Comparison of drinking water quality in terms of relative concentrations and carcinogenic risks of trihalomethanes

M A Malkova¹,², M Y Vozhdaeva¹, E A Kantor¹ and I A Melnitskii¹,²

¹ Ufa State Petroleum Technological University, 1 Kosmonavtov str., Ufa, 450062, Russia
² Center of Analytical Control of Water Quality, Municipal unitary enterprise “Ufavodokanal”, 157/2 Rossyiskaya str., Ufa, 450098, Russia

E-mail: kykyshka2009@mail.ru

Abstract. An assessment of the drinking water quality according to the content of trihalomethanes on the surface and infiltration water intakes of the city of Ufa using threshold and non-threshold methods was carried out. The threshold method was estimated by calculating the summation coefficient. The non-threshold method was based on the calculation of the individual and total carcinogenic risks of the trihalomethanes components: trichloromethane, bromodichloromethane, dibromochloromethane. The summation coefficient, calculated on the content of trihalomethanes, for surface and infiltration water intakes was respectively 0.56 and 0.15. A greater contribution to the summation coefficient is made by trichloromethane. On the surface water intake, the values of carcinogenic risks are within $1.1 \times 10^{-6} - 6.3 \times 10^{-6}$, on the infiltration water intake risks are within $9.1 \times 10^{-7} - 2.8 \times 10^{-6}$, which does not exceed the maximum permissible values. A large proportion of the carcinogenic risk for the two types of water intake accounts for bromodichloromethane. The calculations show the need for measures in order to reduce the total content of trihalomethanes, primarily bromine-containing ones.

1. Introduction
The quality of drinking water plays a special role in ensuring sanitary and epidemiological well-being, quality of life and protection of human health [1-7]. The main requirement for the drinking water quality is epidemiological safety for human health. Therefore, water disinfection is included in the complex of measures taken for the prevention and elimination of infectious diseases [2,6]. To solve the problem, various methods are used, such as ozonation, ultraviolet irradiation, fluoridation, oxychlorination, etc. Chlorination is the most common and reliable method of water disinfection. However, this method leads to the formation of chlorination products - organohalogen compounds.

Organic halogenated compounds include, for example, halogenacetic acids, halogenated phenols, etc. The majority of the organic halogenated compounds are trihalomethanes (TGM). This group of compounds includes chloroform CHCl₃ (CF), bromodichloromethane CHBrCl₂ (BDCM), dibromochloromethane CHBr₂Cl (DBC) and bromoform CHBr₃ (BF). Anthorogenic and natural substances are sources of TGM formation [7-9]. Natural sources include aqueous humus, fulvic acids, humic acid, algae etc. [10]. Waste pulp and paper industry pose a significant risk in relation to the formation of TGM. The danger is related to the fact that the structure of lignins is similar to
humic and fulvic acids. They contain similar structural fragments in their molecules [8]. Wastes of coke production, gold mining, herbicides, solvents can be sources of TGM formation [11]. It is known that TGM components can have a negative impact on public health. The action of the chemical compounds contained in the water is prolonged. Despite the fact that microbiological pollution is a priority cause of the incidence of the population due to the water factor, the presence of TGM components in the drinking water even in relatively low concentrations can harm the health of the water user. TGM have a toxic polymorphism and the ability to cause long-term effects, including carcinogenesis [12-14]. It is important to note that the potential risk to human health from TGM components may also be the entry of these agents into the body when using water for washing, household needs and recreation. The content of TGM in drinking water can cause a violation of reproductive function. In this regard, TGM are controlled substances in drinking water.

2. Materials and research methods
Two methods can be used to assess the impact of drinking water quality on a person by TGM content: threshold and non-threshold. The threshold method for assessing the quality of drinking water according to individual chemical indicators involves the calculation of the summation coefficient (1). The coefficient is the sum of the ratio of the actual to the maximum allowable concentration. Its value should not exceed a critical value equal to one [14,15].

\[ \sum C_i \cdot (MAC_i)^{-1} \leq 1 \]  

\( C_i \) - actual substance concentration, \( \mu g / dm^3 \),  
\( MAC_i \) - maximum allowable concentration of the substance, \( \mu g / dm^3 \).

Along with the threshold method, non-threshold models are used to assess effects on human health. They suggest taking into account the effect of a substance of any concentration on human health. No-threshold models can be used to assess the quality of drinking water for individual substances, for total assessments, as well as for comparative assessments of the risk values magnitude [14,15]. Risk assessment allows to obtain a ratio between the concentration of a polluting the environment substance, the duration of exposure to an adverse factor and the probability of a negative impact on human health (development of carcinogenic and non-carcinogenic effects, death of the disease, etc.) [13].

\[ \text{Risk} = \text{LADD} \cdot SF_0 \]  

\( \text{Risk} \) - carcinogenic risk,  
\( \text{LADD} \) - average daily dose for life,  
\( SF_0 \) - carcinogenic potential factor.

We have compared the calculation results of the relative content of chloroform, bromodichloromethane and dibromochloromethane and the cancerous risk of the compounds listed in drinking water of the surface and infiltration water intakes located on r. Ufa. As the initial, the average annual concentrations of the TGM components in the clean water reservoir of the surface and infiltration water intakes of the Ufa city (1995 - 2015) were taken. It is noted that during the study period, the norms of sanitary rules and regulations (2.1.4.1074-01) were not exceeded even once. Tribromomethane calculations have not been carried out, because its concentration in the clean water reservoir since 2000 is below the limit of determination. The strictest standard was used when calculating the summation coefficient for chloroform (GN 2.1.5.2280-07).

3. Results and discussion
The main criterion for the measures development to protect public health from the effects of adverse environmental factors is the magnitude of the risk to the health of people living in the action zone of these factors.

Calculations of the summation coefficient and carcinogenic risk were carried out. The calculation of the contribution to the summation coefficient from trihalomethanes revealed that a
large proportion is accounted for by chloroform (surface water intake). The contribution of chloroform is more than 75%. Bromodichloromethane is the second largest contributor to the summation ratio. Its share is 21.6%. The contribution of dibromochloromethane to the summation coefficient is less than 3% (Table 1).

Table 1. The results of the relative concentrations and carcinogenic risks assessment determined by the presence of components of trihalomethanes in drinking water.

| №  | Component               | Average content µg / dm³ | MAC µg / dm³ | \( \frac{C_i}{MAC_i} \) % | SF₀ | Risk | %   |
|----|-------------------------|--------------------------|--------------|---------------------------|-----|------|-----|
| 1  | Chloroform              | 25.08                    | 60           | 0.42                      | 75.7| 0.0061 | 4.4 × 10⁻⁶ | 37.1 |
| 2  | Bromodichloromethane    | 3.58                     | 30           | 0.12                      | 21.6| 0.062  | 6.3 × 10⁻⁶ | 53.8 |
| 3  | Dibromochloromethane    | 0.45                     | 30           | 0.02                      | 2.7 | 0.084  | 1.1 × 10⁻⁶ | 9.1  |
| 4  | Total                   | 29.11                    | 0.56         | 100.0                     | 11,8×10⁻⁶ | 100.0 |
| 5  | Chloroform              | 5.45                     | 60           | 0.09                      | 57.9| 0.0061 | 9.5 × 10⁻³ | 20.2 |
| 6  | Bromodichloromethane    | 1.60                     | 30           | 0.05                      | 34.0| 0.062  | 2.8 × 10⁻⁶ | 60.4 |
| 7  | Dibromochloromethane    | 0.38                     | 30           | 0.01                      | 8.1 | 0.084  | 9.1 × 10⁻⁷ | 19.4 |
| 8  | Total                   | 7.43                     | 0.15         | 100.0                     | 4.7 × 10⁻⁶ | 100.0 |

Note. SF₀ - carcinogenic potential factor, Risk - carcinogenic risk.

A similar trend is observed at the water intake of the infiltration type. Chloroform accounts for more than 57%, bromodichloromethane - 34%, dibromochloromethane - over 8%.

At the surface water intake, the values of individual carcinogenic risks caused by the presence of TGM lie within \( 1.1 \times 10^{-6} \div 6.3 \times 10^{-6} \), on the infiltration risk \( 9.1 \times 10^{-7} \div 2.8 \times 10^{-6} \). The values obtained do not exceed the established limits for individual carcinogenic risks of \( 1.0 \times 10^{-5} \) [15-18]. Thus, the individual components of TGM do not pose a danger to humans. Thus, the individual components of TGM do not pose a danger to humans. It is important to note the difference in the distribution of the TGM components contribution when evaluating the coefficient of summation and carcinogenic risk. In the second case, a large proportion of the risk is determined by the presence of BDCM in drinking water, despite the significant excess of trichloromethane relative to bromine-containing TGM [19,20].

4. Conclusion

In general, the data obtained indicate that the coefficient of summation over the analyzed compounds is 0.56 for the surface water intake and 0.15 for the infiltration water, which is significantly less than one. At the surface water intake, the carcinogenic risk from the presence of TGM in drinking water is \( 11.8 \times 10^{-6} \), on the infiltration risk it is \( 4.7 \times 10^{-6} \), while the maximum permissible carcinogenic risk is \( 10^{-6} \). Thus, it is necessary to take measures related to the general reduction of bromine-containing TGM to improve water quality.

Acknowledgments

The work was performed within the framework of the State Task No. 5.12863.2018 / 8.9 “Development of a system for identification and quantitative analysis of environmental risks arising from the water supply of a large urban agglomeration”.

References

[1] Malkova M Some problems of the trihalomethanes formation during chlorination of drinking water Young Scientist Bulletin UGNTU 7 68-74
[2] Rusanova N Preparation of drinking water taking into account microbiological and parasitological indicators Water supply and sanitary equipment 11 13-4
[3] Tul'skaya E Comparative safety of water disinfection Public health and environment 11 22–4
[4] Mullina E Chemical aspects of the process of water chlorination International Journal o Applied and Fundamental Research 12 609-13
[5] Kang D, Lansey K Demand and Roughness estimation in Water Distribution Systems Journal of Water Resources Planning and Management 137 20-30
[6] Sokolova N Means and methods of water disinfection (analytical review) Medical alphabet 5 44-54
[7] Brown D, Bridgeman J, and West J Predicting chlorine decay and THM formation in water supply systems Rev. Environ. Sci. Biotechnol. 10 79-99
[8] Ma D, Gao B, Sun S, Wang Y, Yue Q, and Li Q Effect of dissolved organic matter size fractions on trihalomethanes formation in MBR effluents during chlorine disinfection Bioresource Technology 136 535-41
[9] Vozhdaeva M, Cypysheva L, Kantor L and Kantor E Influence of chlorination on the composition of limited-volatile organic water pollutants Journal of Applied Chemistry 77 952-5
[10] Lui Y, Qiu J, Zhang Y, Wong M, Liang Y Algal-derived organic matter as precursors of disinfection by-products and mutagens upon chlorination Water research 4 1454-62
[11] Nizamutdinova N, Kutliahmetov A, SHajdulina G, SafaroVA V, Dokukin YU Evaluation of the impact of technology on underground leaching of gold on the environment Water: chemistry and ecology 76 8-15
[12] Danileviciute A, Grazuleviciene R, Vencloviene J, Paulauskas A, Nieuwenhuijsen M Exposure to Drinking Water Trihalomethanes and Their Association with Low Birth Weight and Small for Gestational Age in Genetically Susceptible Women Public Health 12 4470–85
[13] Hrudey S Chlorination disinfection by-products, public health risk tradeoffs and me Water research 43 2057–92
[14] Malkova M, Vozhdaeva M, Kantor E Assessment of a carcinogenic risk to public health related to the quality of drinking water of surface water intake and infiltration types Water and Ecology: Problems and Solutions 73 59-64
[15] Guidelines for assessing the public health when exposed to chemicals that pollute the environment (Guideline R 2.1.10.1920-04) Federal center of state sanitary and epidemiological surveillance of the Ministry of Health of Russia 1-143
[16] Lepoma P, Brown B, Hanke G, Loos R, Quevauviller P and Wollgast J 2009 Needs for reliable analytical methods for monitoring chemical pollutants in surface water under the European Water Framework Directive J. Chromatogr. A 1216 302–15
[17] Virius E, Kapinus E, Reveisky I and Borzenko A 2003 Determination of total organochlorinecontent in water, based on microfluid extraction and microcoulometric analysis of the extract Zav. Lab 69 3–6
[18] Bulla R, Reckhow D, Li X, Humpaged A, Joll C and Hrudeyc S 2001 Potential carcinogenic hazards of non-regulated disinfection by-products: Haloquinones, halo-cyclopentene and cyclohexene derivatives, N-halamines, halonitriles, and heterocyclic amines Toxicology 286 1–19
[19] Sun Y-X, Wu Q-Y, Hu H-Y, Tian J 2009 Effect of bromide on the formation of disinfection by-products during wastewater chlorination Water Res. 43 2391–8
[20] Shan J, Hu J, Kaplan-Bekaroglu S, Song H and Karanfil T 2012 The effects of pH, bromide and nitrite on halonitromethane and trihalomethane formation from amino acids and amino sugars Chemosphere 86 323–8