CHAPTER 4

CHEMICAL HAZARDS

Chemicals found in pool water include those that are related to water treatment — both the chemical additives themselves and the by-products that are produced from chemical reactions between the additives (particularly the reactive disinfectants) and organic and inorganic materials in the raw water — and those that are contributed by the swimmers, which include soap residues, cosmetics, suntan oil, sweat and urine.

This chapter briefly reviews the routes of exposure to chemicals in swimming pools, spas and similar recreational-water environments, estimated and measured intakes of chemicals by users, and the hazards associated with exposure to the chemicals.

4.1 Concentrations of chemicals in swimming pool environments

4.1.1 Disinfectants

A variety of disinfectants are used for pool water treatment. Those listed in the first column of Table 4.1 represent the major usage worldwide, especially in public and semi-public pools that are large and heavily used. With the exception of chlorine gas and ozone, these disinfectants are also routinely used in many small private and semi-public pools. Some of these are residual disinfectants — i.e., they persist in water and are present in the water to which pool users are exposed. This provides increased protection against contamination with infectious agents susceptible to disinfection and leads to human exposure to the disinfectant itself. Some others (notably ozone and UV) are effective at the point of treatment only. Non-residual disinfectants are often used in combination with residual disinfectants.

Table 4.1: Disinfectants and disinfecting systems for swimming pools

Disinfectants used most frequently in large, heavily used pools	Disinfectants used less frequently	Disinfectants used infrequently, mainly for small-scale and private pools
Chlorine - Gas - Calcium/sodium hypochlorite - Sodium dichloroisocyanurate - Electrolytic generation Ozone/chlorine in combination Chlorine dioxide Chlorine dioxide/chlorine in combination	Bromine - Liquid bromine - Bromochlorodimethylhydantoin (BCDMH) - Sodium bromide + hypochlorite	Bromine chloride UV UV–ozone Iodine Hydrogen peroxide Silver/copper Biguanide

Disinfectant residuals in swimming pools that have been suggested in various countries are shown in Table 4.2.

Table 4.2: Recommended disinfectant residuals (mg/litre) in swimming pool water

Disinfectant	UK[a]	EC[b]	USA[c]	USA (Michigan)[d]	Germany[e]	Italy[f]
Free chlorine (hypochlorous acid and hypochlorite)	1–2		1.0–3.0	0.4–1.0 (pH)	0.3–0.6 0.7–1.0 (spas)	0.6–1.2
Bromine	1.5–3.5		2–4	1.0–2.0 (pH)		
Chlorocyanurates	2.5–5.0 (free chlorine)			1–1.5 (free chlorine)		
Chlorine dioxide		0.2–0.3		0.3 (dose)		0.3
Ozone	0	<0.1	0.1 (0.05 mg/m^3 air)		0.05	0.03

Disinfectant	UK[a]	EC[b]	USA[c]	USA (Michigan)[d]	Germany[e]	Italy[f]
BCDMH	4–6 (as Br) 200 (max. as BCDMH)					
Copper	1					

[a] PWTAG (1999).
[b] Recommended European Community values; PWTAG (1999).
[c] American National Standards Institute (1991).
[d] State of Michigan (1978). Dose = amount that can be added; pH indicates higher dosage at higher pH.
[e] Deutsches Institut für Normung (1997).
[f] Gazzetta Ufficiale della Repubblica Italiana (1992).

4.1.2 Disinfectant by-products

The formation of by-product chemicals associated with disinfection of pool waters varies with the chemical. Disinfectant by-product chemicals are produced by reactions between disinfectants and other substances present in the pool. These disinfectant by-product precursors may be both inorganic, especially bromide ions (such as may be found in a saltwater pool), and organic, such as amino acids and proteins. Input of reactive organic precursor chemicals is continuous and a function of the number of swimmers, who are contributing urine, perspiration, oils, cosmetics, soap residues and insoluble detritus, which can be reactive.

Many chemical by-products associated with disinfection of pool waters are produced at levels that are at least comparable to those produced in drinking-water disinfection. In fact, as initial and make-up water entering the pool has in most cases already undergone drinking-water treatment and contains disinfectant and by-products, and as typical pool waters are recycled and additional precursors and disinfectant are added, the levels of disinfectant by-products found in disinfected pool water could easily exceed drinking-water levels.

The predominant disinfectants that are used in pool water treatment and some of the by-product chemicals that have been detected are summarized in Table 4.3. Unlike the other disinfectants, the major chlorine dioxide disinfectant by-products are derived from decomposition of the disinfectant as opposed to reaction with precursors.

Table 4.3: Predominant disinfectants used in pool water treatment and their associated disinfectant by-products

Disinfectant	Disinfectant by-products
Chlorine/hypochlorite	trihalomethanes (THMs)
	haloacetic acids
	haloacetonitriles
	haloketones
	chloral hydrate (trichloroacetaldehyde)
	chloropicrin (trichloronitromethane)
	cyanogen chloride
	chlorate
	chloramines
Ozone	bromate
	aldehydes
	ketones
	ketoacids
	carboxylic acids
	bromoform
Chlorine dioxide	chlorite

Disinfectant	Disinfectant by-products
	chlorate
Bromine/hypobromite/BCDMH	THMs, mainly bromoform
	bromal hydrate
	bromate
	bromamines

Chlorate, chlorite and bromate measurements have been conducted in swimming pools in Germany (Strähle, 1998). Chlorate ranged in concentration from <0.0036 to 147 mg/litre. Chlorite was not found in pool waters. Bromate ranged in concentration from <0.0055 to 0.825 mg/litre. The highest bromate levels were found in swimming pools (e.g., saltwater pools) in which ozone had been used to treat bromide-containing pool water; the levels were above the provisional WHO drinking-water guideline value for bromate of 0.025 mg/litre (WHO, 1993).

THMs, haloacetic acids, haloacetonitriles, haloketones, chloropicrin, chloral hydrate and bromal hydrate have all been detected in pool water. Concentrations of THMs, which are significant chlorine and bromine disinfectant by-products, have been measured the most frequently. In general, the THM concentration in the pool water is directly dependent on the chlorine (bromine) dose, the organic content in the pool water, the chlorine (bromine) contact time and the temperature. The main constituent among THMs in freshwater pools is chloroform. In the water and air of seawater pools, the dominant THM is bromoform (Baudisch et al., 1997; Gundermann et al., 1997). The other most commonly found THMs are bromodichloromethane (BDCM) and dibromochloromethane (DBCM).

Tables 4.4–4.7 provide an overview of the concentrations of these various disinfectant by-products measured in different pools.

Table 4.4: Concentrations of trihalomethanes measured in swimming pool water

	Disinfectant by-product concentration (µg/litre)									
	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	spa	
Germany	14.6	2.4–29.8							indoor	Eichelsdörfer et
	43	14.6–111							outdoor	al., 1981
	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	hydro-therapy	
		<0.1–0.9		<0.1–1.4		<0.1–16.4		2.4–132	hydro-therapy	
		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	

	Disinfectant by-product concentration (µg/litre)									
	Chloroform		BDCM		DBCM		Bromoform		Pool	
Country	mean	range	mean	range	mean	range	mean	range	type	
		3–27.8		0.69–5.64		0.03–6.51		0.02–0.83	indoor	
		1.8–28		1.3–3.4		<0.1–1	<0.1		indoor	
		8–11							indoor	
	14	0.51–69	2.5	0.12–15	0.59	0.03–4.9	0.16	<0.03–8.1	indoor	Stottmeister,
	30	0.69–114	4.5	0.27–25	1.1	0.04–8.8	0.28	<0.03–3.4	outdoor	1998, 1999
	4.3	0.82–12	1.3	0.19–4.1	0.4	0.03–0.91	0.08	<0.03–0.22	hydro-	
									therapy	**Reference**
	3.8	6.4 (max.)							spa	Erdinger et al., 1997
Denmark		145–151							indoor	Kaas & Rudiengaard, 1987
Hungary	11.4	<2–62.3	2.9	<1.0–11.4					indoor	Borsányi, 1998

Table 4.5: Concentrations of halogenated acetic acids measured in swimming pool water

	Disinfectant by-product concentration (µg/litre)[a]											
	MCAA		MBAA		DCAA		DBAA		TCAA			
Country	mean	range	mean	range	mean	range	mean	range	mean	range	Pool 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 &
	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	hydro-therapy	Naglitsch, 199
	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 whirl-pool	Lahl et al., 1984
										25–136	indoor	
										2.3–100	indoor	Mannschott et al., 1995

[a] MCAA = monochloroacetic acid; MBAA = monobromoacetic acid; DCAA = dichloroacetic acid; DBAA = dibromoacetic acid; TCAA = trichloroacetic acid.

Table 4.6: Concentrations of halogenated acetonitriles measured in swimming pool water

	Disinfectant by-product concentration (µg/litre)[a]							
	DCAN		DBAN		TCAN			
Country	mean	range	mean	range	mean	range	Pool 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	

[a] DCAN = dichloroacetonitrile; DBAN = dibromoacetonitrile; TCAN = trichloroacetonitrile.

Table 4.7: Concentrations of non-trihalomethane disinfectant by-products measured in swimming pool water

	Disinfectant by-product concentration (µg/litre)							
	Chloropicrin		Chloral hydrate		Bromal hydrate			
Country	mean	range	mean	range	mean	range	Pool type	Reference

	Disinfectant by-product concentration (µg/litre)							
	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	
	0.32	0.03–1.6					indoor	Stottmeister, 1998, 1999
	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

THMs have also been measured in air because they are volatile and vaporize from the pool water. This transport from the liquid phase (swimming pool water) to the gaseous phase (e.g., air of an indoor pool) depends on the following factors:

- vapour pressure of the substance;
- its concentration in water;
- its water solubility;
- its diffusion (substance transport) from water to air;
- the water/air contact area;
- the water temperature; and
- air exchange in the indoor pool (efficacy of the ventilation system).

The higher their vapour pressure and concentration in water, the more readily they escape into the air above the pools. Other factors enhancing the transport of THMs into the air are a low water solubility, high water temperatures and a large contact area between the pool water and the air above it. The diffusion of the THMs is inversely proportional to their relative molar mass and proportional to water turbulence caused by bather movements.

Indoor pools allow a build-up of airborne THMs that would not occur at outdoor pools. The measured air concentrations generally decrease with increasing height above the pool surface (Table 4.8). Attractions such as slides, wave pools, etc., and increased activity on the part of pool users considerably enhance the rate of evaporation of THMs.

Table 4.8: Concentrations of trihalomethanes measured in the air above the pool water surface

	Disinfectant by-product concentration (µg/m^3)									
	Chloroform		BDCM		DBCM		Bromoform			
Country	**mean**	**range**	**mean**	**range**	**mean**	**range**	**mean**	**range**	**Pool type[a]**	**Reference**
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 [2)]	
	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

	Disinfectant by-product concentration (µg/m^3)									
	Chloroform		BDCM		DBCM		Bromoform			
Country	mean	range	mean	range	mean	range	mean	range	Pool type[a]	Reference
	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	spa [3)]	

[a] 1 = measured 20 cm above the water surface; 2 = measured 150 cm above the water surface; 3 = measured 200 cm above the water surface.

Knowledge about the occurrence of organic chloramines in swimming pool waters is very limited. Currently, there are no suitable analytical methods for their determination and study in swimming pool water.

4.1.3 Chemicals contributed by swimmers

A number of nitrogen compounds can be eluted from the skin (Table 4.9). The nitrogen content in sweat is around 1 g/litre, primarily in the form of urea, ammonia, amino acids and creatinine. Depending on the circumstances, the composition of sweat varies within extremely broad ranges. Considerable amounts of nitrogen compounds can also reach pool water via urinary discharges (Table 4.9). The urine release into the swimming pool water of indoor pools has been estimated to be between 25 and 30 ml per bather (Gunkel & Jessen, 1988) and as much as 77.5 ml per bather (Erdinger et al., 1997).

Table 4.9: Nitrogen-containing compounds in sweat and urine

	Sweat		Urine	
Nitrogen-containing compounds	Mean content (mg/litre)	Portion of total nitrogen (%)	Mean content (mg/litre)	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

Source: Jandik, 1977

The distribution of total nitrogen among relevant nitrogen compounds (Table 4.9) has been calculated from statistically determined means of values obtained for 24-h urine samples. Although more than 80% of the total nitrogen content in urine is present in the form of urea, and although that of ammonia, at approximately 5%, is comparatively low, swimming pool water exhibits considerable concentrations of ammonia, which evidently are formed secondarily by urea degradation following chemical reactions with chlorine. The ammonia reacts rapidly with hypochlorous acid to form monochloramine, dichloramine and trichloramine (Hailin et al., 1990), whereas nitrogen-containing organic compounds, such as amino acids, may react with hypochlorite to form organic chloramines (Taras, 1953; Isaak & Morris, 1980). The organic nitrogen compounds found in urine and sweat are also possible precursors for chlorination by-products, such as THMs (Ueno et al., 1996).

At present, no information is available on concentrations of chemicals in swimming pool water from cosmetics, suntan oil, soap residues, etc.

4.2 Exposure to chemicals in swimming pools, spas and similar recreational-water environments

There are three main routes of exposure to chemicals in swimming pools or spa waters:

- inhalation of volatile or aerosolized solutes;
- dermal contact;
- direct ingestion of the water.

Inhalation exposures will be controlled by the water concentrations, turbulence, mass transfer properties, air concentrations, length of time in the vicinity of the pool and physical activity, which will affect breathing rate and other factors. Several of these factors will be increased in indoor as opposed to outdoor pools. In indoor pools, for example, inhalation will be an important pathway for the uptake of THMs and other volatile chemicals. In order to establish the exposure situation of users of indoor pools, it is necessary to determine the concentration of the chemicals in the air above the pool water surface in addition to that in the pool water. In outdoor pools, on the other hand, the atmospheric concentrations of THMs above the pool water surface are very low, even when their concentrations in the water are high. Inhalation is likely to be much less important than resorption via the skin or oral intake under these circumstances.

Dermal exposure will be a function of body surface area, time in water, water concentrations and skin permeability, which is a function of the octanol/water partition coefficient of the chemical and other factors. Direct ingestion is probably the least of the exposure sources for volatile, non-polar chemicals, since it is limited to the amount of water that would be swallowed and the chemical concentration.

Body burdens contributed from ingestion, dermal contact and inhalation are difficult to distinguish experimentally.

4.2.1 Ingestion

Estimations of oral exposures (intake and uptake) are based upon assumed values for swallowing pool water in the course of swimming, as well as an assumption of 50–100% of uptake of the chemical after ingestion. Beech (1980), based upon an unpublished estimate by Datta (1979), assumed that a six-year-old child would take into the mouth and squirt out 5 ml of water with each breath while swimming, and that 1% would be swallowed. It was assumed that 1000 breaths per hour would occur while swimming and up to 0.5 litres of water would be ingested as an extreme for children while playing and diving. Borneff (1979) estimated ingestion of 50 ml of water in "normal swimming." A midpoint ingestion value of 225 ml per 1-h swimming session is assumed in these guidelines for competitive swimmers.

4.2.2 Inhalation

Swimmers inhale actively just above the water's surface, and the volume of air inhaled will be a function of the intensity of effort and time as well as their own physical size and physiology. They, and non-swimmers in the area, also breathe air in enclosed pool structures at lower rates during resting periods. Inhalation exposures of swimmers to volatile chemicals will be functions of the concentrations of those chemicals in the breathing zones, and the uptakes into the body will be

affected by the type of chemical, reactivity and metabolism. Exposure of both swimmers and non-swimmers to volatile substances in the pool area will undoubtedly be greatest in indoor pools (Table 4.10), as modelling and measurements in outdoor pools demonstrate low concentrations of volatile organic chemicals in proximity to outdoor pools (Strähle et al., 2000).

Table 4.10: 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

	THM concentration (mean, range)	
	Indoor pool	**Outdoor pool**
Blood of swimmers (µg/litre)	0.48 (0.23–0.88)	0.11 (<0.06–0.21)
Pool water (µg/litre)	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)

Source: Strähle et al., 2000

An estimation of the concentrations of chemicals in the breathing zone and the physical/chemical factors that are operating has been made by Andelman (1997). If the air concentration of a chemical is known, the inhalation exposure dose in mg/kg body weight per day can be estimated using a simple relationship and standard inhalation values. Most studies assume that a 70-kg adult male inhales approximately 10 m^3 of air per 8-h working day (e.g., IPCS, 1994). Swimming includes periods of significant exertion greater than many working conditions, as well as more quiescent periods of swimming and resting. An average breathing rate of 1 m^3/h for mixed activity is a reasonable index value for comparison purposes for normal adult swimmers and pool attendants or lifeguards; higher and lower breathing rates are assumed for competitive swimmers and children, respectively.

Equilibrium is established between the exposure concentration in air and the blood concentration (and exhaled air concentrations) soon after exposure (Khanna, 1983). The time period is dependent upon air concentrations. The percentage of chemical absorbed is higher at lower concentrations in the early period of exposure.

The exposure factor (EF) — also called a retention factor or absorption factor — is a representation of the actual dose retained by the body in a particular time period. For range-finding purposes, EF values of 50% and 100% can be used in estimates involving short-term, low-concentration exposures.

Inhalation exposure doses (IED) can be estimated as follows:

$$IED = (C \times IR \times T \times EF) / BW$$

where:

IED = inhalation exposure dose (mg/kg body weight per day),
C = contaminant concentration (mg/m^3),
IR = inhalation rate (m^3/h),
T = exposure duration (h/day),
EF = exposure factor (unitless), and
BW = body weight (kg).

4.2.3 Dermal contact

Chemicals present in pool water may diffuse across the surface membranes (skin, stratum corneum) of the swimmer. Two pathways have been suggested for transport across the stratum corneum: one for lipophilic chemicals and the other for hydrophilic chemicals (Raykar et al., 1988). Fick's first law, which is traditionally used to estimate dermal exposure to non-electrolytes in dilute aqueous solutions (Bogen, 1994) at steady state, applies only to highly lipophilic chemicals — i.e., those with octanol/water partition coefficients greater than approximately 50 (log K_{ow} ~1.7) (Anderson et al., 1988).

Estimates of dermal exposure based upon Fick's law and short-term simulated measurements of uptake (i.e., before steady state has been achieved) may significantly underestimate the actual total dermal dose that would be expected from real-world contact with dilute solutions of lipophilic agents, such as from swimming. One way of expressing this relationship for exposure periods too short for steady state to be achieved is as follows:

$$D\ (\text{Exposure}) = A\ K_p^{\text{eff}}\ C_w t$$

where:

D (Exposure) = the total absorbed chemical mass (mg),
A = the body surface area (cm^2),
K_p^{eff} = the effective dermal permeability coefficient (cm/h),
C_w = the chemical concentration in water (mg/cm^3), and
t = the duration of exposure (h).

In the calculations shown below (see section 4.4), body surface areas were assumed to be 10 000 cm^2 for a small child and 18 000 cm^2 for an adult (ATSDR, 1993). K_p^{eff} values for various disinfectant by-products are given in Table 4.11.

Table 4.11: K_p^{eff} values for various disinfectant by-products

Chemical	Molecular mass (MM)	Experimental log K_{ow} [a]	Estimated log K_{ow} [b]	K_p^{eff} [c]
Chloroform	119.4	1.97	1.52	0.144[d]
Bromodichloromethane	163.9	2.00	1.61	0.0519[d]
Dibromochloromethane	208.3	2.16	1.70	0.0225[d]
Bromoform	252.7	2.40	1.79	0.0109[d]
Chloroacetic acid	94.5		0.34	0.0260
Chloroacetaldehyde	78.5		0.09	0.0267
Dichloroacetic acid	128.9		0.52	0.0147
Trichloroacetic acid	163.4		1.44	0.0238
Bromoacetic acid	138.5	0.43	0.41	0.0103[d]
Dibromoacetic acid	218.4		0.70	0.00223
Chloroacetonitrile	75.45	0.45	0.11	0.0479[d]
Dichloroacetonitrile	110.9		0.29	0.0163
Bromoacetonitrile	119.9		0.20	0.0116
Dibromoacetonitrile	199.8		0.47	0.00251
Bromochloroacetonitrile	154.4		0.38	0.00655
Cyanogen chloride	61.47		–0.38	0.0206
Chloropicrin	164.37	2.09	1.32	0.0583[d]
Hypochlorous acid	52.46		–0.87	0.0128
Chlorous acid	84.46		–0.66	0.00800
Formaldehyde	30.0	0.35	–0.17	0.123[d]
Acetaldehyde	44.05	–0.34		0.0332[d]

[a] Log K_{ow} values were determined experimentally by Sangster Research Laboratories, Hansch (1993), Sangster (1994) and Hansch & Leo (1995).
[b] Log K_{ow} values were calculated by the Syracuse Research Corporation using data from the Sangster LOGKOW Databank.
[c] K_p^{eff} values were calculated according to the equation of Bogen (1994): $\log K_p^{eff} = -0.812 - 0.0104\ MM + 0.616 \log K_{ow}$.
[d] Experimental log K_{ow}s were used.

Following exposure, the chemical is transported to the bloodstream. The rate of transfer of a chemical from the epidermis into blood is proportional to the instantaneous amount in the epidermis, the epidermal blood flow rate and the relative solubilities of the chemical in the two compartments (Shatkin & Brown, 1991). Transport may be accelerated during physical activity, such as swimming.

Dermal uptake values calculated using the above equation could be reduced by 10–20% for longer-term exposure (~1 h), according to Bogen et al. (1998). On the other hand, for active swimmers, this reduction might not be appropriate, and the actual uptakes could be higher due to increased surface capillary circulation.

4.2.4 Measured and estimated exposures by all routes

Several studies have estimated intake and uptake of chloroform or other THM compounds in persons exposed in pool environments. THMs are expected to be good surrogates for other volatile substances with similar physical/chemical properties (e.g., trichloramine, chloroacetonitrile).

Beech (1980) carried out a study on a six-year-old boy immersed in water containing 500 µg chloroform per litre for 1 h. They estimated that his exposure corresponding to a 3-h session would be as follows: dermal 1.65 mg; oral 0.079 mg; buccal and sublingual 0.075 mg; orbital and nasal 0.07 mg; aural 0.075 mg; inhalation 0.866 mg: total 2.82 mg.

Shatkin & Brown (1991) calculated dermal absorption rates of chloroform by a swimmer during a 20-min immersion in pool water and estimated a total dose as high as 4.8 mg. Kaas & Rudiengaard (1988) calculated that dermal absorption of 700 µg of chloroform and oral absorption of 200 µg could occur from a 1-h swim in water containing 150 µg/litre and suggested an inhalation dose of 12.9 mg chloroform from a 2-h swim.

Lahl et al. (1981) estimated inhalation exposures and uptakes in two scenarios, assuming a respiration volume of 1 m^3/h and 50% uptake of inhaled chemical. They estimated that a dose of 50 µg of chloroform would be absorbed in a 30-min swim during a 1-h visit inhaling air just above the water surface. Using more extreme conditions, i.e., a 1-h swimming session, maximum water/air exchange of chloroform, chloroform concentrations of 389 µg/m^3 in air, and spending 10 min resting above the water discharge port with maximum chloroform outgassing, they estimated a burden of 500 µg of chloroform per person per visit (about 7 µg/kg for a 70-kg adult). [IPCS (1994), based on ICRP (1974), considers the average body weight of an adult to be 64 kg, based on body weights of 70 kg for an adult male and 58 kg for an adult female. The WHO *Guidelines for Drinking-water Quality* (WHO, 1993) uses 60 kg for an adult body weight.] For children, they estimated a specific dose of 15 µg/kg body weight. All of these estimates are for inhalation exposures alone.

Lévesque et al. (1994) estimated that the daily dose of chloroform resulting from a 1-h swim (65 µg/kg body weight per day) in conditions commonly found in public swimming pools is 141 times greater than that for a 10-min shower and 93 times greater than that for tapwater ingestion.

Lindstrom et al. (1997) measured chloroform and BDCM in breath from two collegiate swimmers during a 2-h training session and 3 h afterward. They concluded that 80% of the blood chloroform concentration was attributable to dermal exposure. This conclusion was based upon comparisons of the concentration of chloroform in the swimmers' exhaled breath with the ambient pool air concentration. They did not measure chloroform levels in the air in the breathing zone close to the water surface.

A number of studies relating concentrations of chloroform and other THMs in indoor swimming pool water, air above pools, plasma of swimmers, plasma of non-swimming employees at pools and alveolar air have been published (e.g., Aggazzotti et al., 1990, 1993, 1995, 1998; Aiking et al., 1994; Sacré et al., 1996; Strähle et al., 2000). Plasma levels have been correlated with chloroform concentrations in water and pool air, number of swimmers in the indoor pools, and duration and intensity of swimming activity (Aggazzotti et al., 1990). Mean chloroform levels of 1.06 µg/litre in plasma drawn 1–40 min past exposure (Table 4.12) were obtained in swimmers for water with mean chloroform levels of 32.7 µg/litre and air with mean chloroform levels of 214 µg/m^3. Mean levels of BDCM and DBCM in plasma were about 10% of the corresponding chloroform levels.

Table 4.12: Concentrations of trihalomethanes in plasma of 127 swimmers

THM	No. positive/no. samples	Mean THM concentration (µg/litre)	Range of THM concentrations (µg/litre)
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

Source: Aggazzotti et al., 1993, 1995

Table 4.13 shows that mean levels of chloroform in alveolar air in swimmers are about two-thirds of the chloroform concentrations in the environmental pool air. Mean levels of BDCM and DBCM, when detected in alveolar air, were similar to the environmental pool air levels.

Table 4.13: Concentrations of trihalomethanes in alveolar air samples from 163 swimmers

THM	No. positive/no. samples	Mean THM concentration (µg/litre)	Range of THM concentrations (µg/litre)
Chloroform	163/163	94	14–312
BDCM	163/163	94	1–42
DBCM	25/163	12.6	2–28

Source: Aggazzotti et al., 1993, 1995

Olivo et al. (1989) calculated lung absorption rates (uptake) in five persons based on the differences in concentrations between environmental air (C_e) and alveolar air (C_A), the time of exposure (t) and estimated pulmonary ventilation (V). Mean chloroform levels of 33.7 µg/litre in water and 161.2 µg/m^3 in air led to mean absorption rates between 374 and 472 µg/h. Air and lung absorption rates of BDCM and DBCM were in similar relative proportion to that for chloroform. These values are specific for the environmental scenarios given (Table 4.14).

Table 4.14: Pulmonary intake of trihalomethanes in swimming pools

	THM absorption (µg/h)[a]				
THM	**Subject A**	**Subject B**	**Subject C**	**Subject D**	**Subject E**
Chloroform					
Mean	459	459	431	374	472
Range	281–696	227–588	351–615	206–547	262–597
BDCM					
Mean	62.2	57.7	61.0	53.7	48.9
Range	49.7–94.4	46.6–58.8	44.9–84.9	39.4–79.4	37.0–60.5
DBCM					
Mean	42.3	50.1	45.2	39.8	37.8
Range	33.1–60.7	39.6–64.0	37.8–51.4	32.6–45.1	35.3–40.3
Bromoform					
Mean	1.1	1.2	–	1.0	1.0

[a] Pulmonary uptake $U = V(C_E - C_A)t$
where:
U = uptake (µg/h),
V = pulmonary ventilation (m^3/min),
C_E = concentration in environmental air (µg/m^3),
C_A = concentration in alveolar air (µg/m^3), and
t = exposure time (min).

Source: Olivo et al., 1989

Cammann & Hübner (1995) compared chloroform levels in blood between competitive swimmers, normal swimmers and pool attendants and found levels of 1.14–5.23 µg/litre, 0.56–1.65 µg/litre and 0.13–2.45 µg/litre, respectively; they also concluded that 3–7% of chloroform uptake was excreted in urine.

The levels of THMs in ambient air and in alveolar air in competitive swimmers have been compared at various times of swimming sessions — i.e., before arrival at the pool, during the swimming session and after the swimming session (Aggazzotti et al., 1998; Table 4.15).

Table 4.15: Comparison of trihalomethane levels in ambient air and alveolar air in swimmers prior to arrival at the swimming pool, during swimming and after swimming

	THM levels (μg/m^3) at various monitoring times[a]				
	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] 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. nq = not quantified.

Source: Aggazzotti et al., 1998

A rapid rise in THM levels in alveolar air while in the pool area prior to swimming and a further elevation after the swim are demonstrated in Table 4.15 (Aggazzotti et al., 1998). It was shown that at 1 and 1.5 h after swimming, alveolar air levels did not return to baseline A, even though the subjects were exposed to ambient air at baseline A. For biological monitoring in plasma, chloroform was detected in 14 samples out of 20 at baseline A, at values ranging from 0.3 to 1.8 μg/litre. The total THM plasma values measured after swimming (point C) ranged from 0.9 to 2.3 μg/litre (mean 1.5 ± 0.5 μg/litre). Chloroform was present at detectable levels in all samples; concentrations ranged from 0.7 to 2.3 μg/litre, which represents approximately 90% of the total plasma THMs. BDCM in plasma was detected in two sampling sessions and in only five samples (range: 0.2–0.3 μg/litre), while DBCM was detected in only one session at very low levels in three subjects (detection limit = 0.1 μg/litre). Bromoform was never found. These results correlated well with the results of an earlier study (Aggazzotti et al., 1995).

Competitive swimmers undergoing intense training sessions have been shown to rapidly absorb chloroform. Aggazzotti et al. (1995), for example, studied the kinetics of chloroform elimination in a 104-kg competitive swimmer after intense practice swims of 45 min each on four different days. Exhaled alveolar air was measured for 10 h after each swim, by which time chloroform elimination had ceased. Chloroform levels in pool water ranged from 106 to 144 μg/litre; ambient pool air values ranged from 92 to 208 μg/m^3, with a mean level of 139 ± 24.6 μg/m^3. Biological half-lives ranged from 20 to 27 min, while area-under-curve values for total elimination over 10 h were 2815, 1777, 1269 and 1136 μg·min/m^3 for chloroform, respectively, for each session. Chloroform absorption has been shown to be rapid, and pulmonary uptake and elimination occur by first-order diffusion processes, with rate constants corresponding to tissue loading or desaturation of at least three distinct compartments (vessel-rich tissues, lean body mass, adipose tissue). Elimination occurs by pulmonary

elimination and by metabolism (Aggazzotti et al., 1995). Some studies have suggested chloroform metabolism on the order of 30% of the absorbed dose (Khanna, 1983).

4.3 Health hazards associated with chemicals in swimming pool environments

The adverse health risks associated with the ingestion of many disinfectants and disinfectant by-products in drinking-water have been well documented (see, for example, WHO, 2000). Guideline values derived on the basis of these health risks could be applied to the accidental swallowing of pool water.

Much less has been written on the health hazards specifically associated with exposure, particularly by inhalation and dermal contact, to these chemicals in swimming pools, spas and similar recreational-water environments.

This section briefly describes the known health risks associated with exposure of pool users to disinfectants and disinfectant by-products, as well as the hazards associated with chemicals that interfere with disinfectant efficiency. Although occupational exposures of individuals working in recreational-water environments are not discussed elsewhere, exposures of pool workers to chemical hazards in swimming pool environments are examined briefly here.

4.3.1 Disinfectants

It is important that all applicable safety and health protocols and regulations are followed when handling disinfectants.

Chlorine gas and chlorine dioxide, for example, are strong respiratory irritants. Although chlorine gas has demonstrated its ability to work well where adequate precautions are taken, its use in swimming pool disinfection has been discouraged in some countries because of the risk of accident, especially in poorly ventilated storage and dosing areas. Because the gas is heavier than air and exposure is rapidly incapacitating, poorly ventilated areas present a particular risk.

Sodium hypochlorite and calcium hypochlorite must also be stored and handled in accordance with regulations. Sodium hypochlorite, for example, should never be mixed with acids, as toxic chlorine gas will be liberated. Particularly in its powder form, irritant calcium hypochlorite dust can be breathed in during handling and can affect the lungs quite severely. Even with granular and tablet forms, personal protection equipment should be used. Chlorinated isocyanurates also need to be stored separately from acids.

Chemicals should not be added directly to the water in a swimming pool or spa pool when the pool is in use. Localized high concentrations of chlorine and bromine can cause bather distress from eye and skin irritation (Government of Victoria, 1999). Episodes of dermatitis have been associated with exposure to chlorine and hypochlorite (US EPA, 1981; Eun et al., 1984).

The presence of slight amounts of ozone in air could potentially contribute to health-related problems, particularly in pool users or pool maintenance personnel with existing respiratory conditions (OSEH, 2000). There must be careful training for pool staff in the safe operation of the ozone equipment and good ventilation in the plant room, and excess ozone must be removed within the treatment system (Massin et al., 1998).

Studies with bromine have shown that less eye irritation and odour occur in brominated pools than in chlorinated pools (Block, 1991). Elemental bromine disinfects and oxidizes in a similar way to

chlorine, but it is more difficult to transport, handle and use safely and is considered to be a greater hazard generally. Users of pools disinfected with BCDMH have reported skin irritation (itch and rash) of a type not found in chlorinated pools (Rycroft & Penny, 1983).

Iodine as a swimming pool disinfectant does not form additional products with ammonia, as do chlorine and bromine. Because of this, less eye irritation occurs in iodinated pools.

4.3.2 Disinfectant by-products

There have been few studies conducted on health effects directly associated with exposure to disinfectant by-products in pool water.

In a pilot study designed to address the potential effects of long-term exposure to chlorination products (using chloroform as an indicator) in indoor and outdoor swimming pools, no hepatotoxic effects (as indicated by serum glutamate oxaloacetate transaminase, serum glutamate pyruvate transaminase and ?-glutamyl transpeptidase enzyme levels) were observed. However, levels of ß-2-microglobulin, an indicator of renal damage, were significantly elevated in urine samples of the slightly, but significantly, younger indoor pool swimmers (Aiking et al., 1994).

Massin et al. (1998) measured trichloramine levels in the atmosphere of indoor swimming pools and examined their relationship to irritant and chronic respiratory symptoms, indices of pulmonary function and bronchial hyperresponsiveness to methacholine in lifeguards working in the pools. The data showed that lifeguards exposed to trichloramine in indoor swimming pools are at risk of developing irritant eye, nasal and throat symptoms. Although no relation was found between bronchial hyperresponsiveness and exposure, the authors did not rule out the possibility that lifeguards may be at risk of developing transient bronchial hyperresponsiveness.

Chloramines in pool water, known collectively as “combined residual chlorine,” are known to cause irritation of the conjunctiva and effects on the mucous membranes of the nasopharynx. The highly irritant and odour-intensive compounds are also responsible for the typical “indoor pool smell.” Due to their different volatilities, pool water releases dichloramine about three times faster and trichloramine about 300 times faster than monochloramine (Holzwarth et al., 1984). Dichloramine imparts a chlorinous odour to water, while monochloramine does not. Trichloramine has a strong unpleasant odour at concentrations in water as low as 0.02 mg/litre (Kirk & Othmer, 1993).

The health effects associated with exposure to certain disinfectant by-products in drinking-water have been recently reviewed (WHO, 2000). Tolerable daily intakes (TDIs) recommended in this review for these disinfectant by-products, as well as for certain drinking-water disinfectants, are summarized in Table 4.16.

Table 4.16: Tolerable daily intakes for disinfectants and disinfectant by-products in drinking-water

Chemical	TDI (µg/kg body weight)	Basis of TDI[a]
Disinfectants		
Chlorine	150 (for free chlorine)	NOAEL in 2-year studies in rats and mice
Monochloramine	94	NOAEL in 2-year rat bioassay
Chlorine dioxide	30	NOAEL for neurodevelopmental effects of chlorite in rats, as chlorine dioxide is rapidly hydrolysed to chlorite in body
Disinfectant by-products		
Chloroform	10	NOAEL for cytotoxicity in mice
DBCM	30	NOAEL based on liver toxicity in rats
Bromoform	25	NOAEL based on liver toxicity in rats
DCAA	40	NOAEL for hepatomegaly and glycogen accumulation in mice
TTAA	40	NOAEL for hepatic toxicity in mice
DBAA	20	NOAEL for effects on reproduction in male rats
Chloral hydrate	16	LOAEL for hepatomegaly
DCAN	15	NOAEL in reproductive toxicity study in rats
DBAN	23	NOAEL for general toxicity in rats
Chlorite	30	NOAEL for adverse effects in two-generation study in rats
Bromate	1	no-effect level for formation of renal tumours in rats

[a] NOAEL = no-observed-adverse-effect level; LOAEL = lowest-observed-adverse-effect level.

Source: WHO, 2000

Thirteen-week toxicological studies for sodium cyanurate, which can accumulate in swimming pools disinfected with sodium dichloroisocyanurate, have indicated no-observed-effect levels (NOELs) of 522 mg/kg body weight per day in mice and 72 mg/kg body weight per day in Charles River rats (Blair et al., 1982; Serota et al., 1982). In a two-year study in Charles River rats, the NOEL was 154 mg/kg body weight per day; tumours were not seen in a 2-year mouse study at 1525 mg/kg body weight per day (Monsanto Co., 1983). Maternal toxicity was seen in pregnant dd strain mice, but not in rats, at 400 mg/kg body weight per day when exposed at days 6–15 of gestation (Hammond et al., 1986). Conservative estimated acceptable doses of 14 mg cyanuric acid per litre and 10 mg/litre for chlorinated isocyanurates have been computed using an uncertainty factor of 50 applied to the dose level of 72 mg/kg body weight per day in rats in a study by Rajasekaran et al. (1981) (J.K. Fawell, Water Research Centre, Medmenham, personal communication with NSF International). [Note: A risk assessment for sodium dichloroisocyanurate and its breakdown products is pending.]

The toxicology of iodination disinfectant by-products is not well known.

4.3.3 Chemicals that interfere with disinfectant efficiency

In the discussion of the health hazards associated with chemicals in swimming pools, most emphasis has been placed on the health risks associated with the use of disinfectants and the adverse health effects caused by exposure to disinfectant by-products.

However, because the microbiological quality of water is so important to human health, the presence of chemicals in water — both inorganic and organic — that interfere with the efficiency of disinfection must also be mentioned. These include, of course, all those chemicals that react with disinfectants to form disinfectant by-products. Reducing substances such as dissolved and particulate

matter, for example, must be eliminated from the water as much as possible by preceding treatment steps if adequate disinfection is to be achieved with low amounts of disinfectant.

The adverse health effects associated with decreased microbiological water quality have been addressed in chapter 3. Factors affecting disinfection efficiency are covered more fully in chapter 5.

4.3.4 Other water quality parameters

pH may have a direct impact on health at very low or very high values. Under these circumstances, pH may have effects on taste as well as on skin irritation or dermatitis, particularly in sensitive subjects. High or low pH may also contribute to and exacerbate irritation of the eye by chemicals.

Other chemical parameters may also affect the swimmers' "comfort zone." For example, calcium hardness between 75 and 150 mg/litre as calcium carbonate is a level that has been found to be comfortable to bathers (PWTAG, 1999).

4.4 Risk assessment

The principal databases on exposure to pool volatiles have focused on chloroform and other THMs, due to their ease of analysis, high concentrations, frequency of occurrence and possible toxicity. They are the only disinfectant by-products for which information is available on concentrations in both pool water and ambient pool air. As exposure to volatile substances such as THMs will undoubtedly be greater in indoor pools than in outdoor pools, the risk characterization developed here will focus on exposure to selected THMs via ingestion, inhalation and dermal contact in indoor pools. Any guidelines developed will be protective for exposure in outdoor pools, as concentrations in ambient air will be lower than those in indoor pool air.

The risk characterization will estimate exposures for four populations:

- the sporadic child swimmer;
- the sporadic adult swimmer;
- the competitive adult swimmer in regular training;
- and the pool attendant or lifeguard.

In order to do so, many assumptions need to be made about the physiological and exposure characteristics of these four groups. These assumptions are shown in Table 4.17.

Table 4.17: Physiological and exposure assumptions for four populations

Parameter	Child swimmer	Adult swimmer	Competitive swimmer	Pool attendant/ lifeguard
Volume of water ingested per hour (litres)	0.5[a]	0.05[b]	0.225[c]	0.0[d]
Exposure duration (h/day)	1	1	4	8 (air only)[d]
Inhalation rate (m^3/h)[e]	0.5	1	1.5	1
Body weight (kg)[f]	10	60	60	60
Body surface area (cm^2)[g]	10 000	18 000	18 000	18 000

[a] Beech (1980).
[b] Borneff (1979).
[c] Estimated as midpoint between values for child swimmer and adult swimmer.

[d] These values assume that the pool attendant/lifeguard does not swim. A more realistic assumption might be that pool attendants/lifeguards receive exposures similar to those of occasional adult swimmers, in addition to their occupationally derived exposures.
[e] Estimated from average 8-h respiratory volumes given in IPCS (1994).
[f] WHO (1993).
[g] ATSDR (1993).

Calculations will be made for three exposure scenarios:

- a worst-case scenario, in which concentrations of disinfectant by-products are assumed to be maximum measured concentrations in indoor swimming pools and where uptake via the ingestion and inhalation routes is considered to be 100%;
- a more moderate exposure scenario, where concentrations are highest mean measured concentrations in indoor swimming pools and uptake via the ingestion and inhalation routes is considered to be 50%; and
- a low exposure scenario, in which concentrations are the mean of the mean concentrations measured in indoor swimming pools and uptake is again considered to be 50%.

4.4.1 Chlorine disinfection

For freshwater swimming pools disinfected using chlorination systems, the THM found most frequently in pool water and ambient pool air and for which the most toxicological information is available is chloroform. Chloroform exposure will be used to represent exposure to disinfectant by-products in chlorinated swimming pools.

For ingestion, the concentration of chloroform in water is assumed to be 980 µg/litre for the worst-case exposure (the highest concentration measured; Lahl et al., 1981), 198 µg/litre for the moderate exposure (the highest mean concentration; Lahl et al., 1981) and 64 µg/litre for the low exposure (the mean of the mean concentrations; see Table 4.4). Using these concentrations, uptake would be as indicated in Table 4.18.

Table 4.18: Daily uptake of chloroform under low, moderate and worst-case conditions in indoor swimming pools

	Ingestion		Inhalation		Dermal		Total	
	µg	% of total	µg	% of total	µg	% of total	µg	µg/kg body weight
Child swimmer								
Low	16	13	13	11	92	76	121	12
Moderate	50	14	16	5	285	81	351	35
Worst-case	490	24	103	5	1 411	70	2 004	200
Adult swimmer								
Low	2	1	26	13	166	86	194	3.2
Moderate	5	1	33	6	513	93	551	9.2
Worst-case	49	2	206	7	2 540	91	2 795	47
Competitive swimmer								
Low	29	3	156	18	664	78	849	14
Moderate	89	4	195	8	2 053	88	2 337	39
Worst-case	882	7	1 236	10	10 161	83	12 279	205
Pool attendant/lifeguard[a]								
Low	0	0	132	100	0	0	132	2.2
Moderate	0	0	144	100	0	0	144	2.4
Worst-case	0	0	1 088	100	0	0	1 088	18

[a] For pool attendants or lifeguards who also swim 1 h per day, exposures would be the sum total of exposures for pool attendants/lifeguards and adult swimmers.

For inhalation, the exposure dose was calculated using the equation in section 4.2.2, assuming, for the worst-case scenario, that the concentration in the air is 206 µg/m^3 for a swimmer (20 cm above the water surface) and 136 µg/m^3 for a pool attendant/lifeguard (150 cm above the water surface), the maximum measured concentrations in a study in which concentrations were measured at various levels above the pool water surface (Stottmeister, 1998, 1999). For the moderate exposure scenario, the assumed concentrations are 65 and 36 µg/m^3, respectively, the highest mean concentrations from a study in which concentrations were measured at 20 and 150 cm above the pool water surface (Jovanovic et al., 1995). For the low exposure scenario, the concentrations are taken to be 52 and 33 µg/m^3, the mean of the mean concentrations in these two studies, the only ones in which concentrations were measured in ambient air at 20 and 150 cm above the surface of indoor swimming pools. The inhalation exposure doses calculated in this way are shown in Table 4.18.

For dermal exposure, the concentrations of chloroform in pool water are again assumed to be 980, 198 and 64 µg/litre for the worst-case, moderate and low exposures, respectively. The K_p^{eff} (0.144) is taken from Table 4.11. The uptake from dermal contact, calculated using the equation in section 4.2.3, is shown in Table 4.18.

The relative importance of the three exposure routes agrees generally with the estimates of Beech et al. (1982), who found that, for exposure of a six-year-old child to chloroform in pool water for 3 h, approximately 60% of the dose came from dermal contact, 30% from inhalation and 10% from ingestion. Inhalation is, of course, the only exposure route for pool attendants/lifeguards, unless they also swim. A more realistic assumption might be that pool attendants/lifeguards receive exposures similar to those of occasional adult swimmers, in addition to their occupationally derived exposures. Ingestion is the least important exposure route for all groups except children, who are more likely than adults to accidentally swallow water. Dermal exposure is the most significant exposure route for all groups, which is somewhat surprising for an indoor swimming pool, given the volatility of chloroform. However, this observation agrees with that of Lindstrom et al. (1997), who found that 80% of the blood chloroform concentration in collegiate swimmers during a 2-h training session and 3 h afterwards was attributable to dermal exposure. It should also be emphasized that these rough estimates are dependent on the assumptions made (i.e., those shown in Table 4.17 as well as the concentrations chosen for use) and may not pertain under different conditions.

To determine whether these uptakes have the potential to be hazardous to health, we can consider the TDI for chloroform in drinking-water, which is 10 µg/kg body weight (see Table 4.16). We will assume that 50% of this TDI, or 5 µg/kg body weight, can come from swimming pool exposure. Using this assumption, we can see that under the low exposure scenario, sporadic children swimmers and competitive swimmers will both exceed the TDI. Under the moderate exposure scenario, all three groups of swimmers exceed the TDI, and under the worst-case scenario, all four groups, including pool attendants/lifeguards, will exceed the TDI.

Guideline values have thus been derived for chlorinated swimming-pool environments. These are intended to be used not for routine monitoring but instead to inform design and operation (see section 4.5).

4.4.2 Ozone disinfection

The disinfectant by-product associated with ozone disinfection about which the most is known is bromoform, which can be formed when waters containing bromide ion are treated with ozone or when

bromide ion is added deliberately to recirculating pool/spa waters to be treated with corona discharge generated ozone. Under such conditions, it has been shown that bromoform concentrations above 100 µg/litre can be produced (Pacik & Rice, 1991).

Performing the same calculations for bromoform as was done for chloroform, and using the same assumptions, gives the results shown in Table 4.19. The concentration of bromoform in indoor pool water under the worst-case scenario is assumed to be 203.2 µg/litre, which is the maximum concentration measured (Biziuk et al., 1993). For the moderate and low exposure scenarios, the concentrations chosen are 1.8 µg/litre (the highest of the mean concentrations in indoor swimming pools; Lahl et al., 1981) and 0.45 µg/litre (the mean of the means in Table 4.4, taking <0.1 to be 0.1 µg/litre). The concentration in ambient pool air is taken as 3.0 µg/m^3 20 cm above the pool surface and 0.7 µg/m^3 150 cm above the water surface for the worst-case exposure scenario (highest measurements in a study in which concentrations were measured at two distances above the pool water surface; Stottmeister, 1998, 1999), 0.2 µg/m^3 for the moderate exposure scenario (measured at 20 cm above pool surface, but also used for 150 cm; Aggazzotti et al., 1993, 1995, 1998) and 0.1 and 0.08 µg/m^3, respectively, for the low exposure scenario (means in study in which concentrations were measured at both distances above the water surface; Stottmeister, 1998, 1999). The K_p^{eff} for bromoform is taken as 0.0109 (Table 4.11).

Table 4.19: Daily uptake of bromoform under low, moderate and worst-case conditions in indoor swimming pools

	Ingestion		Inhalation		Dermal		Total	
	µg	% of total	µg	% of total	µg	% of total	µg	µg/kg body weight
Child swimmer								
Low	0.1	56	0.03	17	0.05	28	0.18	0.018
Moderate	0.5	67	0.05	7	0.2	27	0.75	0.075
Worst-case	101.6	81	1.5	1	22	18	125.1	12.5
Adult swimmer								
Low	0.01	7	0.05	33	0.09	60	0.15	0.0025
Moderate	0.05	9	0.1	18	0.4	73	0.55	0.009
Worst-case	10.2	19	3	6	40	75	53.2	0.89
Competitive swimmer								
Low	0.2	22	0.3	33	0.4	44	0.9	0.015
Moderate	0.8	29	0.6	21	1.4	50	2.8	0.047
Worst-case	183	51	18	5	159	44	360	6.0
Pool attendant/lifeguard[a]								
Low	0	0	0.3	100	0	0	0.3	0.005
Moderate	0	0	0.8	100	0	0	0.8	0.013
Worst-case	0	0	5.6	100	0	0	5.6	0.093

[a] For pool attendants/lifeguards who also swim 1 h per day, exposures would be the sum total of exposures for pool attendants/lifeguards and adult swimmers.

The TDI for bromoform in drinking-water is 25 µg/kg body weight (see Table 4.16). If 50% of this TDI (12.5 µg/kg body weight) is assigned to swimming pool exposure, it can be seen that only for children under the worst-case scenario will the TDI be met (due primarily to the ingestion route of exposure). Under normal circumstances (i.e., low and moderate exposure scenarios), exposure to bromoform will not lead to any exceedances of the TDI, and no guideline values are needed.

4.4.3 Other disinfection systems

There is insufficient information available to perform a similar risk characterization for any other disinfectants or disinfectant by-products present in swimming pool water. It would be preferable to perform such calculations for at least one chemical for each major approach to disinfection. For chlorine dioxide, for example, chlorate has been measured in pool water, but not in ambient pool air. Chlorite, on the other hand, has not been measured in either environment. Sufficient information to allow such calculations is desirable.

4.5 Risk management

The calculations presented in section 4.4 are very preliminary estimates and may not represent the usual situation encountered in swimming pools around the world today. As a result, they are useful for drawing only general conclusions. These conclusions are as follows:

- For swimmers and pool attendants/lifeguards in indoor or outdoor pools where ozone is the primary disinfectant, the presence of disinfectant by-products is generally minimal, and guideline values are not required.
- For sporadic adult swimmers and pool attendants/lifeguards in chlorine-disinfected pools operated under typical conditions, with low chloroform levels in air and water, the presence of disinfectant by-products is a non-issue, and guideline values are not required in indoor or outdoor pools. Where concentrations of chloroform in pool water and air are relatively high (i.e., the moderate and worst-case scenarios), however, pool users may exceed the TDI. This is best controlled by good ventilation, use of alternative disinfectants, pre-ozonation, effective flushing, control of precursor addition through pre-swim showering and toilet use, etc.
- Because of their special conditions of exposure, competitive swimmers may readily exceed the TDI for chloroform in chlorine-disinfected indoor pools. Competitive swimmers and their associations should be aware of this and should investigate means to minimize exposure in pools used (e.g., better low-level ventilation, not sitting poolside, occasional use of non-chlorinated pools).
- As children may exceed the TDI for chloroform in chlorine-disinfected indoor pools, parents should be made aware of this and try to minimize their exposure (e.g., emphasizing importance of not intentionally swallowing water).

As dermal contact is the dominant exposure route for chloroform in swimming pools, design engineers must concentrate on factors that will decrease dermal exposure. This implies very good water quality management, typically involving relatively high dilution rates, possibly ozone plus chlorine, and strong promotion of hygiene (pre-use showering, education on urinating in pool), in order to lower exposures to those of the most optimistic assumptions.

Where there are special pool features involving air and water, such as wave machines, eye and skin irritation may occur as a result of disinfectant by-products released in the presence of relatively high ambient temperatures, humidity and condensation. In these cases, water treatment will need to be carefully controlled. Automatic disinfection and water distribution systems should be used where possible, and risks should be controlled by management of bather load, water treatment systems, temperature, disinfectant residuals and pH, and ventilation.

It must be emphasized that although the use of chemical disinfectants in water treatment usually results in the formation of chemical by-products, some of which are potentially hazardous, the risks to health from these by-products at the levels at which they occur in pool water are extremely small in comparison with both the risks associated with inadequate disinfection and the enormous health

benefits (including relaxation and exercise) associated with pool use. In addition, despite the fact that levels of disinfectant by-products in pools may exceed levels in drinking-water, the contribution to total lifetime exposure to disinfectant by-products is, on average, much lower from pools than from drinking-water. The purpose of the guidelines developed here is not to deter swimming pool use but to ensure that pools are operated as safely as possible in order that the largest possible population gets the maximum possible benefit.

4.6 References

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