

Technology of Water Purification With Chlorinated Derivatives and Assessment of Risk Associated With Human Exposure to These Substances

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Abstract. In the given paper the authors consider the technology of water purification with consideration to the recommendations of the World Health Organization (WHO), European Union (EU) and standards of developed countries. Carcinogenic Unit Risk (UR) magnitude for people constantly exposed to the analyzed carcinogens in the course of a lifetime is estimated. The authors calculate and evaluate unique carcinogenic risk as a complementary probability of cancer development during the whole life of CR when introducing EU standards into water purification technology.

1. Relevance

One of state policy directions is public health protection and improvement of the quality of life by ensuring uninterrupted water supply and water disposal as well as by reducing negative impact upon water objects by means of improving the quality of waste water treatment [1,2].

At present time continuous deterioration of surface sources of drinking water and practically not improving state of water conditioning objects and centralized water supply systems make these problems extremely important. That is why authorities of the Russian Federation are introducing EU standards and WHO recommendations into the technologies of water purification. Due to this the object of the work is estimation of carcinogenic risks associated with implementation of hygienic standards of EU countries.

In the recent years water resources are exposed to intensive pollution. Water conditioning and water disposal facilities where traditional methods and procedures are applied are not always able to ensure the required degree of water purification. This fully refers to water decontamination – the main barrier against water infections [3].

Water treatment in order to prepare it for drinking is a complex of physical, chemical and biological methods of changing its original composition. The great variety of water treatment methods can be divided into the following basic groups: improvement of organoleptic properties of water (clarification and discoloration, deodorization and other); ensuring epidemiological safety (chlorination, ozone treatment, ultraviolet radiation and other); mineral composition conditioning (fluoridation, defluorination, extraction of heavy metals ions, deferrization, demanganation,



demineralization or desalting and other). The method is chosen basing on preliminary study of composition and properties of the considered water resource and their comparison to the customer's requirements [4].

2. Material and methods of research

In the practice of drinking water treatment one of the main methods of treatment ensuring its reliable decontamination and allowing to maintain the sanitary state of waste water treatment systems is chlorination. Alternative technologies of decontamination used for water treatment do not always meet such requirements as prolonging action, low capital costs, formation of toxic agents, safe production process. At the same time chlorination promotes formation of dangerous chemical substances affecting people's health.

Recent research showed that the water contains toxic volatile organohalogen compounds (VHC). These are, mainly, compounds falling into the group of trihalometans (THM): chloroform, dichlorobromometane, dibromochloromethane, bromform and other, having carcinogenic, mutagenic activity and cumulated in living organisms.

For the purposes of harmonization with the recommendations of the World Health Organization (WHO) and European Union (EU) and standards of developed countries in 2002 the Russian Federation corrected hygienic rating for halogen-containing compounds formed in the process of chlorination in the drinking water. As we can see from Table 1 the ratings of ten halogen-containing compounds were harmonized: MPC of four substances were corrected, three of them being carcinogenic, APL of five compounds and MPC of chlorine cyanide were re-established, MPC of chloroform was reduced up to 0.06 mg/l, MPC of carbon tetrachloride was reduced by 3 times and that of chloral hydrate – by 20 times [5].

Pollution with organohalogen compounds is mainly anthropogenic. There are two possible sources of VHC in drinking water:

a) resulting from polluting water sources with industrial waste waters containing VHC. It should be noted that surface water sources, as a rule, contain small quantities of VHC as surface water is characterized by active self-purification processes; besides, VHL are removed from water by surface aeration. The main sources of these substances in the environment are organic synthesis companies, hydrolytic, cellulose and paper mills, woodworking, coke-chemical, varnish-and-paint, pharmaceutical production;

b) formation of VHC in the process of water treatment resulting from reactions between chlorine and substances in the primary water. The main precursors of these toxic compounds are natural humic and fuvic acids. The largest group of organohalogen compounds formed when treating drinking water with disinfecting agents is made up of trihalomethans: chloroform, bromform, dibromochloromethane, dichlorobromometane. Derivatives of bromine are formed when primary water contains bromides or when the chlorinating agent is polluted with bromine [6]. Concentration of the formed VHC is significantly influenced by the amount of plankton in the primary water.

Beside trihalomethans the researchers found chlorinated ketones, chloromethyl cyanides, chloracetic acids, chloral, chloropicrin, chlorophenols. The process of these products formation and their content ratio is influenced by many factors: nature of organic substances in the primary water, bromine content, pH, temperature, nature and amount of chlorinating reagent, time of chlorination, season, also, further transformations of organohalogen compounds in the water-supply system are possible. Influence of the large amount of factors makes it difficult to predict the composition of possible products. It has been shown that presence of humic acids leads to formation of volatile organohalogen compounds, that of fulvic acids leads to formation of chloracetic acids. With Ph increase from 5 to 9 content of trihalomethans, particularly chloroform, significantly increases, and content of chloracetic acids, acetone trichloride, acetone dichloride, chloropicrine decreases [6].

Table 1 – Hygienic normatives of halogen-containing compounds in the drinking water which are formed when the water is chlorinated

Compounds	MPC, APL, mg/l before 2002	Corrected normative, mg/l	Potential health impact	Class of hazard
Trihalomethans				
Chloroform	0.2 s.-t.	0.06 s.-t.	Carcinogenic effect	1
Bromodichloromethane	0.03 s.-t.			2→1
Dibromochloromethane	0.03 s.-t.		Hepatotoxic action	2
Bromform	0.1 s.-t.			2
Chlorophenols				
2.4-dichlorophenol	0.002 org.		Change of water taste	4
2.4.6-trichlorophenol	0.004 org.	0.004 s.-t.	Carcinogenic effect	4→1
Chlorophenol	0.001 org.		Water odor appears	4
Chlorine-containing acetic acids				
Chloroacetic acid	0.06 s.-t.		Hepatotoxic action	2
Dichloroacetic acids		0.05 s.-t.		
Trichloroacetic acids		0.01 s.-t.		
Halogen-containing acetonitriles				
Dibromoacetonitrile		0.1 s.-t.	Weight loss	2
Dichloroacetonitrile		0.1 s.-t.	Teratogenic effect	2
Trichloroacetonitrile		0.001 s.-t.		1
Other compounds				
Chloral hydrate	0.2 s.-t.	0.01 s.-t.	Hepatotoxic action	2
Tetrachloride carbon	0.006 s.-t.	0.002 s.-t.	Carcinogenic effect	2→1
Chlorine cyanide (for cyanide)		0.035 s.-t.	Neurotoxic action	2→1

The basic concentrations of VHC are formed at the stage of primary chlorination of unpurified water. Most times THM and tetrachlorine carbon are formed. The amount of chloroform usually exceeds the amount of other VHC by 1-3 decades.

In 1980-1990s, when a number of works was published on halogen-containing compounds in the drinking water, the problems associated with effects of these substances on human health were considered least of all. For a long time one of the most important sides of their biological effect – delay effect, namely, carcinogenic one, was underestimated. Although the experimental data on chloroform cancer effect on animals were obtained and it was included into group 2B (factors for which there is limited (or insufficient) evidence of their cancer effect upon humans and almost enough evidence of that for animals) according to the classification of International Agency for Research on Cancer (IARC), in half of the cases the epidemiological survey did not clearly show increase of cancer rate for the people who had been drinking chlorinated water. In the middle of the 1990s studies were completed that made the scientists to see the products of water chlorination previously considered not so dangerous in a new light. Modern methods of chemical analysis allowed identifying several dozens of such compounds. Reliable information on epidemiology of cancer cases of bladder, large and straight intestines, pancreatic gland and brain associated with drinking chlorinated water containing THM. A number of epidemiologic surveys revealed effect of VHM upon the female reproductive system: increasing the frequency of impairments of gestation course, of prenatal development and appearance of congenital malformations caused by chlorinated drinking water with THM concentrations over 80-100 mg/l. So, by 2000, much evidence of unfavorable effect of chloroform on public health had been collected [7].

It has been also established that chlorine used for decontamination of running water effects people at home in several ways: not only through swallowing but also through the lungs, with inhaled air.

The results of research presented in Table 2 demonstrate the fact of chloroform passes from running water into the air of the living space when people take a bath or a shower.

According to the data of the research quite high concentrations of chloroform (167-232 mg/l) were also found in the air layer over the indoor swimming pools [8].

Such criteria as toxic and carcinogenic properties (group B2 according to the classification of the International Agency for Research on Cancer), probability of effecting population as a whole, distribution in the environment and capability of the compound for cross-media distribution determined the choice of chloroform, side product of water decontamination with chlorine-containing compounds, as of one preferred pollutants of drinking water characterized by high medical and social significance [8].

Table 2 – Influence of water temperature when filling the bath and type of room when taking a shower upon chloroform content in bathroom air [7]

Water temperature when filling the bath, °C	Chloroform content		
	water, mg/l	air, mg/m ³	
		before	after
	filling the bath with running water		
20	145	5	6
35	160	3	44
Taking a shower in the bathroom	180	4	230
Taking a shower in the shower unit	112	3	296

According to modern international practices the risk assessment methodology is applied for integral assessment of environmental factors effect on personal and public health. Interpreting the quality indices of the drinking water as risk factors will allow forecasting public health and estimate the probability of pathologic processes development determined by water contaminating substances. It should be noted that there is an opinion [8] that the probability of oncological diseases is not the same not only for different water distribution systems but also for different parts of one water distribution system. Due to this fact the risks associated with chlorination side products in the drinking water may differ for the population of the same district.

We have estimated the risks of general effect of drinking water chloroform upon the people's health. The initial data were the monitoring data of Federal Service on Customers' Rights Protection and Human Well-being Surveillance for Irkutskaya region obtained in 2013 when chloroform was included into the list of substances to be controlled in the drinking water of the systems of centralized domestic water supply in the town of Irkutsk.

To estimate the exposition we completed calculations of chloroform intake from the water of domestic water supply into the human organism by three possible routes: oral I_o ; inhalative I_i and through skin (absorbed) I_d . Intake of chemical substances was calculated according to the formulas taking into account effecting concentrations, contact, exposure duration and frequency, body mass and the time of exposure averaging.

The intake established on the base of Federal Service on Customers' Rights Protection and Human Well-being Surveillance data is provided in Table 3.

Unit risk (UR) was assessed as the upper, conservative estimate of carcinogenic risk for a person life-long exposed to constant effect of the analyzed carcinogen in the concentration 1 mg/m³ (atmospheric air) or 1 mg/l (drinking water).

Table 3 – Average daily doses of chloroform intake under multi-route exposure

Sampling point	Actual concentration (average value, mg/dm ³)	Normative, mg/dm ³	I ₀ , mg/(kg×day)	I _i , mg/(kg×day)	I _d , mg/(kg×day)
Irkutsk, water supply point 1	0.009	0.06	11·10 ⁻⁵	0.24	3·10 ⁻⁵
Irkutsk, water supply point 2	0.008	0.06	9·10 ⁻⁵	0.21	3·10 ⁻⁵

Calculation of unique carcinogenic risk as complementary probability of life-long cancer development risk was estimated with consideration to lifetime average daily dose.

Population carcinogenic risks (PCR) reflecting complementary (to background) number of malignant neoplasms cases which may occur in the course of a lifetime due to effect of the studied factor. Unique and population carcinogenic risks characterize the upper estimate of possible carcinogenic risk for the period corresponding to average life expectation of a person (70 years).

Annual population carcinogenic risk (PRCa) was estimated as calculated number of complementary cancer cases during a year.

The results of calculations of the given kinds of carcinogenic risk are given in Table 4.

Table 4 – Results of carcinogenic risk calculations

Sampling point	UR _i , m ³ /mg	UR _o , mg/l	CR _o	CR _i	CR _d	PCR _o	PCR _i	PCR _d	PCR _{ao}	PCR _{ai}	PCR _{ad}
Irkutsk, sampling point 1	0.002	0.0002	6·10 ⁻⁷	2·10 ⁻³	9.8·10 ⁻⁷	0.3	1212	0.59	5·10 ⁻³	17	8·10 ⁻³
Irkutsk, sampling point 2			6·10 ⁻⁷	1·10 ⁻³	8.3·10 ⁻⁷	0,3	606	0.50	5·10 ⁻³	9	7·10 ⁻³

When calculating total carcinogenic risks we should take into consideration the differences in the intensity of carcinogenic activity of chemical substances under different intake routes. As the values of carcinogenic potential factors are different for different intake routes risk calculation on the base of total doses is appropriate only for the similar routes.

The obtained risk esteems show that for oral and percutaneous exposure routes the risk is at minimal level and it is perceived by the people as small to negligible not differing from usual everyday risks (De minimis level). Such risk does not require any additional measures to be reduced

and its level is only to be monitored at regular intervals. The risk of cancer development under inhaled route of exposure makes $1 \cdot 10^{-3} - 2 \cdot 10^{-3}$ and exceeds the values of maximum allowed risk for the population (for example, for the drinking water WHO sets $1 \cdot 10^{-5}$ as allowed risk and for atmospheric air – $1 \cdot 10^{-4}$). The risk magnitude is acceptable for professional groups and unacceptable for population at large.

The values of population carcinogenic risk characterize the long-term trends of alteration of oncological background at the studied territory. The given kind of risk turned insignificant for oral and percutaneous routes of exposure. The population carcinogenic risk is significant under the inhalative route of chloroform exposure. According to the calculations 606 and 1012 of complementary (to background) cases of malignant neoplasms cases could have developed due to effect of inhaled evaporating chloroform. Unique and population carcinogenic risks characterize the risk magnitude in the course of a lifetime of a person.

The given regularity is true for the magnitudes of annual population carcinogenic risk. Its calculation for one year of life also has a large value under inhalative exposure. Annual population risk makes from 9 to 17 complementary cancer cases during the year. The amount of complementary cancer cases during the year for oral and percutaneous routes of exposure allows neglecting annual carcinogenic risk of drinking water effect upon population.

The values of carcinogenic risks reflect mainly the long-term trend for alteration of oncological background. The trend is formed when all reference conditions accepted by the researcher are met (for example, certain duration and intensity of exposure, stationarity of exposure, certain values of the factors of exposure and other).

Analysis of unique carcinogenic risks distribution showed that the main contribution into formation of total unique risk associated with drinking water chloroform is made by the risk formed under the inhalative route of exposure. This risk requires developing and taking health-improving measures. Planning the risk-reducing measures in this case must be based on the results of in-depth assessment of various aspects of integrated effect and priority ranking in relation to other hygienic, ecological, social and economic problems of the region.

Further in the work estimation of non-carcinogenic risks of the integrated effect of drinking water chloroform was completed.

Characteristics of risks of non-carcinogenic effects development for specific substances is completed on the base of Hazard Quotient calculation:

$$HQ = AD/RfD \text{ or } HQ = AC/RfC,$$

where HQ – Hazard Quotient; AD – average dose, mg/kg; AC – average concentration, mg/m³; RfD – reference (safe) concentration, mg/m³.

The maximum permissible concentration of chloroform in the drinking water (0.06 mg/l) was taken as equivalent of reference concentration (RfC). The calculation was completed according to the following formula:

$$HQ = C_{\text{aver.}}/RfC,$$

where $C_{\text{aver.}}$ – real concentration, mg/dm³.

Calculation results are provided in Table 5.

Table 5 – Results of Hazard Quotient calculation

Sampling point	Actual concentration (average value, mg/dm ³)	Normative, mg/dm ³	HQ
Irkutsk, facility № 5	0.009	0.06	0.15
Irkutsk, 2 nd water lift Yershi	0.008	0.06	0.13

3. Conclusion

If Hazard Quotient (HQ) of the substance applied in water purification technologies to eliminate VHC according to the recommendations of World health Organization (WHO), European Union (EU) and standards of developed countries does not exceed one, the probability of harmful effects caused by everyday intake of chloroform in the course of a lifetime is insignificant and such effect is characterized as permissible.

The conducted study of water purification technology according to new standards with account to full route of real drinking water chloroform intake provide evidence of monitoring necessity not only for carcinogenic but also for general toxic risks of chloroform exposure. Quantitative characteristics of multi-medium risk allows developing optimal managing solutions for its reduction on the base of estimation of all contact media and intake routes with consideration to their contribution into levels of exposure.

4. References

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