CHAPTER 4

Chemical hazards

Chemicals found in pool water can be derived from a number of sources: the source water, deliberate additions such as disinfectants and the pool users themselves (see Figure 4.1). This chapter describes the routes of exposure to swimming pool chemicals, the chemicals typically found in pool water and their possible health effects.

While there is clearly a need to ensure proper consideration of health and safety issues for operators and pool users in relation to the use and storage of swimming pool chemicals, this aspect is not covered in this volume.

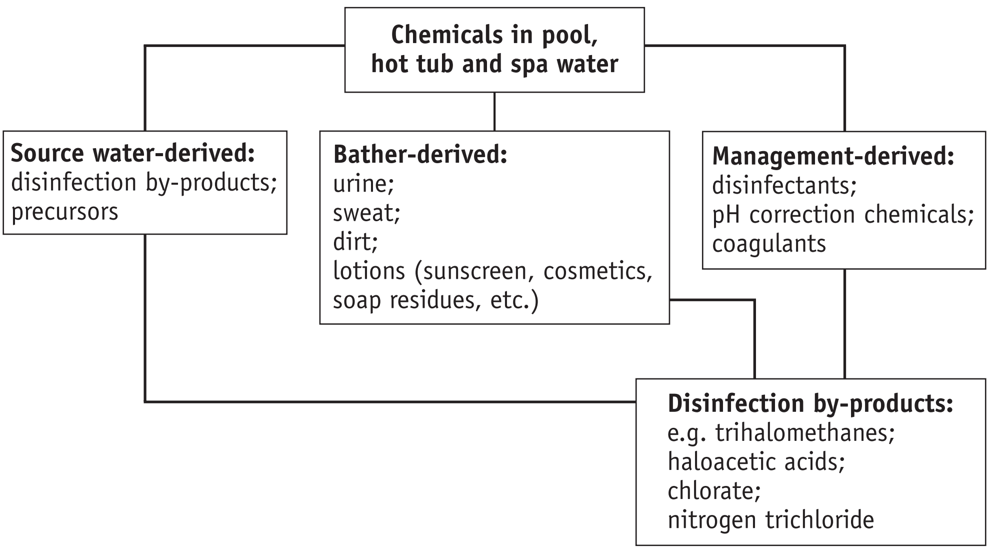

Figure 4.1. Possible pool water contaminants in swimming pools and similar environments

4.1 Exposure

There are three main routes of exposure to chemicals in swimming pools and similar environments:

- direct ingestion of water;
- inhalation of volatile or aerosolized solutes; and
- dermal contact and absorption through the skin.

4.1.1 *Ingestion*

The amount of water ingested by swimmers and pool users will depend upon a range of factors, including experience, age, skill and type of activity. The duration of exposure will vary significantly in different circumstances, but for adults, extended exposure would be expected to be associated with greater skill (e.g. competitive swimmers), and so there would be a lower rate of ingestion in a comparable time than for less skilled users. The situation with children is much less clear. There appear to be no data with which to make a more detailed assessment. A number of estimates have been made of possible intakes while participating in activities in swimming pools and similar environments, with the most convincing being a pilot study by Evans et al. (2001). This used urine sample analysis, with 24-h urine samples taken from swimmers who had used a pool disinfected with dichloroisocyanurate and analysed for cyanurate concentrations. All the participants swam, but there is no information on the participant swimming duration. This study found that the average water intake by children (37 ml) was higher than the intake by adults (16 ml). In addition, the intake by adult men (22 ml) was higher than that by women (12 ml); the intake by boys (45 ml) was higher than the intake by girls (30 ml). The upper 95th percentile intake was for children and was approximately 90 ml. This was a small study, but the data are of high quality compared with most other estimates, and the estimates, are based upon empirical data rather than assumptions. In this volume, a 'worst case' intake of 100 ml for a child is assumed in calculating ingestion exposure to chemicals in pool water.

4.1.2 *Inhalation*

Swimmers and pool users inhale from the atmosphere just above the water's surface, and the volume of air inhaled is a function of the intensity of effort and time. Individuals using an indoor pool also breathe air in the wider area of the building housing the pool. However, the concentration of pool-derived chemical in the pool environment will be considerably diluted in open air pools. Inhalation exposure will be largely associated with volatile substances that are lost from the water surface, but will also include some inhalation of aerosols, within a hot tub (for example) or where there is significant splashing. The normal assumption is that an adult will inhale approximately 10 m^3 of air during an 8-h working day (WHO, 1999). However, this will also depend on the physical effort involved. There will, therefore, be significant individual variation depending upon the type of activity and level of effort.

4.1.3 *Dermal contact*

The skin will be extensively exposed to chemicals in pool water. Some may have a direct impact on the skin, eyes and mucous membranes, but chemicals present in pool water may also cross the skin of the pool, hot tub or spa user and be absorbed into the body. Two pathways have been suggested for transport across the stratum corneum (outermost layer of skin): one for lipophilic chemicals and the other for hydrophilic chemicals (Raykar et al., 1988). The extent of uptake through the skin will depend on a range of factors, including the period of contact with the water, the temperature of the water and the concentration of the chemical.

4.2 Source water-derived chemicals

All source waters contain chemicals, some of which may be important with respect to pool, hot tub and spa safety. Water from a municipal drinking-water supply may contain organic materials (such as humic acid, which is a precursor of disinfection by-products), disinfection by-products (see Section 4.5) from previous treatment/ disinfection processes, lime and alkalis, phosphates and, for chloraminated systems, monochloramines. Seawater contains high bromide concentrations. In some circumstances, radon may also be present in water that is derived from groundwater. Under such circumstances, adequate ventilation in indoor pools and hot tubs will be an important consideration. WHO is considering radon in relation to drinking-water quality guidelines and other guidance.

4.3 Bather-derived chemicals

Nitrogen compounds, particularly ammonia, that are excreted by bathers (in a number of ways) react with free disinfectant to produce several by-products. A number of nitrogen compounds can be eluted from the skin (Table 4.1). The nitrogen content in sweat is around 1 g/l, primarily in the form of urea, ammonia, amino acids and creatinine. Depending on the circumstances, the composition of sweat varies widely. Significant amounts of nitrogen compounds can also be discharged into pool water via urine (Table 4.1). The urine release into swimming pools has been variously estimated to average between 25 and 30 ml per bather (Gunkel & Jessen, 1988) and be as high as 77.5 ml per bather (Erdinger et al., 1997a), although this area has not been well researched.

The distribution of total nitrogen in urine among relevant nitrogen compounds (Table 4.1) has been calculated from statistically determined means of values based on 24-h urine samples. Although more than 80% of the total nitrogen content in urine is present in the form of urea and the ammonia content (at approximately 5%) is low, swimming pool water exhibits considerable concentrations of ammonia-derived compounds in the form of combined chlorine and nitrate. It therefore appears that there is degradation of urea following chemical reactions with chlorine.

Table 4.1. Nitrogen-containing compounds in sweat and urine[a]

	Sweat		Urine	
Nitrogen-containing compounds	**Mean content (mg/l)**	**Portion of total nitrogen (%)**	**Mean content (mg/l)**	**Portion of total nitrogen (%)**
Urea	680	68	10 240	84
Ammonia	180	18	560	5
Amino acids	45	5	280	2
Creatinine	7	1	640	5
Other compounds	80	8	500	4
Total nitrogen	992	100	12 220	100

[a] Adapted from Jandik, 1977

In a study on the fate of chlorine and organic materials in swimming pools using analogues of body fluids and soiling in a model pool, the results showed that organic carbon, chloramines and trihalomethanes all reached a steady state after 200–500 h of operation. Only insignificant amounts of the volatile by-products were found to be lost to the atmosphere, and only nitrate was found to accumulate, accounting for 4–28% of the dosed amino nitrogen (Judd & Bullock, 2003). No information is available on concentrations of chemicals in actual swimming pool water from cosmetics, suntan oil, soap residues, etc.

4.4 Management-derived chemicals

A number of management-derived chemicals are added to pool water in order to achieve the required water quality. A proportion of pool water is constantly undergoing treatment, which generally includes filtration (often in conjunction with coagulation), pH correction and disinfection (see Chapter 5).

4.4.1 Disinfectants

A range of disinfectants are used in swimming pools and similar environments. The most common are outlined in Table 4.2 (and covered in more detail in Chapter 5). They are added in order to inactivate pathogens and other nuisance microorganisms. Chlorine, in one of its various forms, is the most widely used disinfectant.

Some disinfectants, such as ozone and UV, kill or inactivate microorganisms as the water undergoes treatment, but there is no lasting disinfectant effect or 'residual' that reaches the pool and continues to act upon chemicals and microorganisms in the water. Thus, where these types of disinfection are used, a chlorine- or bromine-type disinfectant is also employed to provide continued disinfection. The active available disinfectant in the water is referred to as 'residual' or, in the case of chlorine, 'free' to distinguish it from combined chlorine (which is not a disinfectant). In the case of

Table 4.2. Disinfectants and disinfecting systems used in swimming pools and similar environments

Disinfectants used most frequently in large, heavily used pools	**Disinfectants used in smaller pools and hot tubs**	**Disinfectants used for small-scale and domestic pools**
Chlorine • Gas • Calcium/sodium hypochlorite • Electrolytic generation of sodium hypochlorite • Chlorinated isocyanurates (generally outdoor pools) Bromochlorodimethylhydantoin (BCDMH) Chlorine dioxide[a] Ozone[a] UV[a]	Bromine • Liquid bromine • Sodium bromide + hypochlorite Lithium hypochlorite	Bromide/hypochlorite UV[a] UV–ozone[a] Iodine Hydrogen peroxide/silver/copper Biguanide

[a] Usually used in combination with residual disinfectants (i.e. chlorine- or bromine-based)

bromine, as the combined form is also a disinfectant, there is no need to distinguish between the two, so 'total' bromine is measured.

The type and form of disinfectant need to be chosen with respect to the specific requirements of the pool. In the case of small and domestic pools, important requirements are easy handling and ease of use as well as effectiveness. In all cases, the choice of disinfectant must be made after consideration of the efficacy of a disinfectant under the circumstances of use (more details are given in Chapter 5) and the ability to monitor disinfectant levels.

1. Chlorine-based disinfectants

Chlorination is the most widely used pool water disinfection method, usually in the form of chlorine gas, sodium, calcium or lithium hypochlorite but also with chlorinated isocyanurates. These are all loosely referred to as 'chlorine'.

Practice varies widely around the world, as do the levels of free chlorine that are currently considered to be acceptable in order to achieve adequate disinfection while minimizing user discomfort. For example, free chlorine levels of less than 1 mg/l are considered acceptable in some countries, while in other countries allowable levels may be considerably higher. Due to the nature of hot tubs (warmer water, often accompanied by aeration and a greater user to water volume ratio), acceptable free chlorine levels tend to be higher than in swimming pools. It is recommended that acceptable levels of free chlorine continue to be set at the local level, but in public and semi-public pools these should not exceed 3 mg/l and in public/semi-public hot tubs these should not exceed 5 mg/l. Lower free chlorine concentrations may be health protective when combined with other good management practices (e.g. pre-swim showering, effective coagulation and filtration, etc.) or when ozone or UV is also used.

Using high levels of chlorine (up to 20 mg/l) as a shock dose (see Chapter 5) as a preventive measure or to correct specific problems may be part of a strategy of proper pool management. While it should not be used to compensate for inadequacies of other management practices, periodic shock dosing can be an effective tool to maintain microbial quality of water and to minimize build-up of biofilms and chloramines (see Sections 4.5 and 5.3.4).

Chlorine in solution at the concentrations recommended is considered to be toxicologically acceptable even for drinking-water; the WHO health-based guideline value for chlorine in drinking-water is 5 mg/l (WHO, 2004). Concentrations significantly in excess of this may not be of health significance with regard to ingestion (as no adverse effect level was identified in the study used), even though there might be some problems regarding eye and mucous membrane irritation. The primary issues would then become acceptability to swimmers.

The chlorinated isocyanurates are stabilized chlorine compounds, which are widely used in the disinfection of outdoor or lightly loaded swimming pools. They dissociate in water to release free chlorine in equilibrium with cyanuric acid. A residual of cyanuric acid and a number of chlorine/cyanuric acid products will be present in the water. The Joint FAO/WHO Expert Committee on Food Additives and Contaminants (JECFA) has considered the chlorinated isocyanurates with regard to drinking-water disinfection and proposed a tolerable daily intake (TDI) for anhydrous sodium dichloroisocyanurate (NaDCC) of 0–2 mg/kg of body weight (JECFA, 2004). This would translate into an intake of 20 mg of NaDCC per day (or 11.7 mg of cyanuric acid per day) for a 10-kg child. To avoid consuming the TDI, assuming 100 ml of pool water is swallowed in a session would mean that the concentration of cyanuric acid/chlorinated isocyanurates should be kept below 117 mg/l. Levels of cyanuric acid should be kept between 50 and 100 mg/l in order not to interfere with the release of free chlorine, and it is recommended that levels should not exceed 100 mg/l. However, although no comprehensive surveys are available, there are a number of reported measurements of high levels of cyanuric acid in pools and hot tubs in the USA. Sandel (1990) found an average concentration of 75.9 mg/l with a median of 57.5 mg/l and a maximum of 406 mg/l. Other studies have reported that 25% of pools (122 of 486) had cyanuric acid concentrations greater than 100 mg/l (Rakestraw, 1994) and as high as 140 mg/l (Latta, 1995). Unpublished data from the Olin Corporation suggest that levels up to 500 mg/l may be found. Regular dilution with fresh water (see Chapter 5) is required in order to keep cyanuric acid at an acceptable concentration.

2. *Chlorine dioxide*

Chlorine dioxide is not classed as a chlorine-based disinfectant, as it acts in a different way and does not produce free chlorine. Chlorine dioxide breaks down to chlorite and chlorate, which will remain in solution; the WHO health-based drinking-water provisional guideline value for chlorite is 0.7 mg/l (based on a TDI of 0.03 mg/kg of body weight) (WHO, 2004), and this is also the provisional guideline for chlorate. There is potential for a build-up of chlorite/chlorate in recirculating pool water with time. In order to remain within the TDI levels of chlorate and chlorite, they should be maintained below 3 mg/l (assuming a 10-kg child and an intake of 100 ml).

3. *Bromine-based disinfectants*

Liquid bromine is not commonly used in pool disinfection. Bromine-based disinfectants for pools are available in two forms, bromochlorodimethylhydantoin (BCDMH) and a two-part system that consists of sodium bromide and an oxidizer (usually hypochlorite). As with chlorine-based disinfectants, local practice varies, and acceptable total bromine may be as high as 10 mg/l. Although there is limited evidence about bromine toxicity, it is recommended that total bromine does not exceed 2.0–2.5 mg/l. The use of bromine-based disinfectants is generally not practical for outdoor pools and spas because the bromine residual is depleted rapidly in sunlight (MDHSS, undated).

There are reports that a number of swimmers in brominated pools develop eye and skin irritation (Rycroft & Penny, 1983). However, Kelsall & Sim (2001) in a study examining three different pool disinfection systems (chlorine, chlorine/ozone and bromine/ozone) did not find that the bromine disinfection system was associated with a greater risk of skin rashes, although the number of bathers studied was small.

4. *Ozone and ultraviolet*

Ozone and UV radiation purify the pool water as it passes through the plant room, and neither leaves residual disinfectant in the water. They are, therefore, used in conjunction with conventional chlorine- and bromine-based disinfectants. The primary health issue in ozone use in swimming pool disinfection is the leakage of ozone into the atmosphere from ozone generators and contact tanks, which need to be properly ventilated to the outside atmosphere. It is also appropriate to include a deozonation step in the treatment process, to prevent carry-over in the treated water. Ozone is a severe respiratory irritant, and it is, therefore, important that ozone concentrations in the atmosphere of the pool building are controlled. The air quality guideline value of 0.12 mg/m^3 (WHO, 2000) is an appropriate concentration to protect bathers and staff working in the pool building.

5. *Other disinfectants*
Other disinfectant systems may be used, especially in small pools. Hydrogen peroxide used with silver and copper ions will normally provide low levels of the silver and copper ions in the water. However, it is most important that proper consideration is given to replacement of water to prevent excessive build-up of the ions. A similar situation would apply to biguanide, which is also used as a disinfectant in outdoor pools.

4.4.2 pH correction

The chemical required for pH value adjustment will generally depend on whether the disinfectant used is itself alkaline or acidic. Alkaline disinfectants (e.g. sodium hypochlorite) normally require only the addition of an acid for pH correction, usually a solution of sodium hydrogen sulfate, carbon dioxide or hydrochloric acid. Acidic disinfectants (e.g. chlorine gas) normally require the addition of an alkali, usually a solution of sodium carbonate (soda ash). There should be no adverse health effects associated with the use of these chemicals provided that they are dosed correctly and the pH range is maintained between 7.2 and 8.0 (see Section 5.10.3).

4.4.3 Coagulants

Coagulants (e.g. polyaluminium chloride) may be used to enhance the removal of dissolved, colloidal or suspended material. These work by bringing the material out of solution or suspension as solids and then clumping the solids together to produce a floc. The floc is then trapped during filtration.

4.5 Disinfection by-products (DBP)

Disinfectants can react with other chemicals in the water to give rise to by-products (Table 4.3). Most information available relates to the reactions of chlorine, as will be seen from Tables 4.4–4.11. Although there is potentially a large number of chlorine-derived disinfection by-products, the substances produced in the greatest quantities are the trihalomethanes (THMs), of which chloroform is generally present in the greatest concentration, and the haloacetic acids (HAAs), of which di- and trichloroacetic acid are generally present in the greatest concentrations (WHO, 2000). It is probable that a range of organic chloramines could be formed, depending on the nature of the precursors and pool conditions. Data on their occurrence in swimming pool waters are relatively limited, although they are important in terms of atmospheric contamination in enclosed pools and hot tubs.

When inorganic bromide is present in the water, this can be oxidized to form bromine, which will also take part in the reaction to produce brominated by-products such as the brominated THMs. This means that the bromide/hypochlorite system of disinfection would be expected to give much higher proportions of the brominated by-products. Seawater pools disinfected with chlorine would also be expected to show a high proportion of brominated by-products since seawater contains significant levels of bromide. Seawater pools might also be expected to show a proportion of iodinated by-products in view of the presence of iodide in the water. In all pools in which free halogen (i.e. chlorine, bromine or iodine) is the primary disinfectant, no matter what form the halogen donor takes, there will be a range of by-products, but these will be

Table 4.3. Predominant chemical disinfectants used in pool water treatment and their associated disinfection by-products[a]

Disinfectant	Disinfection by-products
Chlorine/hypochlorite	trihalomethanes
	haloacetic acids
	haloacetonitriles
	haloketones
	chloral hydrate (trichloroacetaldehyde)
	chloropicrin (trichloronitromethane)
	cyanogen chloride
	chlorate
	chloramines
Ozone	bromate
	aldehydes
	ketones
	ketoacids
	carboxylic acids
	bromoform
	brominated acetic acids
Chlorine dioxide	chlorite
	chlorate
Bromine/hypochlorite	trihalomethanes, mainly bromoform
BCDMH	bromal hydrate
	bromate
	bromamines

[a] UV is a physical system and is generally not considered to produce by-products

found at significantly lower concentrations than the THMs and HAAs. The use of ozone in the presence of bromide can lead to the formation of bromate, which can build up over time without adequate dilution with fresh water (see Chapter 5).

While chlorination has been relatively well studied, it must be emphasized that data on ozonation by-products and other disinfectants are very limited. Although those by-products found commonly in ozonated drinking-water would be expected, there appear to be few data on the concentrations found in swimming pools and similar environments.

Both chlorine and bromine will react, extremely rapidly, with ammonia in the water, to form chloramines (monochloramine, dichloramine and nitrogen trichloride) and bromamines (collectively known as haloamines). The mean content of urea and ammonia in urine is 10 240 mg/l and 560 mg/l, respectively (Table 4.1), but hydrolysis of urea will give rise to more ammonia in the water (Jandik, 1977). Nitrogen-containing organic compounds, such as amino acids, may react with hypochlorite to form organic chloramines (Taras, 1953; Isaak & Morris, 1980).

During storage, chlorate can build up within sodium hypochlorite solution, and this can contribute to chlorate levels in disinfected water. However, it is unlikely to be of concern to health unless the concentrations are allowed to reach excessive levels (i.e. >3 mg/l), in which case the efficacy of the hypochlorite is likely to be compromised.

Ozone can react with residual bromide to produce bromate, which is quite stable and can build up over time (Grguric et al., 1994). This is of concern in drinking-water systems but will be of lower concern in swimming pools. However, if ozone were used to disinfect seawater pools, the concentration of bromate would be expected to be potentially much higher. In addition, bromate is a by-product of the electrolytic generation of hypochlorite if the brine used is high in bromide. Ozone also reacts with organic matter to produce a range of oxygenated substances, including aldehydes and carboxylic acids. Where bromide is present, it can also result in the formation of brominated products similar to liquid bromine.

More data are required on the impact of UV on disinfection by-products when used in conjunction with residual disinfectants. UV disinfection is not considered to produce by-products, and it seems to significantly reduce the levels of chloramines.

4.5.1 Exposure to disinfection by-products

While swimming pools have not been studied to the same extent as drinking-water, there are some data on the occurrence and concentrations of a number of disinfection by-products in pool water, although the data are limited to a small number of the major substances. A summary of the concentrations of various prominent organic by-products of chlorination (THMs, HAAs, haloacetonitriles and others) measured in different pools is provided in Table 4.4 and Tables 4.9–4.11 below. Many of these data are relatively old and may reflect past management practices. Concentrations will vary as a consequence of the concentration of precursor compounds, disinfectant dose, residual disinfectant level, temperature and pH. The THM found in the greatest concentrations in freshwater pools is chloroform, while in seawater pools, it is usually bromoform (Baudisch et al., 1997; Gundermann et al., 1997).

1. Trihalomethanes

Sandel (1990) examined data from 114 residential pools in the USA and reported average concentrations of chloroform of 67.1 μg/l with a maximum value of 313 μg/l. In hot spring pools, the median concentration of chloroform was 3.8 μg/l and the maximum was 6.4 μg/l (Erdinger et al., 1997b). Fantuzzi et al. (2001) reported total THM concentrations of 17.8–70.8 μg/l in swimming pools in Italy. In a study of eight swimming pools in London, Chu & Nieuwenhuijsen (2002) collected and analysed pool water samples for total organic carbon (TOC) and THMs. They reported a geometric mean[1] for all swimming pools of 5.8 mg/l for TOC, 125.2 μg/l for total THMs and 113.3 μg/l for chloroform; there was a linear correlation between the number of people in the pool and the concentration of THMs. The pool concentrations of disinfection by-products will also be influenced by the concentration of THMs and the potential precursor compounds in the source and make-up water.

THMs are volatile in nature and can be lost from the surface of the water, so they will also be found in the air above indoor pools (Table 4.5). Transport from swimming pool water to the air will depend on a number of factors, including the concentration in the pool water, the temperature and the amount of splashing and surface

[1] Mean values in Table 4.4 are arithmetic means.

disturbance. The concentrations at different levels in the air above the pool will also depend on factors such as ventilation, the size of the building and the air circulation. Fantuzzi et al. (2001) examined THM levels in five indoor pools in Italy and found mean concentrations of total THMs in poolside air of 58.0 μg/m^3 ± 22.1 μg/m^3 and concentrations of 26.1 μg/m^3 ± 24.3 μg/m^3 in the reception area.

Strähle et al. (2000) studied the THM concentrations in the blood of swimmers compared with the concentrations of THMs in pool water and ambient air (Table 4.6). They showed that intake via inhalation was probably the major route of uptake of volatile components, since the concentration of THMs in the outdoor pool water was higher than the concentration in the indoor pool water, but the concentrations in air above the pool and in blood were higher in the indoor pool than in the outdoor pool. This would imply that good ventilation at pool level would be a significant contributor to minimizing exposure to THMs. Erdinger et al. (2004) found that in a study in which subjects swam with and without scuba tanks, THMs were mainly taken up by the respiratory pathway and only about one third of the total burden was taken up through the skin.

Studies by Aggazzotti et al. (1990, 1993, 1995, 1998) showed that exposure to chlorinated swimming pool water and the air above swimming pools can lead to an increase in detectable THMs in both plasma and alveolar air, but the concentration in alveolar air rapidly falls after exiting the pool area (Tables 4.7 and 4.8).

2. *Chloramines, chlorite and chlorate*

Exposure to chloramines in the atmosphere of indoor pools was studied in France by Hery et al. (1995) in response to complaints of eye and respiratory tract irritation by pool attendants. They found concentrations of up to 0.84 mg/m^3 and that levels were generally higher in pools with recreational activities such as slides and fountains.

Erdinger et al. (1999) examined the concentrations of chlorite and chlorate in swimming pools and found that while chlorite was not detectable, chlorate concentrations varied from 1 mg/l to, in one extreme case, 40 mg/l. Strähle et al. (2000) found chlorate concentrations of up to 142 mg/l. The concentrations of chlorate in chlorine-disinfected pools were close to the limit of detection of 1 mg/l, but the mean concentration of chlorate in sodium hypochlorite-disinfected pools was about 17 mg/l. Chlorate concentrations were much lower in pools disinfected with hypochlorite and ozone, and the chlorate levels were related to the levels in hypochlorite stock solutions.

3. *Other disinfection by-products*

A number of other disinfection by-products have been examined in swimming pool water; these are summarized in Tables 4.9–4.11. Dichloroacetic acid has also been detected in swimming pool water. In a German study of 15 indoor and 3 outdoor swimming pools (Clemens & Scholer, 1992), dichloroacetic acid concentrations averaged 5.6 μg/l and 119.9 μg/l in indoor and outdoor pools, respectively. The mean concentration of dichloroacetic acid in three indoor pools in the USA was 419 μg/l (Kim & Weisel, 1998). The difference between the results of these two studies may be due to differences in the amounts of chlorine used to disinfect swimming pools, sample collection time relative to chlorination of the water, or addition or exchanges of water in the pools.

Table 4.4. Concentrations of trihalomethanes measured in swimming pool water

	Disinfection by-product concentration (µg/l)									
	Chloroform		BDCM		DBCM		Bromoform		Pool	
Country	Mean	Range	Mean	Range	Mean	Range	Mean	Range	type	Reference
Poland		35.9–99.7		2.3–14.7		0.2–0.8		0.2–203.2	indoor	Biziuk et al., 1993
Italy		19–94							indoor	Aggazzotti et al., 1993
	93.7	9–179							indoor	Aggazzotti et al., 1995
	33.7	25–43	2.3	1.8–2.8	0.8	0.5–10	0.1	0.1	indoor	Aggazzotti et al., 1998
USA	37.9								indoor	Copaken, 1990
		4–402		1–72		<0.1–8		<0.1–1	outdoor	Armstrong &
		3–580		1–90		0.3–30		<0.1–60	indoor	Golden, 1986
		<0.1–530		<0.1–105		<0.1–48		<0.1–183	hot tub	
Germany	14.6	2.4–29.8							indoor	Eichelsdörfer et al., 1981
	43	14.6–111							outdoor	
	198	43–980	22.6	0.1–150	10.9	0.1–140	1.8	<0.1–88	indoor	Lahl et al., 1981
		0.5–23.6		1.9–16.5		<0.1–3.4		<0.1–3.3	indoor	Ewers et al., 1987
		<0.1–32.9		<0.1–54.5		<0.1–1.0		<0.1–0.5	hydrotherapy	
		<0.1–0.9		<0.1–1.4		<0.1–16.4		2.4–132	hydrotherapy	
		3.6–82.1		1.6–17.3		<0.1–15.1		<0.1–4.0	outdoor	
	94.9	40.6–117.5	4.8	4.2–5.4	1.8	0.78–2.6			indoor	Puchert et al., 1989
	80.7		8.9		1.5		<0.1		indoor	Puchert, 1994
	74.9		11.0		3.0		0.23		outdoor	
		3–27.8		0.69–5.64		0.03–6.51		0.02–0.83	indoor	Cammann & Hübner, 1995
		1.8–28		1.3–3.4		<0.1–1	<0.1		indoor	Jovanovic et al., 1995
		8–11							indoor	Schössner & Koch, 1995
	14	0.51–69	2.5	0.12–15	0.59	0.03–4.9	0.16	<0.03–8.1	indoor	Stottmeister, 1998, 1999
	30	0.69–114	4.5	0.27–25	1.1	0.04–8.8	0.28	<0.03–3.4	outdoor	
	4.3	0.82–12	1.3	0.19–4.1	0.4	0.03–0.91	0.08	<0.03–0.22	hydrotherapy	
	3.8	6.4 (max.)							spa	Erdinger et al., 1997b
		7.1–24.8							indoor pool	Erdinger et al., 2004
Denmark		145–151							indoor	Kaas & Rudiengaard, 1987
Hungary	11.4	<2–62.3	2.9	<1.0–11.4					indoor	Borsányi, 1998
UK	121.1	45–212	8.3	2.5–23	2.7	0.67–7	0.9	0.67–2	indoor pools	Chu & Nieuwenhuijsen, 2002

BDCM = bromodichloromethane; DBCM = dibromochloromethane

4.5.2 Risks associated with disinfection by-products

The guideline values in the WHO *Guidelines for Drinking-water Quality* can be used to screen for potential risks arising from disinfection by-products from swimming pools and similar environments, while making appropriate allowance for the much lower quantities of water ingested, shorter exposure periods and non-ingestion exposure. Although there are data to indicate that the concentrations of chlorination by-products in swimming pools and similar environments may exceed the WHO guideline values for drinking-water (WHO, 2004), available evidence indicates that for reasonably well managed pools, concentrations less than the drinking-water guideline values can be consistently achieved. Since the drinking-water guidelines are intended to reflect tolerable risks over a lifetime, this provides an additional level of reassurance. Drinking-water guidelines assume an intake of 2 litres per day, but as considered above, ingestion of swimming pool water is considerably less than this; recent measured data (Section 4.1.1) indicate an extreme of about 100 ml (Evans et al., 2001). Uptake via skin absorption and inhalation (in the case of THMs) is proportionally greater than from drinking-water and is significant, but the low oral intake allows a margin that can, to an extent, account for this. Under such circumstances, the risks from exposure to chlorination by-products in reasonably well managed swimming pools would be considered to be small and must be set against the benefits of aerobic exercise and the risks of infectious disease in the absence of disinfection.

Levels of chlorate and chlorite in swimming pool water have not been extensively studied; however, in some cases, high chlorate concentrations have been reported, which greatly exceeded the WHO provisional drinking-water guideline (0.7 mg/l) and which would, for a child ingesting 100 ml of water, result in possible toxic effects. Exposure, therefore, needs to be minimized, with frequent dilution of pool water with fresh water, and care taken to ensure that chlorate levels do not build up in stored hypochlorite disinfectants.

The chloramines and bromamines, particularly nitrogen trichloride and nitrogen tribromide, which are both volatile (Holzwarth et al., 1984), can give rise to significant eye and respiratory irritation in swimmers and pool attendants (Massin et al., 1998). In addition, nitrogen trichloride has an intense and unpleasant odour at concentrations in water as low as 0.02 mg/l (Kirk & Othmer, 1993). Studies of subjects using swimming pools and non-swimming attendants have shown a number of changes and symptoms that appear to be associated with exposure to the atmosphere in swimming pools. Various authors have suggested that these were associated with nitrogen trichloride exposure in particular (Carbonnelle et al., 2002; Thickett et al., 2002; Bernard et al., 2003), although the studies were unable to confirm the specific chemicals that were the cause of the symptoms experienced. Symptoms are likely to be particularly pronounced in those suffering from asthma. Yoder et al. (2004) reported two incidents, between 2001 and 2002, where a total of 52 people were adversely affected by a build-up of chloramines in indoor pool water. One of the incidents related to a hotel pool, and 32 guests reported coughs, eye and throat irritation and difficulty in breathing. Both incidents were attributed to chloramines on the basis of the clinical syndrome and setting. Hery et al. (1995) found that complaints from non-swimmers were initiated at a concentration of 0.5 mg/m^3 chlorine species (expressed in units of nitrogen trichloride) in the atmosphere of indoor pools and hot tubs. It is recommended that 0.5 mg/m^3 would be suitable as a provisional value for chlorine species,

Table 4.5. Concentrations of trihalomethanes measured in the air above the pool water surface

Country	Disinfection by-product concentration (µg/m3)								Pool type	Reference
	Chloroform		BDCM		DBCM		Bromoform			
	Mean	Range	Mean	Range	Mean	Range	Mean	Range		
Italy	214	66–650	19.5	5–100	6.6	0.1–14	0.2		indoor[1)]	Aggazzotti et al., 1995
	140	49–280	17.4	2–58	13.3	4–30	0.2		indoor[1)]	Aggazzotti et al., 1993
	169	35–195	20	16–24	11.4	9–14	0.2		indoor[1)]	Aggazzotti et al., 1998
Canada		597–1630							indoor	Lévesque et al., 1994
Germany	65		9.2		3.8				indoor[1)]	Jovanovic et al., 1995
	36		5.6		1.2				indoor[2)]	
	5.6		0.21						outdoor[1)]	
	2.3								outdoor[1)]	
	3.3	0.33–9.7	0.4	0.08–2.0	0.1	0.02–0.5	<0.03		outdoor[1)]	Stottmeister, 1998, 1999
	1.2	0.36–2.2	0.1	0.03–0.16	0.05	0.03–0.08	<0.03		outdoor[2)]	
	39	5.6–206	4.9	0.85–16	0.9	0.05–3.2	0.1	<0.03–3.0	indoor[1)]	
	30	1.7–136	4.1	0.23–13	0.8	0.05–2.9	0.08	<0.03–0.7	indoor[2)]	
USA		<0.1–1		<0.1		<0.1		<0.1	outdoor[3)]	Armstrong & Golden, 1986
		<0.1–260		<0.1–10		<0.1–5		<0.1–14	indoor[3)]	
		<0.1–47		<0.1–10		<0.1–5		<0.1–14	hot tub[3)]	

BDCM = bromodichloromethane; DBCM = dibromochloromethane
[a] Measured 20 cm above the water surface
[b] Measured 150 cm above the water surface
[c] Measured 200 cm above the water surface

Table 4.6. Comparison of trihalomethane concentrations in blood of swimmers after a 1-h swim, in pool water and in ambient air of indoor and outdoor pools[a]

	THM concentration (mean, range)	
	Indoor pool	Outdoor pool
Blood of swimmers (µg/l)	0.48 (0.23–0.88)	0.11 (<0.06–0.21)
Pool water (µg/l)	19.6 (4.5–45.8)	73.1 (3.2–146)
Air 20 cm above the water surface (µg/m³)	93.6 (23.9–179.9)	8.2 (2.1–13.9)
Air 150 cm above the water surface (µg/m³)	61.6 (13.4–147.1)	2.5 (<0.7–4.7)

[a] Adapted from Strähle et al., 2000

Table 4.7. Concentrations of trihalomethanes in plasma of 127 swimmers[a]

THM	No. positive/no. samples	Mean THM concentration (µg/l)	Range of THM concentrations (µg/l)
Chloroform	127/127	1.06	0.1–3.0
BDCM	25/127	0.14	<0.1–0.3
DBCM	17/127	0.1	<0.1–0.1

[a] Adapted from Aggazzotti et al., 1990

Table 4.8. Comparison of trihalomethane levels in ambient air and alveolar air in swimmers prior to arrival at the swimming pool, during swimming and after swimming[a]

	THM levels (µg/m³) at various monitoring times[b]				
	A	B	C	D	E
Chloroform					
Ambient air	20.7 ± 5.3	91.7 ± 15.4	169.7 ± 26.8	20.0 ± 8.4	19.2 ± 8.8
Alveolar air	9.3 ± 3.1	29.4 ± 13.3	76.5 ± 18.6	26.4 ± 4.9	19.1 ± 2.5
BDCM					
Ambient air	n.q.	10.5 ± 3.1	20.0 ± 4.1	n.q.	n.q.
Alveolar air	n.q.	2.7 ± 1.2	6.5 ± 1.3	2.7 ± 1.1	1.9 ± 1.1
DBCM					
Ambient air	n.q.	5.2 ± 1.5	11.4 ± 2.1	n.q.	n.q.
Alveolar air	n.q.	0.8 ± 0.8	1.4 ± 0.9	0.3 ± 0.2	0.20 ± 0.1
Bromoform					
Ambient air	n.q.	0.2	0.2	0.2	n.q.
Alveolar air	n.q.	n.q.	n.q.	n.q.	n.q.

[a] Adapted from Aggazzotti et al., 1998

[b] Five competitive swimmers (three males and two females) were monitored A: Prior to arrival at the pool; B: After 1 h resting at poolside before swimming; C: After a 1-h swim; D: 1 h after swimming had stopped; and E: 1.5 h after swimming had stopped. D and E occurred after departing the pool area. n.q. = not quantified

Table 4.9. Concentrations of haloacetic acids measured in swimming pool water

	Disinfection by-product concentration (µg/l)											
	MCAA		MBAA		DCAA		DBAA		TCAA		Pool	
Country	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	type	Reference
Germany	26	2.6–81	0.32	<0.5–3.3	23	1.5–192	0.57	<0.2–7.7	42	3.5–199	indoor	Stottmeister & Naglitsch, 1996
	32	2.5–174	0.15	<0.5–1.9	8.8	1.8–27	0.64	<0.2–4.8	15	1.1–45	hydrotherapy	
	26	2.5–112	0.06	<0.5–1.7	132	6.2–562	0.08	<0.2–1.3	249	8.2–887	outdoor	
									30		hot tub	Lahl et al., 1984
										25–136	indoor	
										2.3–100	indoor	Mannschott et al., 1995

MCAA = monochloroacetic acid; MBAA = monobromoacetic acid; DCAA = dichloroacetic acid; DBAA = dibromoacetic acid; TCAA = trichloroacetic acid

Table 4.10. Concentrations of haloacetonitriles measured in swimming pool water

	Disinfection by-product concentration (µg/l)							
	DCAN		DBAN		TCAN		Pool	
Country	Mean	Range	Mean	Range	Mean	Range	type	Reference
Germany		6.7–18.2					indoor	Puchert, 1994
		<0.5–2.5					outdoor	
	13	0.13–148	2.3	<0.01–24	1.7	<0.01–11	indoor	Stottmeister, 1998, 1999
	9.9	0.22–57	0.62	<0.01–2.8	1.5	<0.01–7.8	hydrotherapy	
	45	<0.01–0.02	2.5	<0.01–16	1.3	<0.01–10	outdoor	
	24						indoor	Baudisch et al., 1997
			49				seawater	

DCAN = dichloroacetonitrile; DBAN = dibromoacetonitrile; TCAN = trichloroacetonitrile

Table 4.11. Concentrations of chloropicrin, chloral hydrate and bromal hydrate measured in swimming pool water

	Disinfection by-product concentration (μg/l)							
	Chloropicrin		Chloral hydrate		Bromal hydrate			
Country	Mean	Range	Mean	Range	Mean	Range	Pool type	Reference
Germany		0.1–2.6					indoor	Schöler & Schopp, 1984
		0.32–0.8					indoor	Puchert, 1994
		<0.01–0.75					outdoor	Stottmeister, 1998, 1999
	0.32	0.03–1.6					indoor	
	0.20	0.04–0.78					hydrotherapy	
	1.3	0.01–10					outdoor	
			265				indoor	Baudisch et al., 1997
					230		seawater	Baudisch et al., 1997
				0.5–104			indoor	Mannschott et al., 1995

expressed as nitrogen trichloride, in the atmosphere of indoor swimming pools and similar environments. However, more specific data are needed on the potential for exacerbation of asthma in affected individuals, since this is a significant proportion of the population in some countries. There is also a potential issue regarding those that are very frequent pool users and who may be exposed for longer periods per session, such as competitive swimmers. It is particularly important that the management of pools used for such purposes is optimized in order to reduce the potential for exposure (Section 5.9).

4.6 Risks associated with plant and equipment malfunction

Chemical hazards can arise from malfunction of plant and associated equipment. This hazard can be reduced, if not eliminated, through proper installation and effective routine maintenance programmes. The use of gas detection systems and automatic shutdown can also be an effective advance warning of plant malfunction. The use of remote monitoring is becoming more commonplace in after-hours response to plant and equipment malfunction or shutdown.

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