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Sustained public health protection also via haloacetic acids monitoring

Miroslav Horváth [1,*] and Martina Horváth [2]

[1] *Regional Office of Public Health in Bratislava, Department of chemical analysis, Ružinovská 8, Bratislava, 82009.*
[2] *Medirex, a.s., Galvániho 17/c, Bratislava, 82104, Slovakia.*

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Abstract

Haloacetic acids present in drinking water originate from chlorinated disinfection interacting with organic matter and bromide ions. We delve into the tangled web of these pollutants and monitor levels of five key elements: mono-, di-, trichloroacetic acid, and mono- and dibromoacetic acid. Our research reveals not only the numbers, but also their impact on human health, from skin reactions to oncological diseases. European Union legislation sets a maximum concentration of 60 µg/l, which governs our study in the vibrant Bratislava region, where almost three quarters of a million inhabitants live in four dynamic districts: Bratislava, Pezinok, Malacky and Senec.

This study provides data from a comprehensive analysis of 281 samples from 2019 to 2024. We examine more than just numbers. Our findings reveal not only overall disinfection methods, but also shed light on the unique presence of each haloacetic acid (as the analyte of interest) over time. Our results, visualized through tables and graphs, paint a vivid picture of water quality dynamics.

Keywords: Haloacetic Acids; Disinfection; Monitoring; Legislation

1. Introduction

Haloacetic acids, or HAAs, are derived exclusively from water that undergoes disinfection with chlorine compounds such as Cl_2, ClO_2, NaClO, in situ generated NH_2Cl and contain organic pollutants from water sources, including inorganic bromide anions. In the middle of this chemical mix of substances there are various forms of haloacetic acids containing chlorine and bromine. From a formal perspective, in addition to the most commonly monitored three chlorinated and two brominated acids (monochloroacetic acid - MCA, dichloroacetic acid - DCA, trichloroacetic acid - TCA, monobromoacetic acid - MBA, and dibromoacetic acid - DBA), other acids such as tribromoacetic acid (TBA), dibromochloroacetic acid (DBCA), bromodichloroacetic acid (BDCA), and bromochloroacetic acid (BCA) can also form. However, the latter four are typically below the detection or quantification limits (LOD, LOQ), and regulatory limits on their total presence in drinking water do not apply to them. This trend is also observed in many other countries, where only the aforementioned five HAAs are monitored. For example, in the European Union and the United States, the maximum allowable limit for their sum is set at 60 µg/L, while in Canada and China (where only DCA and TCA are monitored), the limit is less stringent at 80 µg/L (2).

Disinfection by-products in water, such as HAAs, have been shown to have a negative impact on human health with prolonged exposure to higher concentrations. The usual routes of intake are oral (via drinking) and transdermal (via bathing). Among the individual acids, chlorinated acetic acids are well-studied in terms of their entry into the body, metabolism, target tissue selection, mutagenicity, carcinogenicity, overall toxicity, and excretion. However, knowledge about brominated derivatives or interhalogen acetic acids remains insufficiently explored (3).

* Corresponding author: Miroslav Horváth.

It is widely known that long-term exposure to higher concentrations of HAAs can lead to skin problems (eczema, rashes), increase the risk of low birth weight in pregnant women (small for gestational age – SGA), and, as they restrict intrauterine growth, may also affect neonatal length (birth length below the norm) (4). Since HAAs are typically transported in the body as acyl groups, they can act as effective alkylating agents due to the presence of halogens. This poses a risk to both male and female gametes, potentially causing undesired genetic changes. Among chlorinated derivatives, MCA exhibits the highest cyto- and genotoxicity. It affects embryos by inducing dysmorphogenesis in neural tube and eye development and causes anomalies in heart development. DBA disrupts spermatogenesis and impairs testicular steroidogenesis in men (5). In women, it negatively influences the estrogen cycle and suppresses estradiol catabolism, leading to alterations in the production of female sex hormones (6,7). An extreme outcome associated with the effects of HAAs is cancer. These compounds primarily attack the inner lining of rapidly proliferating cells in the excretory system organs (8), making tumors of the colon, rectum, and bladder typical. Additionally, oral intake has been documented to cause toxic effects on endocrine glands such as the liver and pancreas (9, 10).

HAAs are removed from drinking water almost exclusively through additional water treatment processes. Typically, the formed HAAs are removed either chemically (most commonly by ozone) or physically (via UV radiation). In addition to HAAs, ozone also removes other pollutants generated during water disinfection, as well as contaminants from human activities. It also helps regulate the taste and odor of water, and can be used for decolorization. Its stability in water is low, but it generates the strongest oxidant possible in water – the hydroxyl radical (·OH). This radical is capable of oxidizing both small and large (biomacro)molecules, including double bonds and conjugated systems. A disadvantage is that, in the presence of high organic contamination, a large number of oxidation by-products are produced. UV radiation offers undeniable advantages in removing HAAs from water. Degradation occurs without the need for additional chemical reagents and is highly effective microbiologically. Since 2017, it has been used as the sole disinfectant in several municipalities in the Bratislava region (currently in 7 smaller towns and villages) as long-term comprehensive monitoring of drinking water has demonstrated its excellent quality (11). However, its disadvantages include the commercial cost and the necessary technical equipment, which is difficult to implement for large water reservoirs.

2. Experimental Part

The Regional Public Health Office based in Bratislava monitors the quality of drinking water in four districts of the Bratislava region, as geographically illustrated in Figure 1. During the period from 2019 to 2024, 281 samples were analyzed.

Figure 1 Sampling locations in the Bratislava region

The water sources in these locations include the Bratislava Water Company, which uses Sihoť, Pečniansky Forest, Rusovce-Ostrovné Lúčky-Mokraď, Sedláčkov Island, and Čunovo as reservoirs. Other territorial units fall under the so-called group water systems (abbreviated SKV) – Záhorský SKV, SKV Senica, SKV Skalica-Holíč, and Podhorský SKV.

The sample preparation is typically carried out within 3-5 days of receipt. During this period, it is stored in the dark and cool conditions. Figure 2 illustrates the chemical transformation of analytes into methyl esters, which are then identified and quantified using GC-MS with absorption on the stationary phase – a column with a sorbent to fix HAAs.

Derivatization is essential primarily due to the significantly polar nature of the individual HAAs, as well as the potentially lower stability of free HAAs under the conditions of the analysis.

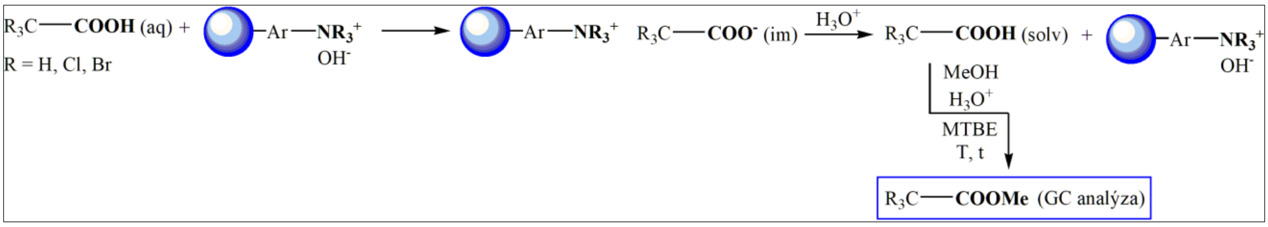

Figure 2 Schematic representation of the derivatization of HAAs into methyl esters (im – immobilized, solv – solvated)

The individual steps of isolation and derivatization can be briefly summarized into six consecutive steps, which are followed by analysis:

- Immobilization on the column (HAAs $_{aq}$ → HAAs $_{im}$) – transformation of dissolved HAAs into insoluble ammonium salts (immobilization),
- Elimination of water-soluble impurities by washing with distilled water,
- Elution from the column with an organic solution of H_3O^+ (HAAs $_{im.}$ → HAAs $_{org.\ solv.}$),
- Esterification – temperature (T), time (t),
- Neutralization with HCO_3^-,
- Dehydration ("drying") of the organic extract,
- Analysis.

Immobilization on the sorbent allows only acidic analytes to be captured, while all neutral and basic compounds are removed by washing the column with the sorbent. HAAs are then released from the sorbent binding using acidified methanol, and in the presence of another organic solvent that is immiscible with water (methyl-*tert*-butyl ether – MTBE), esterification occurs at an elevated temperature. The sorbent is shown in Figure 3.

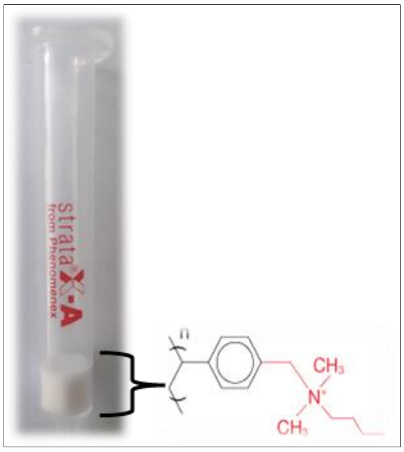

Figure 3 The sorbent with the ammonium residue, which reversibly binds haloacetate anions

3. Results and discussion

The frequencies of occurrence of individual HAAs over the four-year period are summarized in Table 1. Values above the LOQ (values included in the total sum of HAAs) and below the LOD (values not included in the total sum of HAAs) are presented.

Table 1 Frequencies of occurrence of individual HAAs in drinking water samples

Year	Number of samples	MCA		DCA		TCA		MBA		DBA	
		<LOD	>LOQ	<LOD	>LOQ	<LOD	>LOQ	<LOD	>LOQ	<LOD	>LOQ
2019	44	43	1	38	6	44	0	44	0	36	8
2020	49	38	11	8	41	30	19	26	13	11	38
2021	45	6	39	0	45	16	29	10	35	3	42
2022	48	36	12	2	46	17	31	26	22	10	38
2023	47	35	12	3	44	11	36	19	28	16	31
2024	48	33	15	10	38	15	33	16	32	12	36

It is clearly confirmed that the lowest values of individual HAAs were recorded in the period before the Covid-19 pandemic (2019). In the case of MCA, there was only one detection, and for TCA and MBA, there were none. The increased need for disinfection to stop the spread of the virus naturally affected all areas of life, including drinking water. However, the occurrence of MCA has been consistently lower over time. This is mainly due to its higher reactivity (higher δ+ charge on C2 compared to unsubstituted AcOH) and thus increased susceptibility to further halogenation. The same effect can be observed with MBA, which is even more reactive than MCA due to the bulkier and more favorable bromine atom for stabilizing the radical or carbocation (SR or SE mechanism of bromination). This assumption is fully reflected in the frequency of occurrence of DCA and DBA, which are predominantly present. The relatively low representation of TCA is mainly due to the reactivity and chemically lower "willingness" of DCA to undergo a higher degree of halogenation, as well as the consumption of the disinfectant for other (bio)chemical reactions. Steric and electronic effects make this process energetically more demanding and, therefore, less frequent, even with an excess of halogen in the water under the given disinfection conditions. Additionally, it should be noted that the concentration of brominated HAAs depends on the concentration of bromide anions in the water, which are released from the substrate of the water source. Groundwater is generally more mineralized than surface water. And since the Bratislava region draws drinking water almost exclusively from groundwater sources, there is no shortage of naturally occurring inorganic bromine.

It is evident that DCA and DBA are the most prevalently represented in the samples, with the highest measured concentrations. This highlights the significant reactivity of MCA and MBA during further halogenation, which, on the other hand, show the lowest occurrence rates and measured concentrations. Similar results apply to TCA, where, as already mentioned, the substitution of three hydrogen atoms is less favorable. This is even more true for the formation of TBA, which is not monitored by law, even in other countries. It is highly unlikely that under disinfection conditions, a triple substitution with the significantly larger bromine atom will occur. All the results so far are also represented by a graphical visualization of numerical statistical data (mean value, relative deviation, and median - see Figure 4 and Table 2) in the form of a box plot (excluding values below LOQ). From this, the relative proportions of individual HAAs are evident, along with the average concentration values, their distribution, and the frequency of occurrence of HAAs.

Table 2 Statistical data on HAAs and their sum (μg/L) for the period 2019-2024

	MBA	DBA	MCA	DCA	TCA	∑ HAAs
AVERAGE	0.1245	0.8585	0.1136	0.7612	0.4432	1.8016
STDEV	0.1035	0.6774	0.0834	1.0519	0.6651	1.4588
MEDIAN	0.0933	0.7708	0.0857	0.4911	0.2885	1.7555

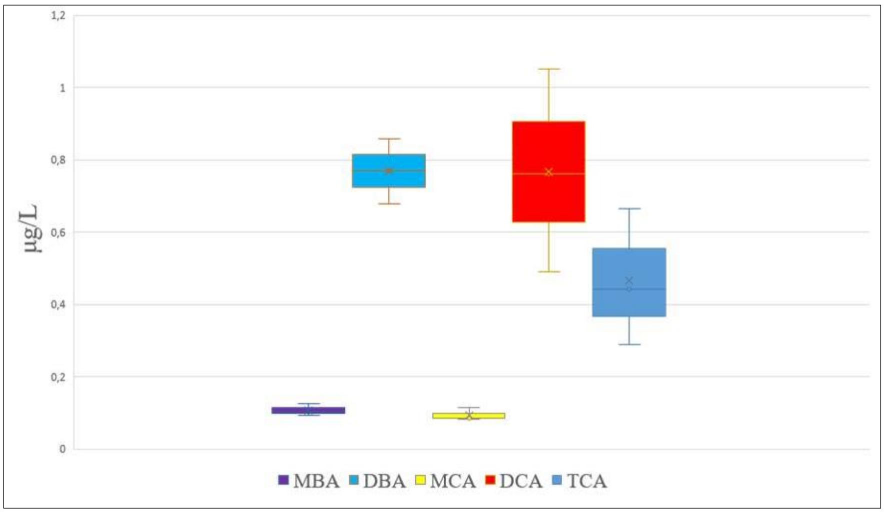

Figure 4 Statistical data on HAAs for the period 2019-2024

Summarizing the results, it was found that the highest quality drinking water source is in the municipality of Malinovo. The Žitný ostrov, from which the drinking water for this locality is primarily sourced, provides high-quality water, and further treatment is minimal. Additionally, the municipality of Dunajská Lužná has been using UV radiation for water treatment since 2017. It is known that this high-energy radiation effectively removes HAAs from the water, resulting in less toxic compounds. The distribution system is also relatively long, and biodegradation as well as gradual chemical breakdown of HAAs may lead to terminal collection points providing residents with water of significant purity. Figure 5 shows the transmission system with additional water sources that supply drinking water to Malinovo.

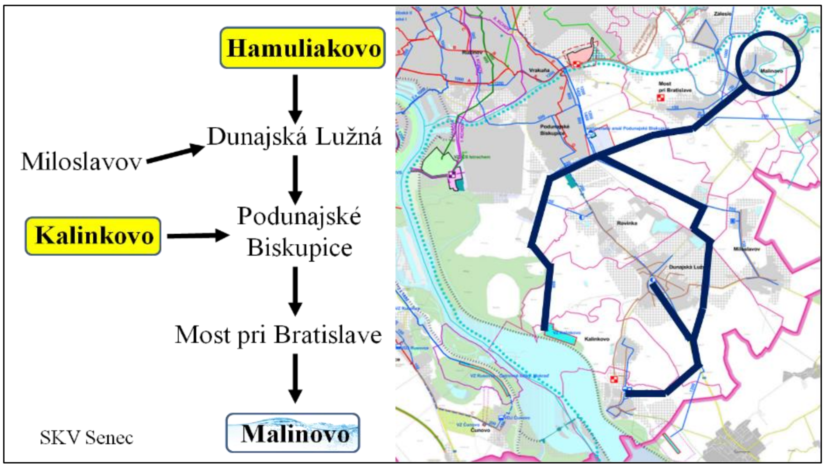

Figure 5 Transmission Water Supply Network Hamuliakovo, Kalinkovo – Malinovo

However, the provided information will continue to be compared with other parameters that indicate the chemical quality of drinking water (free Cl_2, ClO_2, content of trihalomethanes, XO_2^- and XO_3^- - X = Cl, Br). Overall, it can be summarized that none of the samples exceeded the state-mandated limit of 60 µg/L. The highest measured sum of HAAs was only 10.922 µg/L, which is within the norm.

4. Conclusion

During the period from 2019 to 2024, HAAs were monitored in a total of 281 samples. Five analytes and their total sum were tracked. None of the samples exceeded the limit. The highest water quality was recorded in the municipality of Malinovo. Overall, it can be concluded that the quality of drinking water in the Bratislava region during the monitored period is excellent in terms of HAAs content.

Compliance with ethical standards

Disclosure of conflict of interest

The authors declare that they have no known competing financial interests or personal relationships influenced by this work.

Authors contribution statement

Horváth Miroslav * - investigation, data interpretation, software, writing original draft, conceptualization, figures, and tables preparation, formal analysis and editing mail – ba.horvath@uvzsr.sk Horváth Martina - investigation, guided, validation, writing - review, and editing mail- martina.horvath@medirex.sk.

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