investigations have shown, for example, that a diluted aqueous trichloramine solution has a half-life of 218 minutes at a pH of 7. This means that 50 per cent of the substance

'Water attractions such as waterslides, water geysers, flood showers and fountains accelerate the release of trichloramine to the air'

decomposes in water during that time [18]. For example, when the trichloramine concentration in pool water is 0.1 mg/l, then it would be 0.05 mg/l after 218 minutes, if one ignores gaseous emissions of the compound to air.

The outgassing behaviour of a substance dissolved in pool water can be estimated using the air/water partition coefficient (= Henry's law constant, H). The lower the Henry's law constant, the more soluble is the substance in pool water. The higher its Henry's law constant, the more readily it escapes from pool water to air. The Henry's law constants of mono-, di- and trichloramine and hypochloric acid have been determined experimentally by Holzwarth et al. [19] (Table 3).

Contribution of fresh air to ingoing air mass flow	Trichloramine in air	Chloramines (expressed as combined chlorine) in pool water
%	mg/m³	mg/l
0	0.52	0.15
30	0.37	0.15

Table 5: Influence of air renewal on trichloramine concentration in indoor pool air

Pool type	Trichloramine in indoor pool air	Chloramines (as combined chlorine) in pool water
	mg/m³	mg/l
Leisure	0.13	0.07
Leisure	0.16	0.13
Leisure	0.37	0.80
Leisure	2.2	0.12
Conventional	18.8	0.25
Hydrotherapy	0.19	0.01
Hydrotherapy	0.14	0.05
Exercise pool	0.05	0.03
Guideline values	0.50[1)]	0.20[2)]

1) according to INRS [22] ; 2) according to the German standard DIN 19643-1 [23]

Table 4: Trichloramine concentrations in the air of indoor swimming pools and corresponding concentrations of combined chlorine in pool water.

The H values show that trichloramine escapes from pool water 966 times faster than monochloramine and 286 times faster than dichloramine. It 'feels' 435 times 'more comfortable' in indoor pool air than in pool water. This and its odour and taste threshold (Table 2) are the main reasons for the typical chlorine-like smell in swimming pool halls. The H value of dichloramine is only of theoretical interest, as the compound is not stable and decomposes very quickly in pool water [20].

Water attractions such as waterslides, water geysers, flood showers and water fountains accelerate the release of trichloramine to air. Comparing, for example, the outgassing behaviour of trichloramine to that of chloroform, which belongs to the substance group of trihalomethanes, trichloramine escapes from pool water three times faster than that substance.

MEASUREMENT OF TRICHLORAMINE

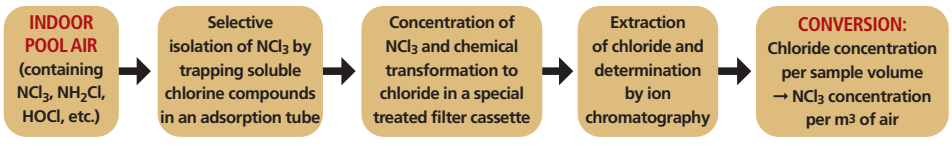
3.1 Measurement in pool water

There is currently no simple on-site method for the selective determination of trichloramine in pool water. One laboratory method to reliably differentiate between and quantify the various inorganic chloramines – mono-, di- and trichloramine – is membrane introduction mass spectrometry (MIMS), whose use remains reserved to specialised water analysis laboratories. The detection limit for trichloramine is reported to be 0.06 mg/l [21].

4.2 Measurement in the air of indoor swimming pools

The German Federal Environmental Agency, Department for Drinking and Swimming Pool Water Hygiene, began measuring trichloramine in the air of indoor swimming pools in summer 1999, for precautionary and the following other reasons: no data whatsoever was available on trichloramine concentrations in the air of German swimming pool halls; the French INRS (Institut National de Recherche et de Sécurité) has published a validated method for the determination of trichloramine in air [22], which was adopted by the Federal Environmental Agency to ensure comparability with INRS measurement data and which is, to this day, the only existing method for determination of trichloramine in air; a health-based guideline value of ≤ 0.50 mg/m3 has been proposed in France for trichloramine in indoor pool air [2, 22]. This value can be used as a basis for assessment of the measurement results.

The principle of the analytical method is shown in the flow chart, left.



Flow chart: the principle of the analytical method.

5. Selected results

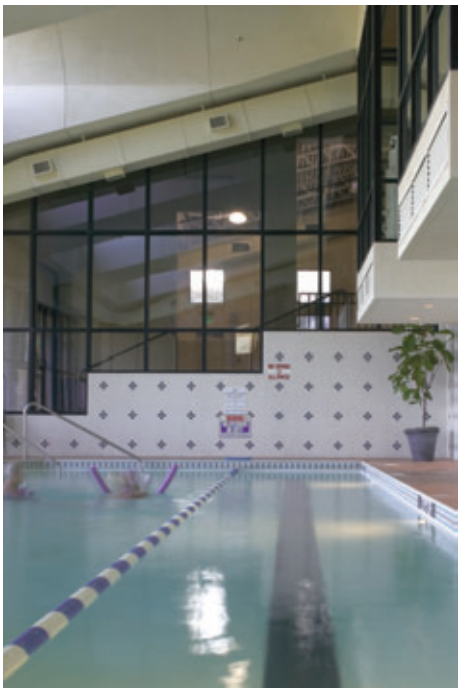
Table 4 presents selected measurement results on trichloramine in the air of indoor swimming pools for different pool types and compares them with

the corresponding measurement data for combined chlorine in pool water.

The values in Table 4 show that measured trichloramine concentrations in the air of indoor swimming pools do not correlate with the values for combined chlorine. There may be cases where the concentration of combined chlorine in pool water, at 0.80 mg/l, exceeds by far the upper value of 0.20 mg/l recommended by the German standard DIN 19643-1 while the trichloramine concentration in the indoor pool air, at 0.37 mg/m3, is below the recommended guideline value of 0.50 mg/m3.

Conversely, there are cases where concentrations of combined chlorine in pool water comply with (0.12 mg/l) or are just slightly above (0.25 mg/l) the recommended upper value while the corresponding results for the trichloramine concentration in indoor pool air (2.2 and 18.8 mg/m3) exceed the guideline value, in the one case, by a substantial amount. This means that a DIN-compliant concentration of combined chlorine in pool water is not automatically linked with trichloramine concentrations in the indoor pool air that are safe for human health.

For this reason, care must be taken to ensure that the ventilation system is designed so that during pool operating hours the proportion of fresh air fed to the air circulating in the pool hall is adjusted to the pool capacity utilisation rate, as prescribed by the technical rule VDI 2089-1 [24]. When the pool is used to maximum capacity (for example, with very high bather loads and with all water attractions switched on) the proportion of fresh air should be at least 30 per cent of the ingoing air mass flow. An example of the influence of air renewal via the contribution of fresh air to the ingoing air mass flow is presented in Table 5. While the upper value in DIN 19643-1 for



combined chlorine in pool water is complied with, at 0.15 mg/l, trichloramine can build up in the indoor pool air to exceed the guideline value of 0.50 mg/m3 if there is no air renewal by a defined proportion of fresh air (no dilution effect).

6. Discussion and conclusions

No direct correlation exists between the trichloramine concentration in the indoor pool air and the corresponding value for the chemical parameter 'combined chlorine' in pool water. This is because the measurement result for this sum parameter does not, unfortunately, indicate how much of the total content is trichloramine. A simple and reliable on-site method for specific measurement of trichloramine as an individual substance in pool water does not yet exist.

A DIN-compliant concentration of combined chlorine in pool water is no automatic guarantee that the trichloramine concentration in the air of the indoor pool will be tolerable from a health perspective. In addition, this means that, during pool operating hours, the airborne trichloramine should be diluted by air renewal via a defined contribution of fresh air to the ingoing air mass flow in accordance with the generally accepted technical standards (VDI 2089 Blatt 1) [24]. This will prevent trichloramine accumulating in the air of the pool hall to an extent as to exceed the guideline value of 0.50 mg/m3.

The concentration of urea in pool water must be minimised, since its reaction with free chlorine in pool water results in the formation of trichloramine, among other substances. This may be achieved by the following:

- With the help of pool users: by using the toilet (elimination of the urea source 'urine') and washing themselves thoroughly (elimination of the urea source 'skin) prior to pool use;
- Removal of urea by water treatment (e.g. ozone-activated carbon treatment [25] [26], photooxidation [27]); and
- Reducing the urea concentration by dilution (adding 30 litres of fresh water per pool user).

If these hints are observed, there need be no concern, according to present knowledge, that trichloramine in indoor swimming pool air may pose a health risk.

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