Study of disinfectant type effect on the organohalogen compounds formation in water treatment

T Krasnova¹, Y Skolubovich² *, D Volkov², I Timoshchuk¹ and A Gorelkina¹

¹Kemerov State University, Stroiteley Av., Kemerovo, 65000, Russia
²Novosibirsk State University of Architecture and Civil Engineering (Sibstrin), 113, Leningradskaya str., Novosibirsk, 630008, Russia
E-mail: *skolubovich@sibstrin.ru

Abstract. In practice of water supply, mainly, chlorine gas is used in the preparation of drinking water supply system, which is toxic, combustible and explosive. In this regard, the urgent problem is the replacement of gaseous chlorine with a safer disinfectant, which provides at least equivalent results at all stages of water treatment. We have studied the possibility and effectiveness of using technical sodium hypochlorite. Contents of organic substances in river water and the concentration of organohalogen compounds in drinking water, regardless of the season (25% on average) with the use of sodium hypochlorite as a disinfectant were established in this research work. It was shown that periodically during 6 months of the year (March- August) the concentration of chloroform and trichlorethylene exceeded MPC normalized values of these substances in drinking water, which necessitated the development of a technology for water purification from organohalogen compounds.

1. Introduction

Water quality control of surface sources in various country regions indicates that the content of chlorine-containing organic compounds in surface waters increases due to natural processes and industrial water in the spring-summer period [1]. Mostly the presence of chloroform and trichlorethylene was noted. In addition, trichlorethylene and other halogen-containing organic compound (HCC): chloroform, carbon tetrachloride, dichloroethane, bromodichloromethane are formed in the natural water treatment process with chlorine agents [2-6]. The existing technology for the drinking water preparation does not provide complete purification from organic substances.

Numerous studies of the recent years have shown that the consumption of such water increases the risk of various pathologies, in particular birth defects [7–13]: a cleft palate, a defect in the septum between two heart ventricles, and heart and brain defects. The carcinogenic effect of HCC on human health was revealed (liver cancer, kidneys, pancreas, bladder, small and rectum) [14-16]. According to Sanitary Rules and Regulations 2.1.4.1074-01 “Drinking water. Hygienic requirements for water quality of central drinking water supply systems. Quality control "MPC of chloroform is 0.060 mg / dm³, trichlorethylene is 0.005 mg / dm³."

2. Materials and methods

Sodium hypochlorite is a liquid containing 40 - 90 g / dm³ of alkali and 120 - 160 g / dm³ of active chlorine, water from a water supply source (river) and drinking water, prepared with gaseous chlorine and sodium hypochlorite as disinfectants.
The content of chloroform, trichlorethylene, dichloroethane, carbon tetrachloride, dibromomethane, bromodichloromethane was determined by liquid chromatography on a Crystal 2000 chromatograph with an electron capture detector and specific sensitivity to halogen-containing compounds (up to 10-13 g).

3. Results
A systematic study of the river water quality of years has established. It is contaminated with phenols, organic compounds of various nature, suspended solids, and nitrogen compounds. Studies on the quality of water sources were conducted in order to assess the contribution of river water to the decrease in the quality of drinking water due to the content of HCC during the year. In the period from December to June, the presence of organohalogen compounds in the river water was not revealed. However, a constant presence of chloroform and trichlorethylene in concentrations not exceeding the MPC was noted in river water from the third decade of June until the end of August. In October - December, traces of chloroform and trichlorethylene were observed in the samples. During the study period, dichloroethane, carbon tetrachloride, dibromomethane, bromodichloromethane were not found in river water.

Hygienic studies have established that sodium hypochlorite in terms of bactericidal action is equivalent to liquid chlorine. A comparative study of the coagulation process indicates the coagulation process proceeds identically regardless of the water impurities oxidation method [1].

A comparative study of the halogen-containing organic compounds was carried out using liquid chlorine and sodium hypochlorite as disinfectants in order to clarify the effect of disinfectant type and seasonal changes in the content of organic substances in river water on the drinking water quality.

The study data, presented on Figure 1, 2, show that in winter the content of organohalogen compounds in drinking water does not exceed 0.03 mg / dm$^3$, and trichlorethylene is 0.001 mg / dm$^3$ and does not undergo sharp fluctuations. During this period, the concentration of HCC in water treated with sodium hypochlorite is on average 7.5% lower than in samples treated with chlorine. The obtained results are stable and unambiguous. At the same time, the change in the concentration of the halogen-containing compounds’ sum and trichlorethylene in water treated with chlorine-containing disinfectants are spasmodic in March-August.

This dependence is obviously associated with a periodic increase in the intake of natural organic compounds with melt water and rains (due to the extraction of humic and fulvic acids from soils, decomposition of animal and plant residues). Halogen-containing organic compounds are formed in water bodies, as a result of microbiological and hydrolytic destruction of humic compounds and fulvic acids. The intensity of the destruction processes increases with high water temperature. A number of studies noted an increase of organohalogen compounds in rivers in the summer season [1, 17, 18].

mg / dm$^3$

Figure 1. Dynamics of changes in the amount of halogen-containing organic compounds in drinking water after treatment with a disinfectant: 1 - sodium hypochlorite; 2 - liquid chlorine.
The obtained data can be explained as follows. It is aqueous humus (humic (HA) and fulvic acids (FA)) suggested by the literature analysis, are responsible for the appearance of organohalogen compounds in drinking water and their structural structure determines the molecular features and chemical properties [19]. The most informative and explaining almost all known experimental data is the structure diagram of humic acids proposed by D.S. Orlov [20] and supplemented by S.N. Chukov [21]. The structural cell is the smallest part of the macromolecule that contains a set of structural fragments according to D.S. Orlov (Figure 3). The characteristic fragments of the molecule non-hydrolyzable part and typical methods of their connection are reflected, and the hydrolyzable periphery is given as a set of structural components, which number and nature of the articulation varies. The composition and structure of the structural cells of entire macromolecule can also vary. Substitutions are also possible in the components’ composition of the molecules hydrolyzable part in the substitution types of “core” six-membered rings, as well as in the set and nature of the these rings articulation. In this case, the core may include highly polymerized forms of aromatic carbon.

The variety of HA and FC structural units explains the appearance of a whole set of chlorine derivatives in drinking water during chlorination (chloroform, trichlorethylene, carbon tetrachloride, dibromochloromethane, bromodichloromethane, etc.) (Figure 3.4). In addition, the precursors of organohalogen compounds in drinking water can be organic substances that have fallen into water bodies from industrial sewage during rains and snowmelt.

Both aliphatic and aromatic structural units of HA and FA enter into reaction reactions, according the identified products with chlorine (Table 1). The appearance of low molecular weight compounds under the action of chlorine on HA and FA macromolecules is obviously possible only through the stage of chlorination products appearance with an intermediate molecular weight. Thus, the oxidation of humic acids [18] was suggested to proceed through an intermediate stage of hypochlorous acid ester formation by the hydroxy groups of humic acids, which decomposes, then under the influence of the OH– ion (Figure 5).
Figure 4. The structural formula of fulvic acids.

Table 1. Reactions of the humic structural groups’ interaction and fulvic acids.

| Structural group | Interaction type          |
|------------------|---------------------------|
| COOH             | carboxylic                |
| CAr – OH         | phenolic                  |
| >C – O           | carbonyl                  |
| C6H5             | benzene                   |
| – CHn             | aliphatic radical         |

Figure 5. Haloform reaction.

It should be noted that the quantitative and qualitative composition of organic components changes due to the constant supply of substances that are unusual for water, including petroleum products because of rain and washout of pollution from city streets, industrial sites from March to September. The content of organohalogen compounds in drinking water turns out to be 2-2.5 times higher than in winter at such moments.

An increase in the content of halogen-containing organic compounds in water sources naturally leads to an increase in their concentration in drinking water.

Chloroform presence in river water in summer caused an increase in its concentration in samples of river water treated with chlorine-containing disinfectants. Thus, the content of chloroform in June, July, and August was 0.07, 0.0682, and 0.074 mg / dm³, respectively, exceeded the MPC by 1.16, 1.13 and 1.24 times in samples of river water treated with liquid chlorine. In samples, treated with sodium hypochlorite, the chloroform content was in the range of 0.0433 - 0.0527, it was high enough, but did not exceed MPC during this period, (Figure 1).
Trichlorethylene in river water also led to an increase in its concentration in samples of drinking water, especially those treated with liquid chlorine. So, in the period from June to July, the content of trichlorethylene in samples treated with chlorine amounted to 0.006-0.009 mg/dm³ exceeded MPC by 1.2-1.8 times, and in samples treated with sodium hypochlorite - 0.004-0.007, exceeded 0.8-1.4 MAC (Figure 2).

In all samples of drinking water, bromodichloromethane is present in quantities significantly lower than MPC, regardless of the chlorine-containing disinfectant used. Dibromochloromethane, carbon tetrachloride and dichloroethane were not detected in any of the samples.

The results show that, regardless of the season, content of organic and mineral components, concentration of organohalogen compounds in water treated with sodium hypochlorite is lower than in water treated with chlorine. In April - August, this difference can reach up to 40%. The decrease in the content of halogen-containing organic compounds, using sodium hypochlorite is obviously due to the inhibitory effect of the sodium ion [17] formed during the hydrolysis of sodium hypochlorite.

\[
\text{NaClO} + \text{H}_2\text{O} \rightarrow \text{HClO} + \text{Na}^+ + \text{OH}^- \\
\text{HClO} \rightarrow \text{HCl} + \text{O}
\]

4. Conclusion
It was established that the content of organic substances in river water and the concentration of organohalogen compounds in drinking water were lower, regardless of the season (25% on average) with the use of sodium hypochlorite as a disinfectant, which made it possible to recommend it for practical use.

It was shown that periodically during 6 months of the year (March-August) the concentration of chloroform and trichlorethylene exceeded MPC normalized values of these substances in drinking water, which necessitated the development of a technology for the water purification from organohalogen compounds.

Acknowledgments
The study was carried out as part of the R&D program of the Scientific Council of the Russian Academy of Sciences in Physical Chemistry No. 20-03-460-27.

References
[1] Krasnova T A and Skolubovich Yu L 2012 Water disinfection in the drinking water supply system, Mon. Novosibirsk, NSUACE (Sibstrin), p 114
[2] Richardson S 2011 Water Analysis: Emerging Contaminants and Current Issues, Anal. Chem, p 83
[3] Richardson S 2011 Disinfection by-products: formation and occurrence of drinking water, in Nriagu, Environmental Health, Elsevier, Burlington, USA, Vol 2,
[4] Richardson S 2012 Mass Spectrometry Identification and Quantification of Toxically Important Drinking Water Disinfection By-Products, in Comprehensive Environmental Mass Spectrometry, ILM Publications, Dorset, UK,
[5] Dmitrenko E A 2010 The processes of formation of trihalomethanes in the water supply networks of Donetsk region, Science Newsletter of the National Medical University, 27, p 121
[6] Mokienko A V 2013 Halogenated compounds (HSS) as products of water chlorination. The first message. General state of the problem (part 2), Actual problems of transport medicine, 1 (31), pp 22-32
[7] Egorova N A, Bukshuk G N and Krasnovsky G N 2003 Hygienic assessment of drinking water chlorinated products, taking into account routes plurality of entry into the body, Hygiene and sanitation, 2, pp18-24 (2003)
[8] Drozdova E V 2016 On the issue of the formation of drinking water by-products disinfection (regulated and emergent), their genotoxic and carcinogenic properties: a problem review and
directions for further research, *Health and the environment: a collection of scientific papers*, Minsk, RSMB, 26, pp 12-16

[9] Kvitka L A 2016 Negative consequences of water preliminary chlorination and methods for their elimination, *Bulletin of the technological and methodical association for education in the field of environmental engineering and water use*, 9, pp 126-131

[10] Kirsanov V V 2012 Sanitary and hygienic characteristics of the possible impact on the public health of by-products of wastewater chlorination and drinking water, *Bulletin of Kazan Technological University*, 4,15, pp 93 – 96

[11] Baytak D 2008 Seasonal variation in drinking water concentrations of disinfection by-products in IZMIR and associated human health risks, *Science of The Total Environment*, 407 (1), pp 286-296

[12] Bruchet A 2008 Where do the odorous halogenated phenols in drinking water resources come from? Water Science & Technology: Water Supply — WSTWS, 3, pp 263 – 269

[13] Krasnova T A 2017 Choice of sorbent for adsorption extraction of chloroform from drinking water, *Foods and Raw materials*, 2, pp 189-196

[14] Boku D S 2012 Production control of swimming pool water on chloroform *Health. Medical ecology. The science*, 3-4, pp 78-79

[15] Bove G E 2007 Case control study of the geographic variability of exposure to disinfectant byproducts and risk for rectal cancer, *International Journal of Health Geographics*, 6,

[16] Hwang B F 2008 Water disinfection byproducts and the risk of specific birth defects: a population-based cross-sectional study in Taiwan, *Environmental Health*, 7 (1), pp 19-29

[17] Nieuwenhuijsen M J 2009 The epidemiology and possible mechanisms of disinfection by-products in drinking water, *Physical, Mathematical and Engineering Sciences*, 367, pp 4043-4076

[18] Gunther L A 1988, The influence of inorganic impurities of natural waters on the formation of chloroform in drinking water, Chemistry and technology of water,T. 10, 2, pp 110-112

[19] Slavinskaya G V 1991 The effect of chlorination on the quality of drinking water, *Chemistry and technology of water*, T.12, 11, pp 1013-1022

[20] Yagovkin A K 2009 Development of ideas about the molecular organization of complex organic systems - humic acids, *Bulletin of Ugra State University*, 3, pp 80-86

[21] Orlov D S 1990 *Humic acids of soils and the general theory of humification*, Moscow Publishing House of MSU,

[22] Orlov D S 2004 Humic acids: functions and structural features, *Sat. abstracts of the IV Congress*, Novosibirsk, 1, p 323