

Disinfection of swimming pools with chlorine and derivatives: formation of organochlorinated and organobrominated compounds and exposure of pool personnel and swimmers

Maria-Cristina Aprea, Bruno Banchi, Liana Lunghini, Massimo Pagliantini, Antonio Peruzzi, Gianfranco Sciarra

Laboratorio di Sanità Pubblica Area Vasta Toscana Sud Est, Azienda USL 7, Siena, Italy; maaprea@tin.it, c.aprea@usl7.toscana.it

Received 12 August 2009; revised 11 September 2009; accepted 5 January 2010.

ABSTRACT

Chlorination of pool water leads to the formation of many by-products, chloroform usually being the most abundant. The paper reports the results of a study evaluating exposure of bathers and pool employees to trihalomethanes (chloroform, bromodichloromethane, dibromochloromethane, bromoform) in four indoor swimming pools with chlorinated water. Chloroform concentrations in environmental air samples when the pool was in use (about 9 h), in the range 1-182 $\mu\text{g}/\text{m}^3$, were greater near the pool than in the change rooms, passageways and offices. Chloroform concentrations in personal air samples of pool employees were in the range 18-138 $\mu\text{g}/\text{m}^3$. Urinary concentrations of chloroform averaged (geometric means) 0.123 and 0.165 $\mu\text{g}/\text{l}$ and 0.404 and 0.342 $\mu\text{g}/\text{l}$ prior and at the end of exposure during in water and out of water activities, respectively. The significant increase in urinary excretion of chloroform confirms that the source of the contaminant was pool water. Absorption of chloroform, estimated from airborne and water concentrations, was significantly correlated with delta chloroform (after/before exposure) and urinary concentrations of chloroform at the end of exposure. As chloroform is a toxic and possibly carcinogenic substance, these observations pose a problem principally for the general population of pool users.

Keywords: Disinfection By-Products; Indoor Swimming Pool; Trihalomethanes; Biological Monitoring; Exposure; Urine

1. INTRODUCTION

This paper is concerned with bathing complexes consisting of one or more artificial pools for recreational, educational, sporting or therapeutic activity carried out in the water. From the health point of view, pools are classified according to environmental and structural characteristics and type of use. Various documents defining guidelines for safe use of recreational facilities such as pools have been published [1-3]. Chemical hazards associated with frequentation of pools are summarized in **Figure 1**.

Chemical agents in pool water depend on the type of water used to fill the pool. Town water, for example, may contain organic matter and by-products of disinfection from previous treatments. Among the chemical agents derived from bathers, nitrogen compounds, especially ammonia, react with free disinfectants to form various by-products. Nitrogen compounds may come from skin secretions: the nitrogen content of sweat is about 1 g/l as ammonia, amino acids, creatinine and urea. Significant quantities of nitrogen compounds can come from urine: urine release by bathers averages 25-30 ml/person [4] but may exceed 77.5 ml/person [5]. No information is currently available about concentrations of compounds from cosmetics. With regard to chemical agents from maintenance, a considerable number of compounds are used to keep water quality acceptable. Disinfectants are added in order to deactivate pathogenic microorganisms. Chlorine in one of its various forms is the most common. Other disinfectants such as ozone and UV radiation kill or inactivate microorganisms at the time of treatment but do not have any residual effect that continues to act in the water. They are therefore used with chlorine or bromine to provide continuous disinfection. Chlorine dioxide is not considered a chlorine disinfectant as it acts differently without producing residual chlorine, through conversion to chlorite

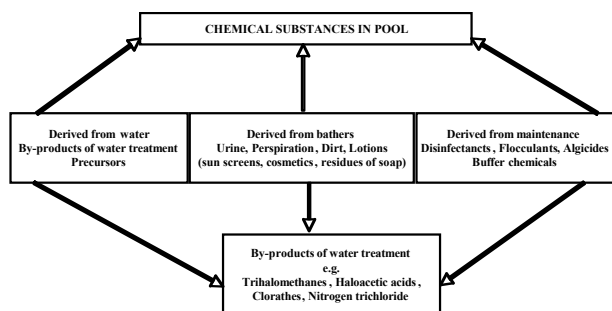


Figure 1. Summary of possible sources of chemical contamination in swimming pools.

and chlorate ions that remain in solution. Liquid bromine is seldom used, whereas sodium bromide and its oxidant (hypochlorite) are more common. Disinfection with bromine compounds is not suitable for outdoor pools because sunlight destroys bromine residues. In all cases, the choice is based on efficacy in the particular circumstances of use, as well as ease of handling and monitoring. Compounds used to correct pH depend on the type of disinfectant and its acidity/alkalinity. Alkaline disinfectants such as sodium hypochlorite only require addition of an acid, which is generally sodium hydrogensulphate, carbon dioxide or hydrochloric acid. Acid disinfectants such as chlorine require addition of an alkaline substance which is generally sodium carbonate solution. At correct doses with maintenance of pH between 7.2 and 8.0, disinfectants should not have adverse effects on health. Flocculants such as polyaluminium chloride can be used to facilitate removal of dissolved or suspended substances and colloids. They trap the substances in flocculate that can be removed by filtration.

The formation of by-products of disinfection is related to the reaction of disinfectants with other chemical substances in the water. The most abundant by-products are trihalomethanes, such as chloroform, the most abundant, together with haloacetic acids of which di- and trichloroacetic acids are the most abundant [6]. The presence of inorganic bromides in the water can induce formation of bromine after oxidation, which can participate in the formation of by-products such as brominated trihalomethanes. Use of ozone in the presence of bromides can lead to formation of bromates that can build up in the water if turnover is poor. Limited information is available on ozonation and its by-products. Ozone can react with organic substances to produce oxygenated compounds such as aldehydes and carboxylic acids. Chlorine and bromine react very quickly with ammonia forming chloramines and bromoamines. Little data is available on the impact of UV on disinfection by-products when used with other chemicals, but UV does not seem to form by-products and appears to significantly reduce chloramine levels.

Exposure of pool personnel and bathers may occur by

ingestion of water, inhalation of aerosol or vapours and cutaneous absorption. The quantity of water ingested by swimmers depends on various factors, including experience, gender, age and type of activity. Estimates show that water intake is higher in children (37 ml) than adults (16 ml), and in men (22 ml) than women (12 ml) [7]. Bathers inhale the air in contact with the water surface. The volume of air inhaled depends on the intensity of physical activity and exposure time. Exposure by inhalation regards substances in vapour form released by the water and aerosols created also by swimmer-induced splashing and stirring of the water. Concentrations at different levels in the air above the pool depends on factors such as ventilation, the size of the building and air circulation. Skin, including eyes and mucous membranes, is extensively exposed to chemical agents in pool water. The intensity of skin absorption depends on a series of factors including contact time, water temperature and concentration of toxic compounds.

Many by-products of disinfection have proven to be mutagenic, genotoxic, carcinogenic, fetotoxic, hepatotoxic, renotoxic, neurotoxic and dysmetabolic [8]. Chloroform and bromodichloromethane are classified by the International Agency for Research on Cancer (IARC) as possible carcinogens for humans (group 2B) [9], whereas the American Conference of Governmental Industrial Hygienists (ACGIH) considers chloroform to be carcinogenic for animals with unknown relevance to humans (Class A3) [10].

Concentrations of trihalomethanes in pool water [11-32] and in the air above the pool [11,14-16,18,26,27,33,34] was examined in several studies. Some authors investigated also the absorption of trihalomethanes during time spent at the pool by measuring blood concentrations of chloroform or those in alveolar air [14-16,29,35,36].

The aim of the present study was to assess exposure levels of swimmers and pool personnel to chlorinated and brominated organic compounds in public indoor pools. Airborne concentrations were determined in different parts of the pool premises, and when possible, by personal air sampling and determination of urinary excretion before and after exposure. Levels of the same compounds were also determined in water, as well as microclimatic and plant conditions. Absorption of chloroform estimated from airborne and water concentrations were compared with the increase in concentrations in urine during exposure.

2. MATERIALS AND METHODS

2.1. Microclimatic and Plant Conditions

Four public indoor pools were monitored. All used drinking water from the town water supply. On days of monitoring, one or more water samples were taken for

determination of brominated and chlorinated organic compounds (chloroform, bromodichloromethane, dibromochloromethane, bromoform).

Pool 1: pool volume 470 m³ plus compensation tank 20 m³, disinfectant calcium hypochlorite 65% and occasionally sodium dichloroisocyanate, air intake 18000 m³/h with aspiration of 15000 m³/h (turnover about 83%). The plant was monitored five times in 2006-2008. On sampling days, mean relative humidity was 51%-68%, mean air temperature 23.5-28.5°C. Mean air speed was 0.10-0.23 m/sec. Water temperature was 28.6-29°C, pH 7.3-7.8, nitrates 8.3-15 mg/l, isocyanic acid 40-75 mg/l, turbidity 0.2-0.3 mg/l, suspended solids 0.9 mg/l and residual free chlorine 0.29-1.12 mg/l. Maximum number of users per hour was 50-60 and total daily users 150-200.

Pool 2: pool volume 476.3 m³ plus compensation tank 24 m³, disinfectant sodium hypochlorite, air intake 30000 m³/h (turnover about 40%). The plant was monitored three times in 2007-2008. Mean relative humidity on sampling days was 70-75%, mean air temperature 23.2-24.5°C, mean air speed 0.06-0.07 m/sec, water temperature 28.4-28.6°C, pH 6.9-7.3, nitrates 0.7-1.1 mg/l, isocyanic acid <20 mg/l, turbidity 0.1-0.6 mg/l, suspended solids <1 mg/l and residual free chlorine 0.81-2.59 mg/l. Maximum number of users per hour 60-100, total daily users 220-240 persons.

Pool 3: pool volume 700 m³ plus compensation tanks 60 m³ disinfectant sodium dichloro-S-triazine-trione (Dichloro 63), air intake 40,000 m³/h without circulation. The plant was monitored twice in 2007-2008. On sampling days, mean relative humidity was 70-75%, mean air temperature 24.5-25.5°C, mean air speed 0.03-0.05 m/sec. Water temperature in adult pool 29-30°C, pH 6.9, nitrates 14 mg/l, isocyanic acid 20 mg/l, turbidity 0.3 mg/l, suspended solids < 1 mg/l, vinyl chloride 5-8 µg/l and residual free chlorine 0.8-1.5 mg/l. Total number of users per day 250-300.

Pool 4: pool volume 400 m³ plus compensation tank 24 m³, disinfectant sodium dichloro-S-triazine-trione and sodium hypochlorite, air input not available, turnover about 30%. The plant was monitored twice in 2007-2008. On sampling days, mean relative humidity was 83-84%, mean air temperature 24°C, mean air speed 0.05 m/sec, water temperature 29-30°C, pH 7.5, nitrates 11.6 mg/l, isocyanic acid 25 mg/l, turbidity 0.5 mg/l, suspended solids < 1 mg/l, vinyl chloride 0.05-0.12 µg/l and residual free chlorine 1.5-1.8 mg/l. Total number of users per day 200.

2.2. Study Population

In the four bathing complexes, six lifeguards and four instructors were monitored: the former worked at the poolside and the latter in the water. Thirty-one bathers underwent biological monitoring (15 swimmers at dif-

ferent levels of expertise, four competitive swimmers and 12 persons enrolled water gym sessions). All filled in a questionnaire about personal details, weight, height, smoking and drinking habits, occupation. This information was used in the statistical analysis of the results. Before enrolment in the study, all subjects gave their informed consent.

2.3. Personal and Environmental Air Sampling

Personal air sampling during the work-shift was performed for poolside personnel by means of radial diffusion air samplers for chloroform assay (Radiello®). In the measurements conducted in 2008, parallel active sampling with carbon vials was carried out at a flow rate of 100 ml/min to determine chloroform, bromodichloromethane, dibromochloromethane and bromoform. Double sampling was carried out to assay bromine compounds, for which the manufacturer of diffusion samplers does not provide equivalent rates.

Fixed (environmental) sampling was carried out about 1.5 m from the pavement at the edge of the pools (3 or 4 samples per bathing complex per day), in the changing rooms, offices and passages between the changing rooms and the pool. Sampling lasting 24 h was carried out with diffusion samplers (Radiello®) and others lasting about 9 h (when the pool was in use) were done using active carbon vials at an air flow of 100 ml/min. The same contaminants as for personal samples were assayed. In Pool 3, the 9-h sampling was divided into two periods of 4.5 h (morning and afternoon) in order to detect any changes in concentrations of the contaminants in the various areas. In this case the data was used as such and after calculation of the weighted mean concentration over the whole period the pool was open.

For the analytical determination, samples were added with carbon disulfide containing deuterated benzene as internal standard and left in contact with the solvent for 30 min. The extract was injected in the GC/MS apparatus (EI-SIM electronic impact, single ion monitoring). The analytical limit of detection (LOD) was 0.1 µg/sample.

2.4. Estimation of Absorption of Chloroform

Absorption of chloroform was estimated for staff and bathers, summing the fractions derived from direct ingestion of water, inhalation of aerosols and vapours, and transcutaneous absorption. For absorption by ingestion, the results of Evans *et al.* 2001 [7] were used. According to the latter, water intake averages 22 ml/h for men 12 ml/h for women. Knowing the concentration of chloroform in pool water, it was possible to calculate the quantity ingested, assuming 100% absorption. The fraction derived from ingestion was assumed to be zero for pool-side staff.

The fraction derived from inhalation was estimated on the basis of time spent in the water, lung ventilation and median concentration of airborne contaminant at the poolside, corrected by a factor of 1.8 because the measurements were made 1.5 m from the pavement instead of 20 cm from the water's surface [11]. A lung retention of 59% was assumed, as proposed by Kuo *et al.* [37]. Lung ventilation was assumed to be 15 l/min for males and 12 l/min for females for tasks involving little exertion (lifeguard) and 30 l/min for males and 25 l/min for females for activity in the water. For poolside personnel, the concentration found by personal air sampling was used.

The fraction derived from skin absorption was estimated on the basis of time spent in the water, chloroform concentration in pool water, body surface area estimated on the basis of weight and height using the Du Bois formula [38] and 80% contact of the skin with water. The permeation constant of skin was assumed to be 0.2 cm/h as proposed by Kuo *et al.* [37]. The fraction derived from skin absorption was assumed to be zero for poolside personnel.

2.5. Urine Sampling

Spot samples of urine were obtained from personnel and bathers before and after exposure. Chloroform, bromodichloromethane, dibromochloromethane and bromoform were determined in all samples. The determination was performed analyzing the head space in GC/MS EI-SIM using deuterated benzene as internal standard. The LOD was 0.050 µg/l.

The data, expressed in µg/l was used as such and as differences between concentrations before and after exposure.

2.6. Statistical Analysis

Statistical analysis was done using Stat View 5.0, Power PC Version (SAS Institute Inc.). Values below the analytical limit of detection (LOD) were analyzed as half the LOD when at least half the data was over the LOD. Values above LOD but not quantifiable (<LOQ) were analyzed as the mean of LOD and LOQ. Parametric tests were used (analysis of variance, regression analysis, Student's t test for paired and unpaired data) and the level of significance chosen was $\alpha = 0.05$.

3. RESULTS

Concentrations of trihalomethanes in pool water on sampling days are shown in **Table 1**. Concentrations of contaminants in the water depended on the type of disinfectants used, on any impurities in the water used to fill the pool and on water characteristics. Brominated compounds seemed to be associated more with use of sodium hypochlorite than with compounds such as calcium hypochlorite or Dichloro 63, irrespective of isocyanates. Chloroform was confirmed to be the most abundant trihalomethane, and was only equal in concentration to bromodichloromethane and dibromochloromethane in pool 2, disinfected with sodium hypochlorite alone.

Table 1. Concentrations of trihalomethanes (µg/l) in water of four public pools.

		Chloroform	BDCM	DBCM	Bromoform
Pool 1	N	5	3	3	3
	N < LOD	0	0	3	3
	Mean ± SD	85.54±35.73	1.87±0.23	-	-
	Median	83.20	2.00	-	-
	GM	75.47	1.86	-	-
	Min-Max	35.7-127.00	1.60-2.01	-	-
Pool 2	N	3	3	3	3
	N < LOD	0	0	0	0
	Mean ± SD	12.33±2.10	17.73±1.56	17.67±2.61	4.60±1.13
	Median	12.40	17.90	17.40	4.0
	GM	12.21	17.69	17.54	4.52
	Min-Max	10.2-14.4	16.1-19.2	15.2-20.4	3.90-5.90
Pool 3	N	6	6	6	6
	N < LOD	0	1	0	0
	Mean ± SD	33.23±9.72	1.48±0.61	0.63±0.09	0.04±0.004
	Median	38.40	1.70	0.61	0.040
	GM	31.83	1.25	0.62	0.042
	Min-Max	19.00-40.80	0.25-1.80	0.52-0.78	0.40-0.50
Pool 4	N	6	6	6	6
	N < LOD	0	0	0	0
	Mean ± SD	11.98±0.80	3.10±0.14	1.47±0.05	0.17±0.02
	Median	11.70	3.10	1.50	0.18
	GM	11.96	3.10	1.47	0.17
	Min-Max	11.10-13.10	2.90-3.30	1.40-1.50	0.13-0.19

BDCM= Bromodichloromethane. DBCM= Dibromochloromethane. GM = geometric mean.

Table 2. Descriptive statistics of concentrations of chloroform ($\mu\text{g}/\text{m}^3$) detected in environmental air samples in four public pools.

TOTAL DATA						
	Poolside		Change rooms and offices		Passageways	
	9 h (a)	24 h (b)	9 h (a)	24 h (b)	9 h (a)	24 h (b)
N	26	40	15	23	3	5
N <LOD	0	0	7	2	1	0
Mean \pm SD	85 \pm 50	52 \pm 30	11 \pm 12	8 \pm 7	34 \pm 29	25 \pm 9
Median	65	46	4	5	50	20
GM	70	43	5	6	14	24
Min-Max	21-182	12-127	1-34	1-29	1-52	18-36
POOL 1						
	Poolside		Change rooms and offices		Passageways	
	9 h (a)	24 h (b)	9 h (a)	24 h (b)	9 h (a)	24 h (b)
N	9	15	3	5	3	5
N <LOD	0	0	1	0	1	0
Mean \pm SD	124 \pm 41	81 \pm 24	14 \pm 11	7 \pm 3	34 \pm 29	25 \pm 9
Median	128	78	18	6	50	20
GM	118	77	7	6	14	24
Min-Max	66-182	39-127	1-22	3-10	1-52	18-36
POOL 2						
	Poolside		Change rooms and offices		Passageways	
	9 h (a)	24 h (b)	9 h (a)	24 h (b)	9 h (a)	24 h (b)
N	9	9	6	6	0	0
N <LOD	0	0	3	0	-	-
Mean \pm SD	35 \pm 15	25 \pm 10	5 \pm 6	5 \pm 1	-	-
Median	32	23	2	5	-	-
GM	33	23	3	5	-	-
Min-Max	21-62	12-39	1-14	4-7	-	-
POOL 3						
	Poolside		Change rooms and offices		Passageways	
	9 h (a)	24 h (b)	9 h (a)	24 h (b)	9 h (a)	24 h (b)
N	4	8	3	6	0	0
N <LOD	0	0	0	0	-	-
Mean \pm SD	132 \pm 11	56 \pm 14	29 \pm 4	18 \pm 8	-	-
Median	130	53	27	16	-	-
GM	131	55	29	17	-	-
Min-Max	120-147	39-76	26-34	11-29	-	-
POOL 4						
	Poolside		Change rooms and offices		Passageways	
	9 h (a)	24 h (b)	9 h (a)	24 h (b)	9 h (a)	24 h (b)
N	4	8	3	6	0	0
N <LOD	0	0	3	2	-	-
Mean \pm SD	61 \pm 4	26 \pm 12	-	4 \pm 4	-	-
Median	63	26	-	3	-	-
GM	61	24	-	2	-	-
Min-Max	55-64	14-40	-	1-10	-	-

(a) Sampling conducted for 9 h in the presence of bathers; (b) Sampling conducted for 24 h in the presence and absence of bathers.

Chloroform concentration detected in environmental samples are summarized in **Table 2**, where the poolside, change room, office and passageway data is presented separately. The table also shows 9-h and 24-h sampling data separately. The sampling site and bathing complex significantly affected chloroform concentrations when the pools were open and over 24 h.

For 9-h sampling, the model explained 76% of the variance, with bathing complex explaining 31% and sampling site 45%, whereas for 24-h sampling the corresponding percentages were 70%, 28% and 42%. Twenty-four-hour values were less than those measured when the pools were open, especially at the poolside, indicating that movement of the water increased airborne

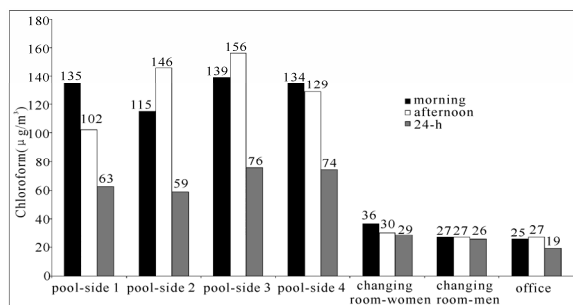


Figure 2. Concentrations of chloroform in morning, afternoon and 24-h environmental samples at pool 3.

chloroform.

Confirming this, **Figure 2** shows chloroform concentrations found in environmental samples at pool 3: sampling when the pool was open in the morning and afternoon gave values much higher than 24-h data at the poolside, whereas those obtained in changing rooms and offices did not vary.

Chloroform concentrations measured at the poolside when the pool was in use showed a statistically significant correlation ($p < 0.0001$) with chloroform concentrations in the water and with the number of pool users per day (N). Multiple regression analysis showed that 74% of the variance was explained according to the following Equation:

$$\text{CHCl}_3 \text{ air } (\mu\text{g}/\text{m}^3) = -101.6 + 1.70 \text{ CHCl}_3 \text{ water } (\mu\text{g}/\text{l}) + 0.57 \text{ N}$$

Temperature did not contribute significantly to the regression.

Chloroform concentrations in personal air samples in the three bathing complexes where they were obtained are summarized in **Table 3**. As expected, they were lower than at the poolside because these personnel did not spend the whole shift beside the pools but also spent time in offices etc. where airborne concentrations of the contaminant were often less.

Table 3. Descriptive statistics of concentrations of chloroform ($\mu\text{g}/\text{m}^3$) detected in personal air samples.

	TOTAL DATA	POOL 1	POOL 3	POOL 4
N	17	8	6	3
N<LOD	0	0	0	0
Mean \pm SD	68 \pm 35	89 \pm 35	61 \pm 17	25 \pm 10
Median	61	95	61	20
GM	58	82	59	23
Min-Max	18-138	37-138	34-84	18-36

Table 4. Descriptive statistics of concentrations di bromodichloromethane (BDCM) and dibromochloromethane (DBCM) ($\mu\text{g}/\text{m}^3$) detected in poolside air samples of the two pools in which at least 50% of the data was detectable.

	POOL 2		POOL 4	
	BDCM	DBCM	BDCM	DBCM
N	9	9	4	4
N<LOD	2	3	0	4
Mean \pm SD	16 \pm 10	8 \pm 6	10 \pm 3	-
Median	18	8	9	-
GM	10	5	9	-
Min-Max	1-27	1-17	7-13	-

With regard to airborne concentrations of brominated compounds, bromoform was never detected whereas bromodichloromethane (BDCM) and dibromochloromethane (DBCM) were only detectable in poolside samples of pools 2 and 4, where significant concentrations of the same contaminants were also found in the water (**Table 4**). The amount of data was therefore insufficient for multiple regression analysis between airborne and water concentrations. However, it can be said that the chemophysical characteristics of contaminants strongly affect dispersal dynamics. In other words, for a given water concentration, chloroform passes much more readily into the vapour phase (vapour pressure 21.2 kPa at 20°C) than bromodichloromethane (vapour pressure 6.6 kPa at 20°C) and other brominated compounds that have even lower vapour pressures.

Concentrations of BDCM, DBCM and bromoform were undetectable in all urine samples. Descriptive statistics of chloroform concentrations detected in urine before and after exposure are summarized in **Table 5** which also shows differences in concentration (delta) between the two times. The data is separated for persons carrying on activity in the water, for whom inhalation, ingestion and cutaneous absorption are likely, and personnel working out of the water, for whom only respiratory exposure is likely.

A quick look at **Table 5** shows that delta after/before was higher for subjects carrying on activity in the water, confirming the hypothesis of skin and digestive absorption. In **Table 6**, the difference in concentrations after/before exposure is shown in a differentiated manner depending on the type of activity and/or the pool frequented. Despite the small number of data items available the table shows that for a given activity, delta after/before depended on the bathing complex and therefore on water and airborne concentrations of this contaminant.

Table 5. Descriptive statistics of concentrations of chloroform ($\mu\text{g/l}$) detected in urine.

	Type of exposure (a)	Start of exposure (before)	End of exposure (after)	Delta after/before
N	In water	35	35	35
	Out of water	6	6	6
N<LOD	In water	11	0	-
	Out of water	1	0	-
Mean \pm SD	In water	0.262 \pm 0.351	0.659 \pm 0.667	0.397 \pm 0.455
	Out of water	0.265 \pm 0.236	0.563 \pm 0.627	0.297 \pm 0.480
Median	In water	0.100	0.420	0.208
	Out of water	0.189	0.329	0.091
GM	In water	0.123	0.404	-
	Out of water	0.165	0.342	0.141
Min-Max	In water	0.025-1.676	0.025-3.327	0-2.227
	Out of water	0.025-0.615	0.100-1.746	0.052-1.271

(a) Exposure in water: swimmers, competitive swimmers, water gym participants, instructors; Exposure out of water: lifeguards and attendants.

Table 6. Differences between concentrations at the end and start of exposure ($\mu\text{g/l}$) detected in urine during activity in and out of the water by pool and specific activity.

	N	Mean \pm SD	Median	GM	Min-Max	
Competitive swimming (a)	4	0.065 \pm 0.047	0.074	-	0-0.113	
Total swimmers	15	0.506 \pm 0.585	0.250	-	0-2.227	
Pool 1	9	0.768 \pm 0.635	0.672	0.490	0.025-2.227	
	Pool 4	6	0.112 \pm 0.077	0.107	-	0-0.207
Water gym course	12	0.311 \pm 0.326	0.204	-	0-1.301	
	Pool 3	8	0.231 \pm 0.154	0.186	-	0-0.426
Pool 4	4	0.472 \pm 0.554	0.223	0.309	0.142-1.301	
	4	0.580 \pm 0.225	0.511	0.550	0.408-0.887	
Instructor	Pool 1	3	0.637 \pm 0.238	0.609	0.607	0.414-0.887
	Pool 3	1	-	-	-	0.408
Lifeguard/attendant	Pool 1	3	0.529 \pm 0.645	0.209	0.305	0.107-1.271
	Pool 3	2	-	-	-	0.052-0.071
	Pool 4	1	-	-	-	0.075

(a) only pool 3.

Table 7. Absorbed chloroform (μg) estimated on the basis of concentrations in water and in poolside air while the pool was open.

	N	Mean \pm SD	Median	GM	Min-Max
Total doses	41	358.9 \pm 301.9	173.6	267.2	109.4-1248.4
Doses ingested	35	1.4 \pm 1.8	0.35	0.66	0.12-5.82
Transcutaneous doses	35	194.6 \pm 217.5	85.5	108.4	25.4-844.0
Respiratory doses	41	191.5 \pm 132.3	160.1	158.7	89.9-716.7
% ingested dose	35	0.3 \pm 0.2	0.2	0.2	0.1-0.7
% cutaneous dose	35	42.5 \pm 17.1	45.7	39.2	17.1-78.6
% respiratory dose	35	57.2 \pm 17.2	54.1	54.3	17.2-77.9

Table 7 shows estimated absorbed doses of chloroform and the percentages of the total constituted by digestive, skin and inhalatory doses. Our estimates produced absorption values up to about 1.25 mg for swimmers or instructors in the water for long periods (2-3 h). For those carrying on activity in the water, the ingested percentage of the total dose was negligible compared to respiratory and skin doses that were 57% and 43%, respectively.

Estimates of absorbed dose were analysed by linear regression model with chloroform delta after/before exposure and urinary concentrations of chloroform at the

end of exposure. The results are shown in **Figures 3** and **4**. Both regressions were highly significant and the variance explained by the model was 53% and 71%. The intercept with the ordinate was very close to zero in **Figure 3**, as expected, and at 0.084 mg/l in **Figure 4**. In the latter case, the intercept should indicate the urinary concentration of chloroform not due to time spent in the pool (pre-exposure value) and indeed it was close to the median for urinary chloroform at the beginning of exposure for subjects carrying on activity in the water, shown in **Table 5** (this data was also the most numerous). The better correlation obtained in **Figure 4** between

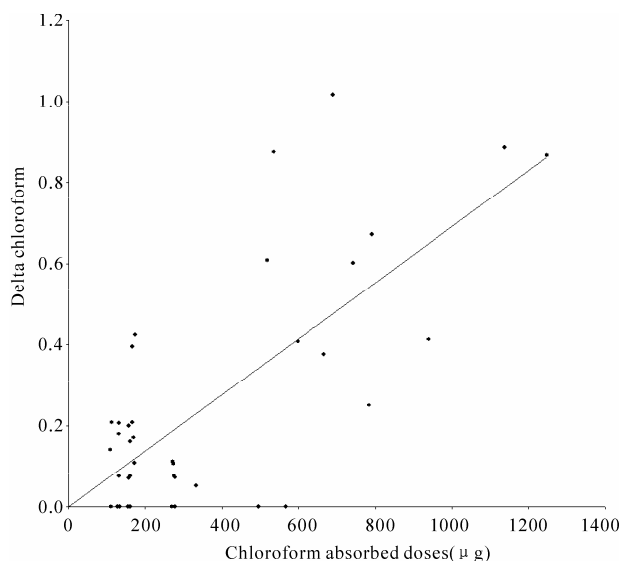


Figure 3. Linear regression analysis between estimated absorbed doses and delta chloroform after/before exposure ($y = 0.00069x + 0.0004$, $r^2 = 0.534$, significant $p < 0.0001$).

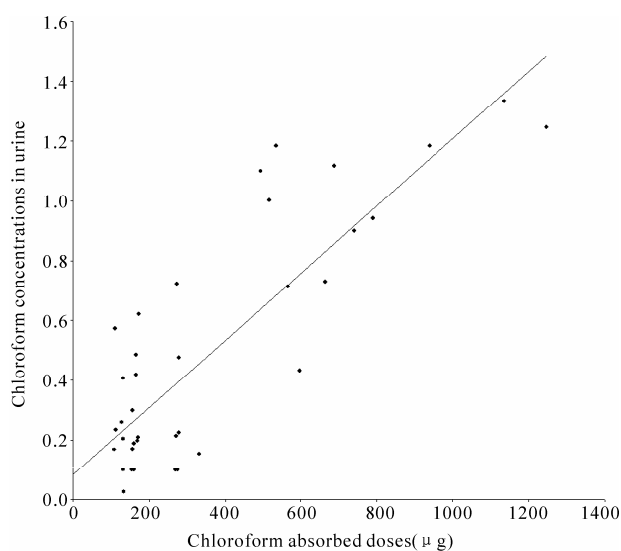


Figure 4. Linear regression analysis between estimated absorbed doses and chloroform concentrations in urine at the end of exposure ($y = 0.0011x + 0.084$, $r^2 = 0.706$, significant $p < 0.0001$).

estimated absorbed dose of chloroform and urinary excretion of chloroform at the end of exposure with respect to the delta for chloroform can probably be ascribed to the further factor of variability due in the second case to the pre-exposure value of chloroform. The slope of the two regressions was very low, probably due to the fact that chloroform eliminated in urine at the end of exposure is only a limited part of the total absorbed, whereas a greater fraction is presumably eliminated by exhalation and stored in body fat.

4. DISCUSSION

Concentrations of trihalomethanes reported in pool water vary from study to study but the results are not dissimilar to ours: Sandel [12] examined data from 114 home pools in the USA, obtaining a mean concentration of chloroform of 67.1 µg/l and a maximum of 313 µg/l. Most other available data on trihalomethanes in pool water is summarized in **Table 8**. In the pools monitored by us, formation of brominated trihalomethanes seemed prevalently associated with the use of sodium hypochlorite for water treatment. Ignoring bromide ions in the water used to fill these pools (town water in the case of pools 3 and 4), the presence of these compounds is presumably due to bromide impurities in the treatment reagents. This evidence makes it important to use only high purity reagents to treat town water.

Water-air transport of trihalomethanes depends on a number of factors that include concentrations in pool water, temperature and water disturbance and splashing by bathers. In our study, the concentration of chloroform detected at the poolside showed a good correlation with chloroform concentrations in pool water and with the number of swimmers present. Air and water temperatures were excluded from the regression model because they did not seem to have a significant effect on environmental concentrations of chloroform. Trihalomethane concentrations at different levels in the air above the pool should also depend on factors such as ventilation, size of pool building and air circulation. Most of the data available on concentrations of trihalomethanes in air above the pools is summarized in **Table 9**, which shows that measurements taken 20 cm above the water were on average 1.8 times higher than those taken 150 cm above the water.

In our study, concentrations of airborne trihalomethanes depended on where the measurements were taken (poolside, change rooms and offices, corridors) as found in other studies: Fantuzzi *et al.* [34] studied total trihalomethane concentrations in five Italian indoor pools, finding mean concentrations in poolside air of $58.0 \pm 22.1 \mu\text{g}/\text{m}^3$ and $26.1 \pm 24.3 \mu\text{g}/\text{m}^3$ at the reception.

Absorption of trihalomethanes during time spent at the pool was investigated by comparing urinary excretion of chloroform before and after exposure. Levels observed at the start of exposure were slightly less than detected in the general population. A study conducted in Italy in 1994 [39] found median concentrations of 194 ng/l in the rural population (115 subjects) and 490 ng/l in the urban population (87 subjects). Most previous studies on absorption of trihalomethanes at swimming pools measured blood concentrations of chloroform or those in alveolar air. Strähle *et al.* [35] compared concentrations

of trihalomethanes in blood of swimmers with those in pool water and air. The results, summarized in **Table 10**, demonstrate that inhalation is probably the main route of absorption of volatile components, since concentrations in water of indoor pools are greater than those of outdoor pools, while concentrations in ambient air are higher indoors, as are blood concentrations. Good ventilation of pool premises should therefore significantly reduce exposure. Erdinger *et al.* [29] confirmed that exposure is prevalently respiratory, showing a ratio of 3:1 with re-

spect to skin absorption. Aggazzotti *et al.* [14-16,36] showed that exposure in chlorinated pools can cause an increase in trihalomethane concentrations in plasma and alveolar air, but the latter declines soon after leaving the pool. Plasma concentrations of chloroform were detectable in 100% of the 127 samples analyzed, showing a mean concentration of 1.06 µg/l, whereas BDCM, detectable in only 25 samples, showed a mean of 0.14 µg/l and DBCM, detectable in only 17 samples, showed a mean of 0.1 µg/l.

Table 8. Concentrations of trihalomethanes in pool water (µg/l).

country	Chloroform		BDCM		DBCM		Bromoform		Type of pool	Ref.
	Mean	Range	Mean	Range	Mean	Range	Mean	Range		
Poland		35.9-99.7 19-94		2.3-14.7		0.2-0.8		0.2-203.2	Indoor	[13] [14]
Italy	93.7 33.7 37.9	9-179 25-43	2.3	1.8-2.8	0.8	0.5-10	0.1	0.1	Indoor	[15] [16] [17]
USA		4-402 3-580		1-72 1-90		<0.1-8 0.3-30		<0.1-1 <0.1-60	Outdoor Indoor	[18] [19]
	14.6 43 198	2.4-29.8 14.6-111 43-980	22.6	0.1-150	10.9	0.1-140	1.8	0.1-88	Indoor	[20]
Germany		0.5-23.6 3.6-82.1		1.9-16.5 1.6-17.3		<0.1-3.4 <0.1-15.1		<0.1-3.3 <0.1-4.0	Indoor Outdoor	[21] [22]
	94.9 80.7 74.9	40.6-117.5	4.8 8.9 11.0	4.2-5.4	1.8 1.5 3.0	0.78-2.6	<0.1 0.23		Indoor Indoor Outdoor	[23] [24] [25]
		3-27.8 1.8-28 8-11							Indoor Indoor Indoor	[11] [25]
Germany	14 30 3.8	0.51-69 0.69-114 6.4 max	2.5 4.5	0.12-15 0.27-25	0.59 1.1	0.03-4.9 0.04-8.8	0.16 0.28	<0.03-8.1 <0.03-3.4	Indoor Outdoor	[26,27]
		7.1-24.8 145-151							Indoor Indoor	[28] [29] [30]
Denmark		<2-62.3	2.9	<1-11.4					Indoor	[31]
Hungary	11.4								Indoor	[32]
UK	121.1	45-212	8.3	2.5-23	2.7	0.67-7	0.9	0.67-2	Indoor	[32]

Table 9. Concentrations of trihalomethanes in air above the pool surface (µg/m³).

country	Chloroform		BDCM		DBCM		Bromoform		Type of pool	Ref.
	Mean	Range	Mean	Range	Mean	Range	Mean	Range		
Italy	214 140 169	66-650 49-280 35-195	19.5 17.4 20	5-100 2-58 16-24	6.6 13.3 11.4	0.1-14 4-30 9-14	0.2 0.2 0.2		Indoor (a)	[15] [14] [16]
Canada		597-1630							Indoor	[33]
	65 36 5.6 2.3		9.2 5.6 0.21		3.8 1.2				Indoor (a) Indoor (b) Outdoor (a) Outdoor (a)	[11]
Germany	3.3 1.2 39 30	0.33-9.7 0.36-2.2 5.6-206 1.7-136	0.4 0.1 4.9 4.1	0.08-2.0 0.03-0.16 0.85-16 0.23-13	0.1 0.05 0.9 0.8	0.02-0.5 0.03-0.08 0.05-3.2 0.05-2.9	<0.03 <0.03 0.1 0.08	<0.03-3.0 <0.03-0.7	Outdoor (a) Outdoor (b) Indoor (a) Indoor (a)	[26,27]
USA		<0.1-1 <0.1-260		<0.1 <0.1-10		<0.1 <0.1-5		<0.1 <0.1-14	Indoor (c) Outdoor (c)	[18]

(a) 20 cm above water surface; (b) 150 cm above water surface; (c) 200 cm above water surface.

Table 10. Comparison of concentrations of trihalomethanes (THM) in blood of swimmers after 1 h of exercise, in pool water and in ambient air of indoor and outdoor pools [35].

	THM (mean - range)	
	indoor pools	outdoor pools
Blood of swimmers ($\mu\text{g/l}$)	0.48(0.23-0.88)	0.11(<0.06-0.21)
Pool water ($\mu\text{g/l}$)	19.6(4.5-45.8)	73.1(3.2-146)
air 20 cm above water surface ($\mu\text{g/m}^3$)	93.6(23.9-179.9)	8.2(2.1-13.9)
air 150 cm above water surface ($\mu\text{g/m}^3$)	61.6(13.4-147.1)	2.5(<0.7-4.7)

Absorptions estimated by us confirmed that the quantity of chloroform taken up by inhalation was a major portion of the total dose for bathers and instructors, being 57% compared to 43% absorbed through the skin. These estimates are based on the results of other studies in the literature, from which we obtained lung retention and skin penetration. They are undoubtedly associated with errors because respiratory dose is greatly affected by lung ventilation which was assumed by us without any precise indications about the real volume of air inhaled and without considering differences between subjects due to physical exertion and age. As far as we are aware, no similar estimates have been reported in the literature and therefore our data forms an excellent basis for further research, including epidemiological studies. The data should be implemented in this way to make it more representative. The good correlation observed with urinary concentrations at the end of exposure and with delta after/before exposure confirms that even if our estimates were not quantitatively exact, they are highly indicative of exposure.

5. CONCLUSIONS

This study shows that concentration of trihalomethanes in pool water vary as a consequence of the type of disinfectants used and of the impurities in the treatment reagents. Trihalomethanes are lost from the surface of the water and are found in the air above the pool. Water-air transport depends on a number of factors that include concentrations in pool water, temperature and water disturbance by bathers. The sampling site and bathing complex significantly affect air concentrations. Absorption of trihalomethanes for workers and swimmers, during time spent at the pool, evaluated by urinary excretion of the same compounds before and after exposure, is higher for subjects carrying on activity in the water, confirming the importance of skin and digestive absorption, although inhalation is on average the major portion of the total absorbed dose.

The results show that even “healthy” places like pools can pose chemical agent management problems that are far from simple. Since the aim of water treatment is to control biological risk for users, it is senseless to categorically condemn swimming pools or water chlorination. “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” [1]. It is therefore to be hoped that more attention be paid to the design and management of pools, as well as to correct behaviour, in order to improve our living and occupational environments.

This study considers all the aspects related to the trihalomethanes exposure in indoor swimming pool disinfected with chlorine and derivatives, and the results can be generalized and applied in similar situations.

REFERENCES

- [1] WHO (2006) Guidelines for safe recreational water environments. Swimming pools and similar environments, *World Health Organization*, **2**.
- [2] Istituto Superiore di Sanità, (2007) Piscine ad uso natatorio: aspetti igienico-sanitari e gestionali per l'applicazione della nuova normativa. Rapporti ISTISAN 07/11.
- [3] ISPESL (2005) Quaderni per la salute e la sicurezza “Le piscine”. Osservatorio Nazionale Epidemiologico sugli ambienti di vita. Istituto Superiore Prevenzione e Sicurezza sul Lavoro.
- [4] Gunkel, K. and Jessen, H-J. (1988) The problem of urea in bathing water. *Zeitschrift für die Gesamte Hygiene*, **34**, 248-250.
- [5] Erdinger, L., Kirsch, F. and Sonntag, H-G, (1997) Potassium as an indicator of anthropogenic contamination of swimming pool water. *Zentralblatt für Hygiene und Umweltmedizin*, **200(4)**, 297-308.
- [6] WHO (2006) Guidelines for Drinking-water Quality, first addendum to third edition. Recommendations, *World Health Organization*, **1**.
- [7] Evans, O., Cantú, R., Bahymer, T.D., Kryak, D.D. and Dufour, A.P. (2001) A pilot study to determine the water volume ingested by recreational swimmers. Paper presented to 2001 Annual Meeting of the Society for Risk Analysis, Seattle, Washington, 2-5 December 2001.
- [8] Meek, M.E., Beauchamp, R., Long, G., Moir, D., Turner, L. and Walker, M. (2002) Chloroform: exposure estimation, hazard characterization, and exposure-response analysis, *J Toxicol Environ Health B Crit Rev*, **5(3)**, 283-334.
- [9] International Agency for Research on Cancer (1999) IARC Monographs on the evaluation of carcinogenic risk to humans. Some chemicals that cause tumors of the kidney or urinary bladder in rodents and some other sub-

- stances, *IARC Monographs*, **73**.
- [10] American Conference of Governmental Industrial Hygienists (2007). Threshold limit values for chemical substances and physical agents and biological exposure indices, *ACGIH. Cincinnati OH, USA*.
- [11] Jovanovic, S., Wallner, T. and Gabrio, T. (1995) Final report on the research project "Presence of haloforms in pool water, air and in swimmers and lifeguards in outdoor and indoor pools". Stuttgart, Landesgesundheitsamt Baden-Württemberg.
- [12] Sandel, B.B. (1990) Disinfection by-products in swimming pools and spas. Olin Corporation Research Center (Report CNHC-RR-90-154) (available from Arch Chemical, Charleston).
- [13] Biziuk, M., Czerwinski, J. and Kozlowski, E. (1993) Identification and determination of organohalogen compounds in swimming pool water, *Int J Environ Anal Chem*, **46**, 109-115.
- [14] Aggazzotti, G., Fantuzzi, G., Righi, E., Tartoni, P.L., Casinadri, T. and Predieri, G. (1993) Chloroform in alveolar air of individuals attending indoor swimming pools, *Arch Environ Health*, **48**, 250-254.
- [15] Aggazzotti, G., Fantuzzi, G., Righi, E. and Predieri, G. (1995) Environmental and biological monitoring of chloroform in indoor swimming pools, *J Chromatogr A*, **710(1)**, 181-190.
- [16] Aggazzotti, G., Fantuzzi, G., Righi, E. and Predieri, G. (1998) Blood and breath analyses as biological indicators of exposure to trihalomethanes in indoor swimming pools, *Sci Total Environ*, **217 (1-2)**, 155-163.
- [17] Copaken, J. (1990) Trihalomethanes: Is swimming pool water hazardous? In: Jolley RL, Condie LW, Johnson.
- [18] Armstrong, D.W. and Golden, T. (1986) Determination of distribution and concentration of trihalomethanes in aquatic recreational and therapeutic facilities by electron-capture GC, LC-GC, **4**, 652-655.
- [19] Eichelsdörfer, D., Jandik, J. and Weil, L. (1981) Formation and occurrence of organic halogenated compounds in swimming pool water. *A.B. Archiv des Badewesens*, **34**, 167-172.
- [20] Lahl, U., Bätjer, K., Duszeln, J.V., Gabel, B., Stachel, B. and Thiemann, W. (1981) Distribution and balance of volatile halogenated hydrocarbons in the water and air of covered swimming pools using chlorine for water disinfection, *Water Research*, **15**, 803-814.
- [21] Ewers, H., Hajimiragha, H., Fischer, U., Böttger, A. and Ante, R. (1987) Organic halogenated compounds in swimming pool waters, *Forum Städte-Hygiene*, **38**, 77-79.
- [22] Puchert, W., Prösch, J., Köppe, F-G. and Wagner, H. (1989) Occurrence of volatile halogenated hydrocarbons in bathing water. *Acta Hydrochimica et Hydrobiologica*, **17**, 201-205.
- [23] Puchert, W. (1994) Determination of volatile halogenated hydrocarbons in different environmental compartments as basis for the estimation of a possible pollution in West Pommern. Dissertation, Bremen, University of Bremen.
- [24] Cammann, K., Hübner, K. (1995) Trihalomethane concentrations in swimmers' and bath attendants' blood and urine after swimming or working in indoor swimming pools. *Arch Environ Health*, **50(1)**, 61-65.
- [25] Schössner, H., Koch, A. (1995) Investigations of trihalogenmethane-concentrations in swimming pool water. *Forum Städte-Hygiene*, **46**, 354-357.
- [26] Stottmeister, E. (1998) Disinfection by-products in German swimming pool waters. Paper Presented to the 2nd International Conference on Pool Water Quality and Treatment, 4 March 1998, School of Water Sciences, Cranfield University, Cranfield, UK.
- [27] Stottmeister, E. (1999) Occurrence of disinfection by-products in swimming pool waters. *Umweltmedizinischer Informationsdienst*, **2**, 21-29.
- [28] Erdinger, L., Kirsch, F., Hoppner, A., Sonntag, H.G. (1997) Haloforms in hot spring pools. *Zentralblatt für Hygiene und Umweltmedizin*, **200**, 309-317.
- [29] Erdinger, L., Kuhn, K.P., Kirsch, F., Feldhues, R., Frobel, T., Nohynek, B., Gabrio, T. (2004) Pathways of trihalomethane uptake in swimming pools. *International Journal of Hygiene Environmental Health*, **207(6)**, 1-5.
- [30] Kaas, P. and Rudiengaard, P. (1987) Toxicologic and epidemiologic aspects of organochlorine compounds in bathing water. Paper Presented to the 3rd Symposium on Problems of Swimming Pool Water Hygiene, Reinhardbrunn.
- [31] Borsányi, M. (1998) THMs in Hungarian swimming pool waters. Budapest, National Institute of Environmental Health, Department of Water Hygiene (unpublished).
- [32] Chu, H. and Nieuwenhuijsen, M.J. (2002) Distribution and determinants of trihalomethane concentrations in indoor swimming pools. *Journal of Occupational Environmental Medicine*, **59(4)**, 243-247.
- [33] Lévesque, B., Ayotte, P., LeBlanc, A., Dewailly, E., Prud'Homme, D., Lavoie, R., Allaire, S., Levallois, P. (1994) Evaluation of dermal and respiratory chloroform exposure in humans. *Environmental Health Perspectives*, **102(12)**, 1082-1087.
- [34] Fantuzzi, G., Righi, E., Predieri, G., Ceppelli, G., Gobba, F., Aggazzotti, G. (2001) Occupational exposure to trihalomethanes in indoor swimming pools. *Science of Total Environment*, **264(3)**, 257-265.
- [35] Strähle, J., Sacre, C., Schwenk, M., Jovanovic, S., Gabrio, T., Lustig, B. (2000) [Risk assessment of exposure of swimmers to disinfection by-products formed in swimming pool water treatment. Final report on the research project of DVGW 10/95, Landesgesundheitsamt Baden-Württemberg, Stuttgart.
- [36] Aggazzotti, G., Fantuzzi, G., Tartoni, P.L., Predieri, G. (1990) Plasma chloroform concentration in swimmers using indoor swimming pools. *Archives of Environmental Health*, **45A(3)**, 175-179.
- [37] Kuo, H.W., Chiang, T.F., Lo, I.I., Lai, J.S., Chan, C.C., Wang, J.D. (1998). Estimates of cancer risk from chloroform exposure during showering in Taiwan. *Science of Total Environment*, **218(1)**, 1-7.
- [38] Du Bois, D. and Du Bois, E. (1916). A formula to estimate the approximate surface if height and weight be known. *Clinical Calorimetry*, tenth paper. *Archives of International Medicine*, 863-871.
- [39] Brugnone, F., Perbellini, L., Giuliani, C., Cerpelloni, M., Soave, C. (1994) Blood and urine concentrations of chemical pollutants in the general population. *Med Lav*. **85(5)**, 370-389.