

# **Analysis of Swimming Pool Water – Assessment of Results According to German Regulations**

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## **Abstract**

In Germany, quality of swimming pool water is regulated by DIN19643. In this paper we present results of microbiological and chemical analysis of pool water and show correlations between parameters. In total, more than 500 pool analysis from 100 different pools have been performed within a two-year period. Results have been evaluated using statistical methods. Next to microbiological parameters (Colony count, E. coli, Coliforms, Pseudomonas aeruginosa and Legionellae), chemical (including free and combined chlorine, KMnO<sub>4</sub> consumption, NO<sub>3</sub>, Cl, SO<sub>4</sub>, PO<sub>4</sub>) and physico-chemical parameters (ORP, pH, T) have been analysed in pool water and after water treatment. Results obtained within this study clearly indicate interdependencies between parameters and show that chlorine concentrations of 0.3 to 0.6 mg/l are sufficient to guarantee adequate swimming pool water quality.

## **Introduction**

Since the beginning of the last century, techniques for swimming pool water preparation have been developed which are capable of maintaining the quality of swimming pool water over long periods. Many countries introduced regulations on the quality of swimming pool water, usually these regulations include at least microbiological and several chemical parameters to guarantee long term hygienic quality of the water.

In Germany, technical regulations for the operation of swimming pools are summarised in DIN19643 „Preparation and Disinfection of swimming- and bathing pools”. These regulations contain threshold limits for the examination of pool water according to parameters listed in table 1.

Frequency of examination of swimming pool water depends on the size of the pool. In large indoor pools microbiological analyses are performed once per month and chemical analysis at least 2 times per year. Outdoor pools are inspected once per month during the bathing season. The purpose of this presentation is to present data of swimming pool analysis and to show dependencies of parameters. Another aim is to show that indoor pools can be operated safely using chlorine concentrations as low as 0.3 to 0.6 mg/l.

## **Methods**

*Chemical and physico-chemical analysis of swimming pool water:* All chemical and microbiological analysis were performed according to German standard methods. Free and combined chlorine were measured using the DPD method and a portable photometer (Allcon). Anions were analysed using a Dionex DX-120 chromatograph. All photometrical analysis were performed using a Hitachi U-2000 spectrophotometer. DPBs were measured using a purge-and-trap method (Tekmar Purge and Trap analyser) in connection with a GC and ECD detection (Fisons GC8000).

*Measurement of ORP:* According to technical regulations public swimming pools have to record free chlorine as well as ORP (Oxidation-Reduction-Potential) permanently. While data for free chlorine have been measured on site, data for ORP have been taken from on site instruments.

*Microbiological analysis:* Heterotropic plate count was performed using standard agar. E.coli, Coliforms and P. aeruginosa were examined using enrichment broth.

**Table 1:** Microbiological, physico-chemical and chemical threshold values for swimming pool water according to DIN19643.

Parameter	Pool water	Cleaned water	Filtrate
E.coli	n.d. in 100 ml	n.d. in 100 ml	
Pseudomonas aeruginosa	n.d. in 100 ml	n.d. in 100 ml	
Colony count (20± 2)°C, (36 ±1)°C	100/ml	20/ml	
Legionella sp.	n.d. in 1 ml		n.d. in 100 ml
Free chlorine	0.3-0.6 mg/l	Min. 0.3 mg/l	
Combined chlorine	Max. 0.2 mg/l	Max 0.2 mg/l	
ORP	Min 730 mV		
pH	6.5-7.2*		
Acid capacity		Min. 0.7 mmol/L	
Aluminium		0.5 mg/L	
Chloride			
Coloration	0.5/m	0.2/m	
Nitrate		20 mg/L <sup>#</sup>	
Phosphate			
Sulfate			
Temp.		Max 32°C	
Trihalomethanes		Max. 20 µg/L	
Turbidity	0.5 FNU	0.2 FNU	

\*if Aluminium salts are used for flocculation <sup>#</sup>above Filling water

## Results

Microbiological quality is the most important parameter for the safety of swimming pool water. Therefore there is broad consent that disinfection of pool water is indispensable. Ideas about chlorine concentrations necessary to achieve this goal vary widely between different countries. WHO suggests for public pools a minimum concentration of free chlorine of 1 mg/L and a maximum level of 2 mg/L (WHO 2000). However, scientific background for these concentrations is only limited and experiences in different countries on microbiological quality of swimming pool water have not been published so far.

### Chlorine and ORP

Concentration of free chlorine is most important for disinfection capacity, whilst combined chlorine is much less active. Additionally, the pH of the water is of crucial importance for the disinfecting activity of hypochlorites since only hypochlorous acid is the active component in this system. Oxidation-Reduction-Potential theoretically depends on concentrations of the oxidizing disinfectants as well as on pH value and concentration of reducing compounds in the water (soil). Therefore this parameter can be useful for the evaluation of the overall disinfection capability of the water. Average data for ORP, free and combined chlorine are given in table 2.

Mean values for free and combined chlorine were within the limits defined in DIN19643 and the mean value for ORP was significantly higher than required by DIN19643. A Pearson product moment correlation shows significant correlation between concentration of free

chlorine in the pool water and ORP ( $p=0,0019$ ). However, there is no correlation between  $KMnO_4$  consumption of the pool water or the cleaned water and ORP.

**Table 2:** Statistical data for ORP, free and combined chlorine in German indoor pools. All data in [mg/L],  $n=897$  (each).

	Free Chlor. (Pool)	Comb. Chlor. (Pool)	Free Chlor. (Cleaned water)	Comb. Chlor. (Cleaned water)	ORP
Median	0.47	0.08	0.53	0.07	777
Mean	$0.51 \pm 0,22$	$0.10 \pm 0.07$	$0.65 \pm 0.58$	$0.08 \pm 0.07$	$774 \pm 55$

Results of microbiological water analysis have been compared to results of physico-chemical and chemical water analysis ( $n=435$ , data from one year). Results indicate that 7.1% of all samples did not fulfill the required limits. There were 12 cases regarding pool water, 14 cases regarding cleaned water and 5 cases regarding both sampling sites that did not fulfill one or more microbiological demands of the DIN19643.

**Table 3:** Chlorine concentration and ORP in pools without microbiological problems.

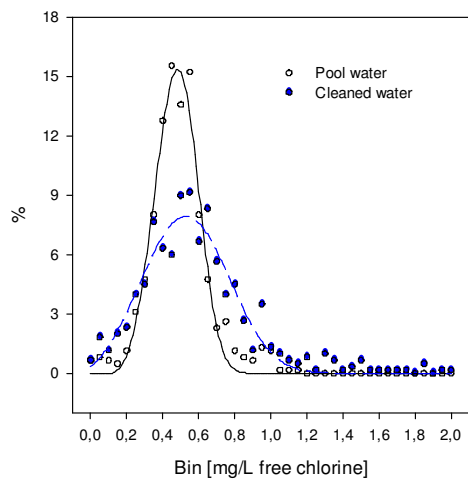
		Too low ( $<0,28$ mg/L)	Number (n)	Percent (%)
Free Chlor.	Cleaned water	54	393	13,7
	Pool water	34	403	8,4
ORP		46	381	12,1

**Table 4:** Chlorine concentration and ORP in pools not fulfilling microbiological requirements.

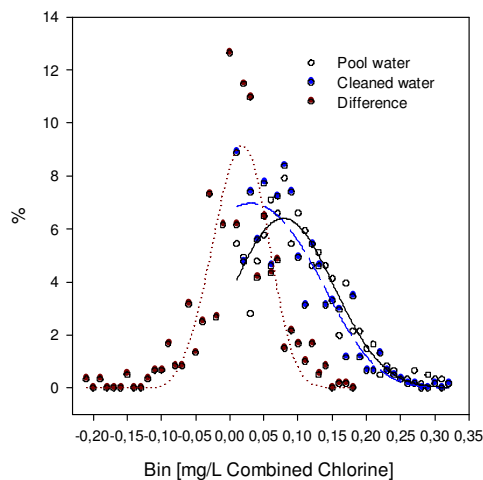
		Too low ( $<0,28$ )	Number (n)	Percent (%)
Free Chlor.	Cleaned water	5	20	25,0
	Pool water	2	17	11,8
ORP	Cleaned water	8	29	27,5
	Pool water	4	15	26,7

In order to assess significance of ORP for the evaluation of pool water, data for ORP and chlorine concentrations in pools are compared. In table 3 data for pools fulfilling all microbiological requirements chlorine concentrations are compared to results of ORP measurements, table 4 depicts the same data for pools where microbiological parameters were not conform to regulations. However, the data pool for swimming pools not fulfilling microbiological requirements is very limited and therefore results have to be interpreted with caution.

Distribution of free and combined chlorine in pool water and cleaned water are depicted in figures 1 and 2, respectively. For the purpose of these diagrams data have been grouped and %-frequency has been plotted on the y-axis.



**Figure 1:** Free chlorine in pool water and in cleaned water.

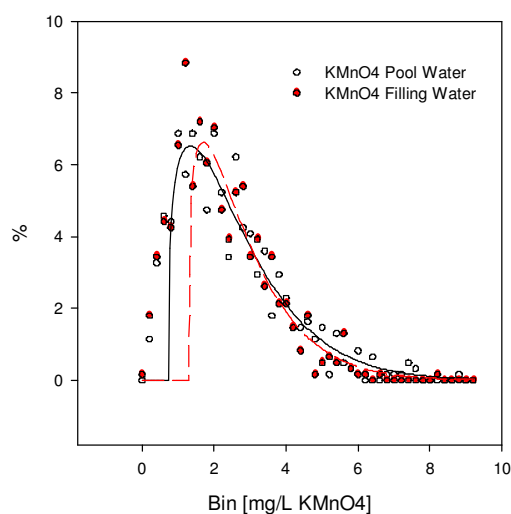


**Figure 2:** Combined chlorine in pool water, in cleaned water and difference between both.

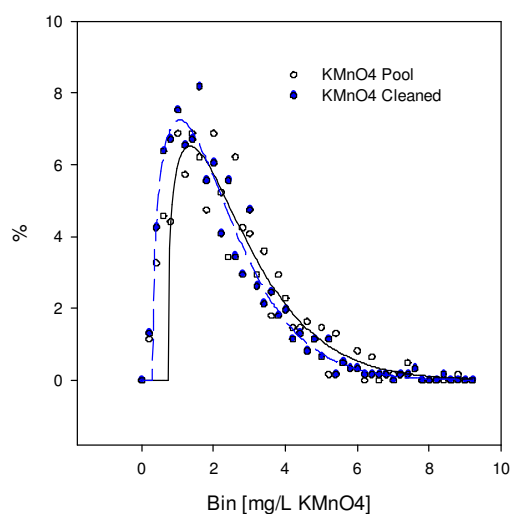
In all cases a Weibull distribution was employed to fit the data. For free chlorine in the pool water, distribution of data is narrow compared to the concentrations of free chlorine in the cleaned water. Obviously the standard of DIN19643 for a minimum chlorination of 0.3 mg/L in the cleaned water is not met. Data distribution of combined chlorine shows a maximum at 0.1 mg/L, and concentrations of combined chlorine seem to be a little lower in cleaned water. Distribution of the difference between concentration of combined chlorine in the pool water and in the cleaned water is nearly normal and shows that combined chlorine can be reduced or can raise by water filtration, probably depending on the backflush status of the sand filters.

### *KMnO<sub>4</sub> consumption*

KMnO<sub>4</sub> consumption is a parameter indicating polluting organic compounds in the water and thus reflecting quality of water preparation. This parameter is traditionally used in water chemistry although TOC (Total Organic Carbon) indicates the same information. KMnO<sub>4</sub> consumption is significantly different between pool water and filling water.



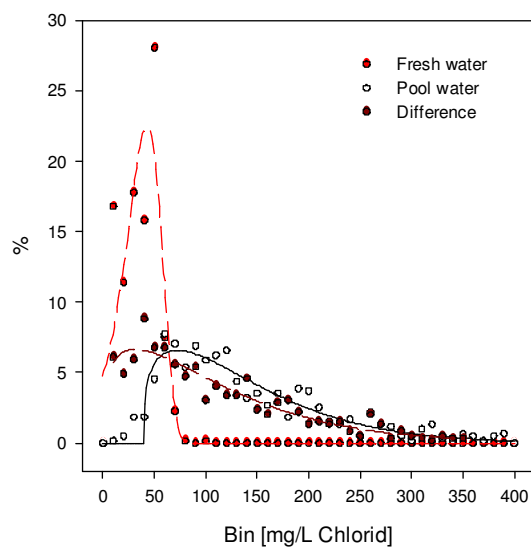
**Figure 3:** Comparison of KMnO<sub>4</sub> consumption of filling water and pool water (n=611).



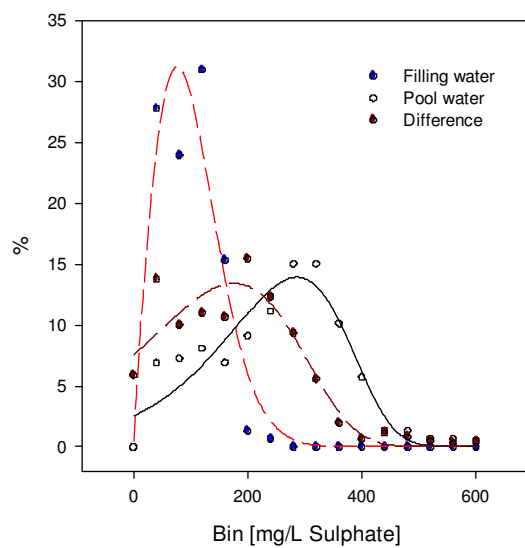
**Figure 4:** Comparison of KMnO<sub>4</sub> consumption of cleaned water and pool water (n=611).

Figure 3 indicates that maximum of the density function for  $\text{KMnO}_4$  consumption of the pool water is slightly lower than maximum for the filling water. That means that certain organic compounds from the filling water are removed through the water preparation process in the swimming pool. Figure 2 elucidates the effect of water filtration on  $\text{KMnO}_4$  consumption in pool water: The maximum is lower in cleaned water compared to pool water; there is no enrichment of  $\text{KMnO}_4$  consumption causing organic compounds.

Other inorganic parameters like sulphate or chloride can only be removed from the water by dilution because water filtration will not affect their concentration. Figures 5 and 6 compare chloride and sulphate concentrations in pool water with filling water.



**Figure 5:** Comparison of chloride concentration of filling water and pool water

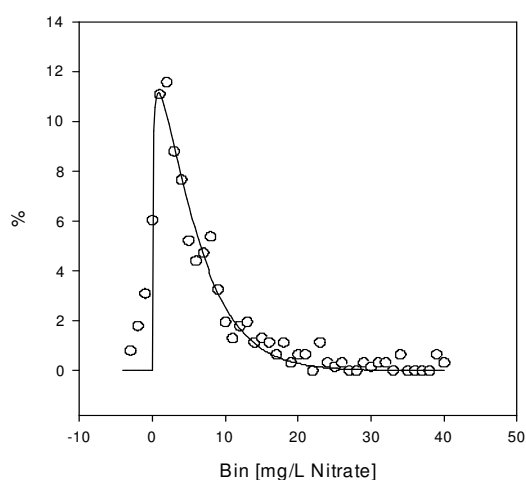


**Figure 6:** Comparison of sulphate concentration of filling water and pool water

The source for the enrichment of chloride in pool water is mainly the disinfectant, an additional source is present if hydrochloric acid is used for pH-stabilisation of the water. Finally, a certain amount of chloride will be brought in by the bathers. Distribution density of chloride concentration in the pool water reflects this situation. Distribution of data for sulphate looks different compared to chloride. The main source for sulphate in the water is sulfuric acid which can be used instead of hydrochloric acid for pH stabilisation of pool water. Another aspect is that chloride can at least partially escape from the water in form as nitrogen trichloride and other halogenated DBPs, whilst sulphate cannot.

### Nitrate

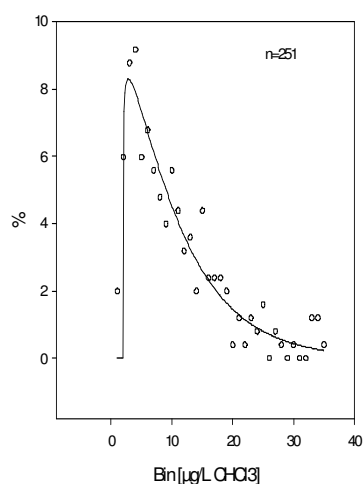
Figure 7 shows the distribution of differences of nitrate data (pool water-filling water). Compared to filling water, the concentration of nitrate in pool water is elevated. In contrast to sulphate and chloride, nitrate is not added deliberately to the pool water but it will be formed by oxidation of nitrogen containing organic and inorganic molecules. Like concentrations of sulphate and chloride, nitrate can only be removed by substitution of pool water. However, nitrate formation rate will depend on the oxidising capability of the water preparation system and other factors and therefore nitrate formation cannot be taken as a measure of freshwater addition to pool water.



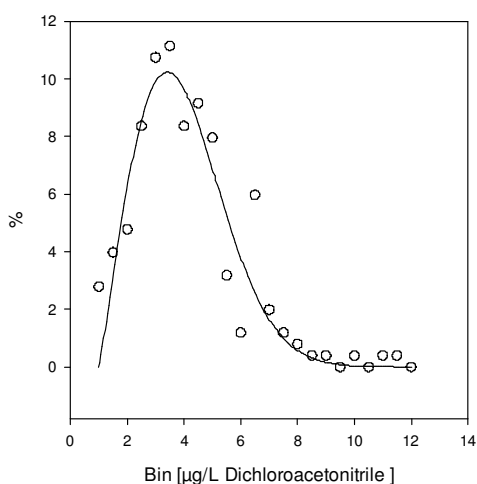
**Figure 7:** Difference of nitrate concentration in pool water and filling water.

### *Disinfection Byproducts*

According to regulations of DIN19643, total THM concentration should not exceed 20  $\mu\text{g/L}$ . No regulations or threshold limits are given for other organic DBPs. In swimming pools not containing bromide in the water, chloroform is the main component of total THM load. In figure 8 distribution of  $\text{CHCl}_3$  concentrations in pool waters is given, and in figure 9 data from the same pools for dichloroacetonitril is depicted. Because chloroform is a relatively unpolar compound compared to dichloroacetonitrile, it can escape from the water more easily. Actually the main pathway for the uptake of chloroform by swimmers is inhalation from indoor pool air. Compared to chloroform, dichloroacetonitril will remain longer in the pool water, the fate of this compound is not known.



**Figure 8:** Distribution of  $\text{CHCl}_3$  concentrations in swimming pools.



**Figure 9:** Distribution of Dichloroacetonitril distribution in swimming pools.

## Discussion

Swimming pool water is recycled over more or less specified periods and various chemicals are used to conserve water quality. Whilst there are numerous publications describing microbiological hazards in swimming pools (Yoder et al. 2002), chemical aspects of swimming pool water chemistry have not drawn much interest. If chemical aspects are addressed, in most cases only compounds to be added for a special purpose are centered, whilst their fate in the water is neglected. However, since epidemiological studies indicated that Clara cell protein is significantly lowered in children regularly visiting chlorinated swimming pools (Lagerkvist et al. 2004; Bernard et al. 2003) swimming pool water chemistry is gaining interest.

The chemistry of swimming pool water completely differs from drinking water chemistry. Some of the chemical components of pool water will be transformed after their release in the pool, others remain stable and can only be removed by water dilution, by addition of fresh water. Inorganic and organic nitrogen containing compounds released into the water by bathers will be transformed, at least partially, to combined chlorine. However, the chemical identity of individual compounds hiding behind this sum parameter is only known to a limited degree. Results show, that compounds forming combined chlorine do not concentrate in the water. Some of them will be transformed to nitrate, others will probably escape (as e.g. nitrotrichloride) to the atmosphere. Other components of the disinfectant, like chlorate, can concentrate in the water and reach high levels comparable to concentrations of other inorganic components of the water (Erdinger et al. 1999).

Inorganic compounds like sulphate and chloride which are added as disinfectant or in order to stabilize the pH of the water, will mainly remain unchanged and concentrate in the water. However, at least a small portion of the chlorine will react with organic or inorganic compounds and some of these reactions products are volatile and will escape from the pool. Hot whirl pools, for example, show lower chloroform concentrations in the water than other pools due to the intensive aeration of the water (Erdinger et al. 1997).

In order to avoid production of DBPs organic compounds should be removed from the water. Traditionally,  $\text{KMnO}_4$  consumption of the water is used to estimate burden of organic compounds. In Germany, flocculation using aluminium salts and sand filtration is usually employed to filtrate particles and organic compounds. Some public swimming pools use ozonation of the water in order to achieve better oxidation of organic compounds. Results indicate that in all swimming pools organic compounds do not concentrate over the course of time. On average, oxidizability of the pool water is reduced compared to filling water, and the effect of water filtration on removal of oxidizable compounds can be demonstrated.

Although chlorine concentrations as low as 0.3 to 0.6 mg/l are used in German swimming pools, microbiological quality is guaranteed. Only in a limited number of pools microbiological standards of DIN19643 have not been met. However, chlorine concentration of the water or measurement of ORP is not a reliable predictor of microbiological water quality: in about 75% of cases of microbiological contamination of the water chlorine concentration and/or ORP met the standards. Positive microbiological results may be accidentally. Therefore only repeated analysis of the water can prove that the water filtration process is working correctly.

## **Literature**

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