Investigations on the concentrations of volatile halogenated hydrocarbons in swimming pool water, surrounding air and bath attendants' blood using GC methods

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Abstract

GC methods were established to investigate the correlations between volatile halogenated hydrocarbons (VHH) in indoor swimming pool water, ambient air and bath attendants' blood and a survey over some of the results is given.

Introduction

The method of choice for disinfection of swimming pool water is still the application of chlorine, hypochlorite or chlorine dioxide. However, since 1974 it has been known that haloforms and other chlorinated products are formed by the reaction of chlorine with humic and fulvic acids in water[1,2]. Also it was described that the presence of bromide in water leads to corresponding brominated and mixed halogenated products[3].

Our interest was focused on volatile halogenated hydrocarbons (VHH), especially four trihalomethanes (trichloro-, bromodichloro-, dibromochloro and tribromomethane) and four commonly used solvents (tetrachloromethane, 1,1,1-trichloroethane, trichloro- and tetrachloroethene).

First water and air analyses of three indoor pools in a small city in Hessia were performed during complete weeks or whole days to establish correlations between water and air values. Then the blood of bath attendants was drawn both before and after their daily shifts to see if the VHH concentrations in blood were influenced by the duration of exposure to the pool area. So far trichloromethane concentrations in swimmers' blood ranging from 0.10-2.99 μg/L and 50 μg/L can be found in literature[4,5].

Experimental

I. Water analysis

2 mL were taken from the pool at a depth of 10 cm and directly delivered into HS-vials. To degrade the remaining chlorine in the water 0.4 g sodium thiosulfate was added to each vial before sampling. The vials were capped with PTFE-coated butylgumsepta and stored at -20°C in a freezer until headspace (HS) analysis. The temp. in the HS sampler (HP 13895 A) was 60°C, the equil. time 5 h, the vial press. 1 bar and the sample loop volume 1 ml (split 15:1). The GC was a HP 5890 series II and the column a SE 52 (50 m, 0.32 mm ID, 0.25 μm film thickn.). The GC column temperature was 11 min 40°C, 10°C/min to 80°C, 6 min 80°C. The carrier gas was helium, the makeup gas argon/methane (90:10) and the column flow 1 mL/min. Detection was accomplished using a ^{63}Ni-ECD (HP 19233 B). In calibration purposes, seven standards (0.30-200 μg/L Trichloromethane and 0.03-20 μg/L other VHH) were prepared in distilled water. SD values depended on the concentration and ranged from about 3 % for >100 ppb up to more

than 10 % below 1 ppb near the quantification limits (LOQ see also table 1).

II. Air analysis

Either Tenax TA cartridges for short sampling periods (a few minutes) or charcoal tubes for long sampling periods (several hours) were used for enrichment. The TA cartridges required subsequent thermal desorption; whereas the charcoal tubes involved solvent elution. During the blood investigation long-time sampling on charcoal was preferred to get averaged values representing the entire human dwell time near the pool. A sampling pump (AMA PN 7300) with a variable flow-rate was placed by the pool at a height of 1.2 m. The sampling rate was 35 mL/min and, thus, the sample volume ≥ 12 L. For analysis, each charcoal tube was emptied into immediately septum-capped vials, and under ice-cooling, 1.6 mL of a 1:1 mixture of n-pentane/toluene were injected slowly. After 15 min in an ultrasonic-bath and 30 min of resting a 1 μL-aliquot was injected into the GC (split 20:1). The GC column temperature was 8 min 40°C, 10°C/min to 55°C, 20°C/min to 80°C, 3 min 80°C, 40°C/min to 220°C, 2 min 220°C. Nitrogen was used as carrier and makeup gas, the column flow was 3.5 mL/min and the detector was an ECD. External calibration was performed by using a commercial VHH-standard (Promochem, FRG) diluted in n-pentane.

III. Blood analysis

The blood samples were collected in 10 mL vacutainers which contained potassium-EDTA as an anticoagulent and later transferred to HS-vials in 2 mL portions with a multipipette. The blood samples were then treated the same way as the water samples, with the exception that a HS-temperature of 40°C was used. The external standards were made with donorblood (free of VHH) to which, for example, 1 μL of a VHH-standard in water was added with a syringe.

Results

The most important and frequent compound among the VHH was undoubtedly trichloromethane. Its concentration in the water reached up greater than 150 μg/L (ppb). Also of importance were the three brominated trihalomethanes (THM), while the other VHH usually were far below 0.1 ppb and often very close to the limit of quantification or even detection. Table 1 shows the concentration ranges of the four THM during the most recent sampling sessions as well as the limits of quantification.

sample type	$CHCl_3$			$CHBrCl_2$			$CHBr_2Cl$			$CHBr_3$		
	bath I	bath II	bath III	bath I	bath II	bath III	bath I	bath II	bath III	bath I	bath II	bath III
fresh water	0.04-0.10	0.21-0.62	0.31-1.64	<0.05	0.07-0.14	<0.05-0.74	0.07-0.83	0.47-1.26	0.06-0.92	0.33-0.66	1.92-4.01	0.03-0.49
pool water	34.71-56.84	14.16*-79.73	56.17-134.44	4.98-13.95	1.17-2.98	2.74-5.14	4.06-9.76	0.68-1.28	0.15-0.31	0.69-2.32	0.24-0.53	<0.10-0.14
ambient air	6.69-16.78	1.77-63.52	78.73-108.06	1.16-2.17	n.d.-1.73	2.84-5.75	1.16-2.17	n.d.-1.73	n.d.-1.81	0.28-0.54	n.d.-0.81	n.d.-0.59
blood	<0.05-2.45	0.06-0.57	0.20-2.83	n.d.-0.58	n.d.-0.05	n.d.-0.21	n.d.-0.53	n.d.-0.12	n.d.-0.18	n.d.-0.52	n.d.-0.24	n.d.-0.44
LOQ water		0.04			0.05			0.07			0.10	
blood		0.05			0.05			0.07			0.12	
air	depends on the sample volume											
n.d.:not detected	*:low values in the beginning after several weeks the bath was closed											

Table 1: Concentration ranges of THM and limits of quantification (water and blood in μg/L; air in ng/L)

Usually the ranges were not a consequence of any week- or day-trend, but more likely the normal fluctuation during a certain period. These variations might correlate with the number of swimmers in the pool or the chlorine dosage which also variied depending on the number of visitors.

The blood samples of bath attendants registered only trichloromethane concentrations high enough to measure alterations during the stay in the pool. Other substances usually were close to or even below the limit of quantification. Figure 1 shows the blood concentrations of trichloromethane before and after the daily shifts. Table 2 includes the water and air concentrations as well. The given air concentrations are averaged values evaluated from long-time samplings.

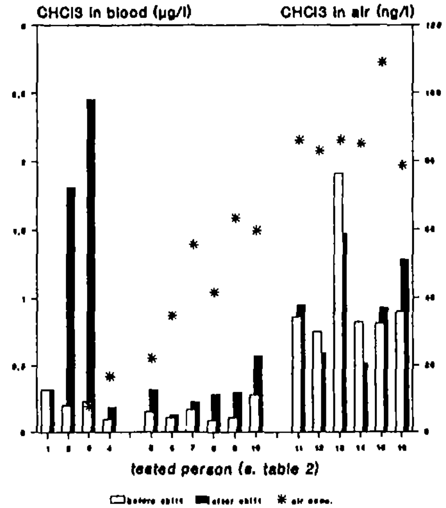

Figure 1: Trichloromethane concentrations in bath attendants' blood before and after their daily shifts and corresponding air levels

No.	test person, bath, duration of expos.	blood conc.(µg/L) before shift	blood conc.(µg/L) after shift	water conc. range (µg/L)	air conc.(ng/L) pool area	air conc.(ng/L) pool att.'s room
1	bath attendant 1, bath I, Nov.11, 8h	0.32	0.32	47.59-51.13	-	-
2	bath attendant 1, bath I, Nov.14, 6h	0.20	1.81	48.71-48.96	-	-
3	bath attendant 2, bath I, Nov.13, 7h	0.23	2.45*	45.88-46.90	7.77	-
4	bath attendant 3, bath I, Nov.15, 6h	0.10	0.19	39.77-40.90	16.78	-
5	bath attendant 4, bath II, Nov.25, 5h	0.15	0.32	14.16-17.12	22.09	-
6	bath attendant 4, bath II, Nov.27, 5.5h	0.11	0.13	45.43-61.53	34.86	4.71
7	bath attendant 4, bath II, Nov.29, 9h	0.17	0.23	74.99-79.73	55.75	-
8	bath attendant 5, bath II, Nov.26, 13h	0.09	0.29	28.76-36.76	41.81	-
9	bath attendant 5, bath II, Nov.28, 4.5h	0.11	0.30	65.37-77.38	63.52	-
10	bath attendant 5, bath II, Dec.1, 9.25h	0.28	0.57	54.97-65.49	59.65	-
11	bath attendant 6, bath III, Jan.20, 5.2h	0.86	0.95	99.74-125.13	86.11	71.33
12	bath attendant 6, bath III, Jan.22, 5.75h	0.75	0.59	12.18-129.33	83.00	54.90
13	bath attendant 7, bath III, Jan.20, 8h	1.91	1.47	99.74-129.36	86.11	71.33
14	bath attendant 8, bath III, Jan.21, 6.7h	0.82	0.51	92.44-108.54	84.94	58.39
15	bath attendant 8, bath III, Jan.22, 7.75h	0.81	0.93	98.12-134.44	109.06	-
16	bath attendant 8, bath III, Jan.25, 5h	0.90	1.28	90.14-133.19	78.73	49.56

*: high degree of physical activity due to scrubbing the flagstones of the pool

Table 2: Trichloromethane concentrations in swimming pool water, ambient air and bath attendants' blood

Conclusions

As table 1 and 2 show it is difficult to find easy correlations between water, air and blood levels. While the values in water might be dependent on the number of swimmers, their input of organic substances, the resulting chlorine dosage and the bromide-concentration, the air levels will be influenced by room ventilation or the turbulence at the surface of the water (again depending on the number of swimmers). Though the blank values of donorblood (below limit of detection) support the theory that the trichloromethane in the blood is a consequence of working in an indoor swimming pool and though in most cases the levels in blood increased during a bath attendant's working shift, neither the bath attendants' shift duration nor the concentrations of trichloromethane in air were the only decisive parameters. It was found that the air concentration varies from the pool area to the bath attendant's room so the incorporation of THM into the body is dependent on the time a bath attendant spend either in the pool area or in his room. In bath III the bath attendant's room was not completely separated from the pool area, its air concentrations were higher than in other bathes and higher trichloromethane concentrations in blood were found. According to investigations on agonistic swimmers also the differring degree of physical activity might be a factor influencing the uptake of THM[6] (see also test person 3 in table 2). Anyway it can be concluded that already the contact with indoor swimming pool air without any water contact leads to higher trichloromethane concentrations in blood.

The other chlorinated solvents were present in air in concentrations similar to the normal background values[7] which demonstrates that they are not formed during chlorination and do not origin in the water as the THM do.

Finally it should be mentioned that new techniques of disinfection are required to avoid those high concentrations as found here. The discussed recommended value for German pool water which might be valid for the EC as well, is a total of 25 μg/L THM in water which was exceeded in all of the three baths.

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