



Evaluation of health risk caused by chloroform in drinking water

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ABSTRACT

In this paper, the results of cancer risk evaluation for chloroform in tap water at Cracow city (Poland) are presented. Cracow is a large city which is mostly supplied with surface water. The raw water seasonally has a high content of organic matter. Since chlorine is the basic disinfectant, organic compounds react with chlorine which results in the disinfection byproducts formation, such as trihalomethanes, in delivered water. Calculations were made, separately in male and female, for average chloroform concentration in the whole city as well as with respect to the season and supply zone. The study is based on the multipathway method which takes into account three ways in which chloroform contained in the tap water enters the human body (oral ingestion, dermal absorption, and inhalation exposure). The total cancer risk is at the acceptable level (between 10^{-6} and 10^{-5}) because the chloroform concentration in water supply system only incidentally exceeds the maximum allowable concentration regulated by Polish Ministry of Health, i.e. 30 µg/L.

Keywords: Cancer risk; Chloroform; Trihalomethanes; Water supply system; Tap water

1. Introduction

The organic matter contained in natural water ecosystem poses the main threat to human health. Since the law related to drinking water quality protects consumers' health [1], water companies have to apply high-efficient technologies to remove organic compounds contained in the raw water. The last element of the treatment process is disinfection during which chlorine is commonly used because it is cheap, effective, and convenient in usage. However, some part of organic matter contained in water reacts with

chlorine and disinfection byproducts is the result of this chemical reaction. In the group of secondary micropollutants [2,3] essential are trihalomethanes which are probably carcinogen—they are classified as the cancer group B2 by the United States Environmental Protection Agency and the World Health Organization.

Trihalomethanes are formed not only at water treatment plant but also in the distribution subsystem where residual chlorine reacts with organic matter present in water pipes. The process of their formation is not well recognized despite many attempts to model it (the brief chronological review may be found in [4]). The problem of trihalomethanes formation is

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very important due to their potential threat to human health and because of decreasing water demand in the water supply system which causes that time of water delivery to consumers is longer.

The estimation of cancer risk caused by trihalomethanes is an essential problem studied in many papers, e.g. [5–12]. In this study, the cancer risk from trihalomethanes in Polish city Cracow is evaluated. The chloroform is taken into account because it constitutes the largest part of trihalomethanes in the Cracow Water Supply System (other trihalomethanes appear in trace amounts). The main exposure of the human body to the harmful effects of chloroform is related to the respiratory system, the digestive system, and skin. It is assumed that up to 50% of chloroform daily dose absorbed by citizens comes from the water. The chloroform absorption rate depends on exposure paths, the medium (water or air), and the age and health of human. Chloroform is conveyed by the blood to all body parts, and reaches the highest concentration in the lipid-rich tissues (removal from which is very slow).

Thus, the risk is calculated for three exposure pathways (oral ingestion, dermal absorption, and inhalation exposure), separately in male and female, including the seasonal variation on trihalomethanes concentration in tap water and the distance from water treatment plant to consumer. The obtained values are at the acceptable level because in Cracow the concentration of chloroform is regularly monitored and rarely exceeds the maximal allowable concentration, i.e. 30 µg/L [13].

2. Materials and methods

2.1. Study area

Cracow city is one the largest cities in southern Poland. Its current water supply system is a result of constructing the water treatment plants for over 100 years, their modernization, and as well as the water-pipe network development resulting from building new housing at outskirts of the city. The water supply system consists of water production subsystem and the water distribution subsystem.

There are five separated treatment lines feeding on surface water sources (from Rudawa, Dłubnia, and Sanka Rivers, Dobczyce reservoir) and underground water (from intake in Mistrzejowice) which form the whole water production subsystem. Long-standing issue of decreasing water demand in the city caused that currently the Cracow water supply system is with excess (the maximal system's reserve is about 74% of average 24 hours water demand).

The Raba Water Treatment Plant is the most significant part of the water supply system—its average daily production is 80,760 m³ (approximately 48% of daily water demand). During emergency periods, this water treatment production could cover the full demand of citizens.

The Raba Water Treatment Plant takes the raw water from Dobczyce reservoir, which is a seasonally unstable and non-homogeneous surface water resource. Its waters undergo typical qualitative and quantitative changes. The total phosphorus, chlorophyll, and oxygen sag are the most important parameters that seasonally reduce the class of water quality. The eutrophication process results in domination of green algae and diatom phytoplankton that intensively develop from the spring to the late autumn. Late summer in the water depth there blue-green algae appears. These processes cause that the content of organic matter is high and its major part consists of precursors of trihalomethanes.

In the Raba Water Treatment Plant, the following technological processes are applied: preliminary ozonation (the maximal ozone dose 4 g/m³), coagulation (PAX or aluminum sulfate in a dose of 0–40 g/m³, Magnaflok in a dose of 0–0.5 g/m³, and sometimes the active carbon in a dose of 0–10 g/m³), rapid filtration (average filtration speed 3 m/h), and finally disinfection using chlorine (chlorine dose 0.5–2 g/m³).

Drinking water is transported from the Raba Water Treatment Plant to the distribution subsystem of Cracow via transit (diameters Ø1,000 and Ø1,400, length about 17 km) where water tanks in Gorzków (with the capacity of 22,500 m³) and tanks complex in Siercza (with the capacity of 158,500 m³) are localized. The water delivered to consumers is additionally chlorinated in water pipe network due to its large supply area. The total length of the distribution subsystem of the city area is 1,849.26 km. The water supply network is characterized by a great age diversity (the largest share have the pipe built after 1975—56%) as well as diversity of the material used (steel 32%, cast iron 26%, PCV 23%). Inseparable elements of the distribution subsystem are equalizing reserve tanks. The Cracow water supply system uses 11 water tanks with the total capacity of over 276,200 m³. These tanks capacities back up 165% actual average 24 hour water demand in the city [14].

The complex structure of the water supply system in Cracow, a long distance from the main water treatment plant (Raba), and decreasing water demand in the city result in increasing time of delivering drinking water to consumers. Additionally, using chlorine in the disinfection process as well the content of organic

matter including a significant part of trihalomethanes precursors in treated water cause the danger of harmful and carcinogenic disinfection byproducts formation. Thus, higher concentrations of chloroform in drinking water are periodically observed.

2.2. Sample collection

In this study, results of laboratory analyses of various water quality parameters obtained by the Central Water Quality Laboratory in Cracow Water Company were used. The analyses were results of regular control monitoring procedures conducted by the company as well as an additional study carried out within the framework of the project supported by Polish State Committee for Scientific Research under the contract No. 5T07E 044 25 [14].

Data were collected from January 2007 to December 2013. Water samples were taken at the Water Treatment Plant Raba and at selected 23 sampling points on the water distribution network. Basic parameters such as pH, residual chlorine, chlorine dose, chemical oxygen demand, UV absorbance in 272 nm, and temperature were tested daily at water treatment plant, however, disinfection byproducts parameters were analyzed once a month. Water quality parameters that characterize the process of disinfection byproducts formation (such as pH, temperature, UV absorbance in 272 nm, the total organic carbon, residual chlorine, chloroform, and the sum of trihalomethanes) in water pipes were analyzed on average once a month. Additionally, for the purposes of this research, the supply area was divided into five supply zones depending on its distance from the water treatment plant (the zones were designated every 5 km, i.e. the first zone was from 0 to 5 km, and the last zone—greater than 20 km). Thus, each sampling point was matched with one of these zones.

Water samples at the Cracow water supply system were collected according to the Polish Standard PN-87/C-04632/01-04. The concentrations of chloroform and other trihalomethanes were specified according to 75-PB-NJL-W-06 procedure using gas chromatograph HP-5890GC/5970MSD.

2.3. Exposure assessment and risk calculation

In Cracow, the chloroform is the predominant of total trihalomethanes, its fraction is about 80% (Fig. 1). For this reason, the cancer risk was calculated only for this one compound.

In this paper, the method of cancer risk assessment is based on the approach proposed by the United States

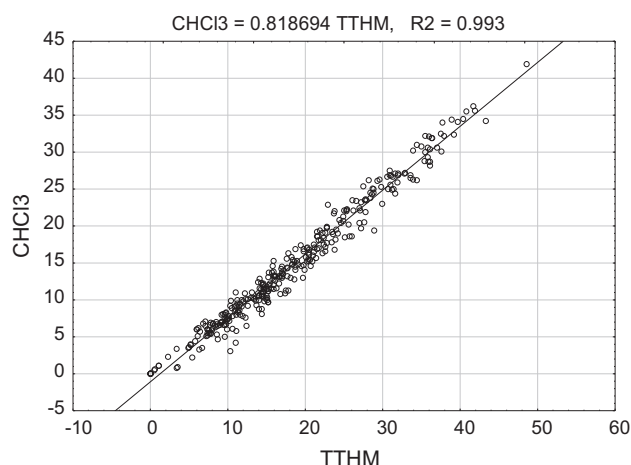


Fig. 1. Relation between concentrations of total trihalomethanes and chloroform at sample points.

Environmental Protection Agency [15,16] which is commonly used by many researchers (e.g. [5–12]). Namely, this method applies formulas (1)–(6) cited below.

There are three paths through which chloroform contained in the tap water enters the human body: oral route (ingestion), dermal absorption, and inhalation exposure (bathing or showering). The total cancer risk TR is defined as the sum of cancer risks CR from all these paths [15,16]:

$$TR = CR_{\text{oral}} + CR_{\text{dermal}} + CR_{\text{inhalation}} \quad (1)$$

where

$$CR_{\text{oral}} = CDI_{\text{oral}} \times PF_{\text{oral}}$$

$$CR_{\text{dermal}} = CDI_{\text{dermal}} \times PF_{\text{dermal}} \quad (2)$$

$$CR_{\text{inhalation}} = CDI_{\text{inhalation}} \times PF_{\text{inhalation}}$$

Potency (slope) factors of chloroform in units of kg day/mg are following [10–12]:

$$PF_{\text{oral}} = 6.10 \times 10^{-3}, \quad PF_{\text{dermal}} = 3.05 \times 10^{-2}, \\ PF_{\text{inhalation}} = 8.05 \times 10^{-2}.$$

Chronic daily intakes CDI are defined as:

$$CDI_{\text{oral}} = \frac{CW \times IR \times EF \times ED}{BW \times AT} \quad (3)$$

$$CDI_{\text{dermal}} = \frac{CW \times SA \times PC \times ET \times EF \times ED \times CF}{BW \times AT} \quad (4)$$

$$CDI_{\text{inhalation}} = \frac{C_{\text{air}} \times VR \times ET \times EF \times ED \times CF}{BW \times AT} \quad (5)$$

In formulas above CW is the concentration of contaminant in water, IR —the ingestion rate, EF —exposure frequency, ED —exposure duration, BW —body weight, AT —average time, SA —skin area, PC —permeability constant, CF —conversion factor, ET —exposure time, VR —ventilation rate, and C_{air} —the concentration of volatile contaminant in air calculated as in [17]:

$$C_{\text{air}} = \frac{a}{2b} (1 - e^{-bt}), \quad (6)$$

where $a = \frac{Q_L CW (1 - e^{-Nt})}{V_s}$, $b = \frac{Q_L (1 - e^{-Nt}) + HQ_G}{HV_s}$, $N = \frac{K_{OLA}}{Q_L}$, H is the Henry law constant, K_{OLA} —overall mass transfer coefficient, V_s —bathroom volume, Q_L —water flow rate, and Q_G —air flow rate.

For risk calculations most of typical values were assumed except some specific to Poland (such as average lifetime or body weight). A detailed description of input parameters is contained in Table 1.

3. Results and discussion

The concentration of chloroform at water treatment plant was changing from 0 to 28.6 $\mu\text{g/L}$ and from 0 to 41.9 $\mu\text{g/L}$ at sampling points on the network, but large concentrations were detected rather incidentally. Basic descriptive statistics of chloroform concentration are given in Table 2. The table presents data for the whole city and with respect to the particular zone and season. The greatest values were observed during summer because then the temperature is usually higher. The average chloroform concentration increases with distance from the water treatment plant, except for the zone 1. It may be due to two factors: water samples from this zone form the set which is smaller than others (so incidental large concentrations affect the mean value of a greater extent) or this zone should be subdivided into subzones. Moreover, in studied data temperature was changing from 1.7 to 23.6°C, pH from 7.2 to 8.4, the total organic carbon from 1.09 to 3.25 mg C/L (at water treatment plant) and from 0.64 to 4.68 mg C/L (on network), UV absorbance at 272 nm from 0.008 to 0.037 per cm (at water

Table 1
Input parameters used to cancer risk estimation of chloroform

Parameter	Unit	Value	Source
<i>Common parameters</i>			
CW	mg/L	See Table 2	This study
EF	d/y	365 365/4 (one season)	[16]
ED	y	82 (female) 75.1 (male)	[18]
BW	kg	65 (female) 80 (male)	[19]
AT	d	82×3 (female) 75.1×3 (male)	Formula from [16]
<i>Oral ingestion</i>			
IR	L/d	2	[15,20]
<i>Dermal absorption</i>			
SA	cm^2	$\frac{4BW + 7}{BW + 90} \times 10^4$	[9]
PC	cm/h	0.0089	[6,11]
ET	h	0.33	Assumed in this study
CF	L/cm^3	0.001	
<i>Inhalation exposure</i>			
C_{air}	mg/L	Model (6) calculations	[17]
Q_L	L/min	4	[17]
Q_G	L/min	50	[17]
H	dimensionless	0.15	[21]
K_{OLA}	L/min	7.4	[17]
V_s	m^3	6.6	[9]
VR	m^3/h	0.51 (female) 0.62 (male)	[20]
CF	L/m^3	1,000	

Table 2
Basic descriptive statistics of chloroform concentration (WSS Cracow)

	Mean	Median	Minimum	Maximum	Standard deviation
Zone 1	14.84	18.2	0	31.9	10.78
Zone 2	13.79	12.6	4.2	35.5	9.35
Zone 3	15.72	13.2	0.5	32.1	7.03
Zone 4	16.91	13.5	1.1	35.6	8.78
Zone 5	17.51	14.4	6.0	41.9	10.63
Winter	10.80	10.0	5.0	25.6	5.23
Spring	14.51	14.1	0	35.5	8.42
Summer	23.23	22.1	4.2	41.9	8.19
Autumn	14.37	12.1	0.5	28.0	6.64
Whole city	15.75	13.2	0	41.9	8.35

Table 3
Cancer risk with respect to location

Location		Cancer risk			
		Oral	Dermal	Inhalation	Total
Male	Zone 1	2.26×10^{-6}	3.23×10^{-7}	1.17×10^{-6}	3.75×10^{-6}
	Zone 2	2.10×10^{-6}	3.00×10^{-7}	1.08×10^{-6}	3.49×10^{-6}
	Zone 3	2.40×10^{-6}	3.42×10^{-7}	1.24×10^{-6}	3.98×10^{-6}
	Zone 4	2.58×10^{-6}	3.68×10^{-7}	1.33×10^{-6}	4.28×10^{-6}
	Zone 5	2.67×10^{-6}	3.81×10^{-7}	1.38×10^{-6}	4.43×10^{-6}
	Whole city (mean)	2.40×10^{-6}	3.43×10^{-7}	1.24×10^{-6}	3.98×10^{-6}
	Whole city (median)	2.01×10^{-6}	2.87×10^{-7}	1.04×10^{-6}	3.34×10^{-6}
Female	Zone 1	2.78×10^{-6}	3.56×10^{-7}	1.18×10^{-6}	4.32×10^{-6}
	Zone 2	2.59×10^{-6}	3.31×10^{-7}	1.10×10^{-6}	4.02×10^{-6}
	Zone 3	2.95×10^{-6}	3.77×10^{-7}	1.25×10^{-6}	4.58×10^{-6}
	Zone 4	3.17×10^{-6}	4.06×10^{-7}	1.35×10^{-6}	4.93×10^{-6}
	Zone 5	3.29×10^{-6}	4.20×10^{-7}	1.39×10^{-6}	5.10×10^{-6}
	Whole city (mean)	2.96×10^{-6}	3.78×10^{-7}	1.25×10^{-6}	4.59×10^{-6}
	Whole city (median)	2.48×10^{-6}	3.17×10^{-7}	1.05×10^{-6}	3.85×10^{-6}

Table 4
Cancer risk with respect to season

Season		Cancer risk			
		Oral	Dermal	Inhalation	Total
Male	Winter	4.12×10^{-7}	5.87×10^{-8}	2.12×10^{-7}	6.83×10^{-7}
	Spring	5.53×10^{-7}	7.90×10^{-8}	2.86×10^{-7}	9.18×10^{-7}
	Summer	8.86×10^{-7}	1.26×10^{-7}	4.57×10^{-7}	1.47×10^{-6}
	Autumn	5.48×10^{-7}	7.82×10^{-8}	2.83×10^{-7}	9.09×10^{-7}
Female	Winter	5.07×10^{-7}	6.48×10^{-8}	8.60×10^{-7}	1.43×10^{-6}
	Spring	6.81×10^{-7}	8.70×10^{-8}	1.16×10^{-6}	1.92×10^{-6}
	Summer	1.09×10^{-6}	1.39×10^{-7}	1.85×10^{-6}	3.08×10^{-6}
	Autumn	6.75×10^{-7}	8.62×10^{-8}	1.15×10^{-6}	1.91×10^{-6}

treatment plant) and from 0.012 to 0.058 per cm (on water pipe network), and chemical oxygen demand from 0.42 to 2.10 mg O₂/L. The total chlorine dose used to water disinfection was between 0.495 and 2.390 mg/L, the residual chlorine in water samples was between 0 and 0.5 mg/L, and the observed chlorine consumption was between 0.533 and 2.234 mg/L.

Evaluations of cancer risk due to formulas (1)–(5) are collected in Tables 3 and 4. The risks were calculated for all seasons and for all zones, separately for males and females. Additionally, the risk was evaluated for the mean chloroform concentration in the entire city as well as for the median of its concentration. The last risk may be more meaningful for the risk assessment because incidental norm exceeding causes the increment of the mean value.

The total cancer risk in all considered cases is between 10⁻⁶ and 10⁻⁵ which means that these values are public health protective at low doses for the range of human variation [15].

The greatest part of the total cancer risk is related to the oral ingestion, followed by inhalation exposure, and lastly dermal absorption. The average risk for female is about 15% higher than for male. The total risk in zone 5 is 27% higher than in zone 2 (both in males and females). The highest risk occurs during summer and it is equal to 2.15 risk during winter (both in males and females).

4. Conclusion

Estimations of cancer risk, presented above, show that the cancer risk is at the acceptable level, i.e. between 10⁻⁶ and 10⁻⁵ [15], and the exposure from chloroform dermal absorption is not significant comparing to oral and inhalation exposures. The real risk may be even less because in Poland people drink more boiled water, whereas the oral route is most significant in the total cancer risk assessment. However, women are more exposed because they take similar doses of disinfection byproducts but have smaller body weight and live longer.

Methodology applied in this study indicates that cancer risk caused by chloroform is a linear function of chloroform concentration in tap water. If one assumes that the chloroform concentration in water delivered to consumers is continuously equal to maximal allowable chloroform concentration (i.e. 30 µg/L), then the total cancer risk would be 7.59 × 10⁻⁶ in males and 8.74 × 10⁻⁶ in females. These values do not exceed 10⁻⁵ therefore it confirms the fact that the maximal allowable concentration of chloroform established by Polish law is safe for water consumers in Cracow. In Poland,

legislation acts allow chloroform concentration to be 100 µg/L for short time, but then the cancer risk increases—it is possible that it will be greater than 10⁻⁵. Since the change of water disinfection method in the near future is not expected, the concentration of trihalomethanes (especially chloroform which is the predominant compound) in drinking water has to be regularly monitored. The monitoring frequency should be greater in summer when the temperature is higher and reaction between chlorine and organic matter is more intensive. Obviously, some preventive actions which improve the effectiveness of precursor removal from water are desirable.

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