Application of mathematical models for predicting the trihalomethanes content in drinking water in the city of Kumanova, North Macedonia

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Abstract – Trihalomethanes (THMs) are created as a result of the reaction between chlorine used to disinfect drinking water and natural organic matter in water. At high levels, THMs have been associated with cancer. As a consequence, THMs must be constantly monitored. They are mainly determined by the method of gas chromatography, which is a more difficult procedure and at a higher cost. In recent years, however, mathematical models have been used to predict THMs. These models work by measuring some physico-chemical parameters of drinking water, those values of these parameters are replaced in mathematical models and the THMs content in drinking water can be predicted. The main purpose of this paper was to predict the content of THMs in the drinking water of the city of Kumanova. The measured parameters were: temperature, residual chlorine, pH, electrical conductivity, chemical oxygen, total dissolved solids and chlorides. Measurements were made during the spring season 2022 in the four sampling points. Ten mathematical models were used for prediction and of them the average value with standard deviation of THM was 26.9532 ± 10.03 µg/L. From the result we can conclude that content of THM does not pose a risk to the health of the population.

Keywords - THMs, Physico-Chemical Parameters, Drinking Water, Mathematical Models for Prediction, Health

I. INTRODUCTION

Disinfection by-products (DBPs) are a class of chemicals that are formed when disinfectants react with organic compounds of drinking water [1]. Some of the DBPs may be carcinogenic and some are suspected of causing health effects. They are undesirable chemical compounds that are created as a result of water disinfection and oxidation. According to Krasner et al., DBPs are classified into
four major classes: trihalomethanes (THMs), haloacetic acids (HAAs), haloacetonitriles (HANs) and halocetones (HKs) [2]. So, a special class of DBPs are THMs, which in addition to carbon, they also contain chlorine and bromine.

THMs were discovered in 1974 by Rook (Netherlands) and Bellar (USA). They first identified chloroform (CHCl$_3$), which is the main THMs in drinking water and are in trace concentration (μg/L). After that date, many other DBPs were identified in chlorinated drinking water, eg. brominated THMs, haloacetic acids, halocetones etc. More than 500 DBPs have been identified in tap waters and since 1980 they have raised great concern due to the fact that they cause side effects in human health, cancer and reproductive disorders [3].

Interest in studying organic substances in drinking water began in 1974 with the detection of haloforms or trihalomethanes by Rook J. during the quality control of water treatment at the Berenplaat, Netherlands [4]. THMs as synthetic organic compounds are created by replacement of three hydrogen atoms in the methane molecule with the atoms of the halogen elements. Chloroform or trichloromethane (CHCl$_3$), bromochloromethane (CHBrCl$_2$), dibromochlormethane (CHBr$_2$Cl) and bromoform or tribromomethane (CHBr$_3$) can be formed during chlorination. Their formation during chlorination represents a very serious health problem as chloroform, main subspecies of THMs formed in this process, implicated in several types of cancers in laboratory animals.

In recent years, modeling for predicting of THM concentration is the contemporary trend. Relevant models are developed with adequate statistical processing of THMs data with the help of statistical programs. Statistical software used for this purpose are, Statistical Package for the Social Sciences (SPSS), Statgraphics etc. The models confirm the empirical or mechanical correlation between THMs contents in drinking water and water quality parameters and their control may be related to the formation of THMs. These models are applied based on routine measurements of some drinking water parameters and with their help predict (calculate) the concentration of THMs in drinking water. These models are use friendly and can be used by any worker in the drinking water plant to estimate the concentration of THM at any given time.

A number of models have been developed to predict mathematically the total THMs (TTHMs) from the water source characteristics. This enables the calculation of TTHMs without the need for intensive sampling. Golfinopoulos et al. developed a model for TTHMs depending on chlorophyl a, pH, bromine concentration, season, temperature and chlorine concentration [5]. The model showed that the concentration of TTHMs increases with the concentration of chlorophyl a, bromine ion concentration, temperature, chlorine concentration, and whether the samples were taken in spring or summer. According to him TTHMs concentration decreases with pH and temperature of the samples in the spring and summer season. Rodriguez and Serodes developed a model for predicting TTHMs in finished water in three plants and TTHMs producing at distribution system points [6]. In two plants it was found that the temperature was the only significant variable and TTHMs concentration increased with temperature. For the third plant the temperature, pH and flow rate were important variables. It was noted that the concentration of TTHMs increased with temperature, and decreased with pH and flow. Villanova et al., developed a model in two Torres river water treatment plants in the city of Salamanca, Spain [7]. This one-year research showed that temperature and pH were the only variables important for the formation of chloroform. Observed results versus calculated values had a high value of $R^2 = 0.99$. As we can see, simple and some very complicated models for the THMs prediction have been developed.

Statistical analysis of results with multifactor variance analysis has revealed the influence of the parameters in the formation of THMs. The simple and multiple regression were used to develop predictive models for THMs formation. These models serve to predict concentrations of THMs in drinking water after monitoring the THMs and following relevant experiments on the impact of various factors on THMs concentration in drinking water. Each developed model is suitable only for
drinking water with similar characteristics. So, a similar model cannot be used to predict THMs in drinking water of different locations with different characteristics and qualities [1].

Thus, Elshorbagy has modeled the formation of different THMs under strictly extreme conditions of chlorine concentration, temperature and bromine ion concentration [8]. Clark and Mano developed a mathematical model that predicts THMs concentration as a function of pH, temperature, initial chlorine concentration and total organic carbon (TOC) [9]. Montgomery Watson Consulting Engineering modeled the THMs formation associated with TOC, pH, temperature, chlorine concentration, bromine ion concentration and contact time [10]. Some other researchers such as Clark et al., studied the effect of the bromine ion concentration on THMs formation [11]. Other researcher studying the effect of other factors in THMs formation. Karimi and Singer reported a strong correlation between algae productivity and THM formation potential (THMFP) [12]. Canale et al., link THMFP with chlorophyll, zooplankton, water depth, dissolved oxygen and total phosphorus [13]. The aim of this paper was the prediction of the THMs content in drinking water in the city of Kumanova for the spring 2022.

II. MATERIALS AND METHODS

Sampling stations, periods and sampling
Drinking water sampling stations are appropriately selected. Four stations (K1 - K4) have been designated in the city of Kumanova. Serious account has been taken of the distance between the stations in order to cover a certain part of the city's territory as well as possible and to enable logical conclusions to be drawn. The stations were: K1 - Street Josko Ilievski No. 45; K2 - General Hospital, K3 – Sirova voda station and K4 - Green Market. From the mentioned stations, drinking water samples were taken every week in the months of March, April, May and June of 2022 (spring season) to determine the values of some of the most necessary drinking water quality parameters. These parameters have been imperative for predicting the concentration of THMs with mathematical models.

The method of sampling has a great influence on the obtained results of the analyses. Sampling was done according to the recommendations of the State Regulation on drinking water of the Republic of North Macedonia, which is harmonized with WHO and EU recommendations [14]. Drinking water samples were taken in polyethylene and glass bottles with a volume of 1.5 L. We filled the bottles up to the lid without leaving space and air bubbles in the sample.

Measured parameters, reagents and instruments
In this paper, in the spring season, the monitoring of the seven most important drinking water parameters was carried out: water temperature (WT), residual chlorine (RC), pH, electrolytic conductivity (EC), total dissolved solids (TDS ), chemical oxygen demand (COD) and chlorides.

The experimental part of the paper was carried out in the field, while COD and chlorides were measured in the laboratories of the University of Tetova. For the realization of this research, relevant methodology has been used and standard methods and techniques of measuring parameters have been used in accordance with the State Regulation for drinking water. Standard physico-chemical methods were used to determine the parameters.

The following reagents were used to measure the parameters: 1) tetra-methyl-benzidine (reagent for residual chlorine), 2) buffer solutions 4, 7 and 9 (for pH-meter calibration), 3) standard KCl solution (for calibration of the conductometer), 4) H₂SO₄ solution (1:3), 5) KMnO₄ solution with c = 0.002 mol/dm³, 6) H₂C₂O₄ solution with c = 0.002 mol/dm³, 7) 10% K₂Cr₂O₇ solution (indicator for determination of chlorides) and 8) AgNO₃ solution with c = 0.0281 mol/dm³.

The following equipment and instruments were used to determine the physico-chemical parameters: a thermometer was used to measure the temperature (an integral part of the conductometer), a portable Conductivity Meter, WTW LF 320, was used to measure EC and TDS; pH measurement was done with a portable pH meter 330i, WTW; RC was measured colorimetrically with a comparator; chlorides were determined by argentometric titration and COD was determined by standard
procedure using oxidizing reagents KMnO₄ and H₂C₂O₄.

### III. RESULTS AND DISCUSSION

The results of the measurements of this paper are presented in Figure 1 and Table 1.

**Water Temperature (WT)**

Temperature plays a crucial role in the physico-chemical and biological behavior of the water system [15]. Chemical reactions depend on water temperature and it controls the metabolic and reproductive processes of aquatic species. The water samples analyzed from the drinking water of the city of Kumano had approximate temperatures, but some exceeded the recommended value of the State Regulation. The range for WT was 8.50 - 13.00 °C. The lowest temperature of 8.50 °C was found in the month of March in K1, while the highest temperature of 14.0 °C was found in the month of April and June in K1 and K4. The average water temperature values in the months of March, April, May and June were 9.675, 12.175, 10.125 and 12.125 respectively. The average seasonal value with standard deviation was 11.025 ±1.3121 °C. Some values of this parameter were higher compared to the State Regulation for drinking water (Fig. 1).

**Residual Chlorine (RC)**

RC is of great importance to determine the presence or absence of microorganisms in drinking water. Its presence in drinking water indicates that a sufficient amount of chlorine has been added to the water first to inactivate bacteria and some viruses that cause diseases such as diarrhea and also to protect the water from recontamination during storage. The range for RC was 0.20 - 0.50 mg/L (Fig. 1). The average values in the months of March, April, May and June were 0.4125, 0.3375, 0.3500 dhe 0.3125 mg/L, respectively. The average seasonal value with standard deviation was 0.3531±0.0425 mg/L, which was higher than the recommended value of the state regulation.

**pH Value**

The pH value of aquatic ecosystems depends on the chemical and biological activity of the water. Natural waters usually have a pH value higher than 7. This results from CO₂ from the atmosphere and from that which is released from the decomposition of organic matter as well as from human activity. CO₂ dissolves in water and forms H₂CO₃. This acid acts with CaCO₃ of surface water and forms CaHCO₃ and as a result natural waters have a value of pH>7. The water samples that we analyzed had pH values with a range of 7.1 - 7.69. The lowest value was in the month of April in K1, while the highest value was in May in K3. The average values in March, April, May and June were 7.41, 7.24625, 7.47375 and 7.28 respectively (Fig. 1). The average seasonal value with standard deviation was 7.3525±0.1070, which was in accordance with the state regulation.

**Electrical Conductivity (EC)**

Chemically pure water has low EC. The higher the EC of natural water, the more polluted it will be. In natural waters, mineralization and productivity reactions are similar. Natural water will have less or more mineral matter depending on when these two processes dominate. EC of water indicates the general presence of chemical compounds and is an indicator of water pollution. This parameter in the four stations was different but not very pronounced. Thus, EC values ranged from 214.00 - 286.00 μS/cm. The lowest value was measured in April in K2 and K3, while the highest value was in May in K4. The average values in March, April, May and June were 278.25, 229.75, 273.625 and 233.5 respectively (Fig. 1). The average seasonal value with standard deviation was 253.7813±25.7014 μS/cm, which was within the allowed values of the state regulation.

**Chemical Oxygen Demand (COD)**

COD is usually used for the indirect measurement of the amount of organic compounds in water. The main application of COD is to quantify organic pollutants found in surface water or wastewater, making COD a useful measure of water quality. COD is the amount of oxygen required to carry out the oxidation of organic pollution using a strong
oxidizing agent. Research conducted on organic pollution of drinking water and liver cancer shows that mortality due to liver cancer is positively correlated COD of with drinking water. COD measurements have varied monthly with a range of 1.25 - 3.79 mg/L. Thus, the lowest values were in K1 and K3 in April, while the highest value was in K2 and K3 in May and June (Fig. 1). Average values during the months of March, April, May and June were 2.5525, 2.0325, 2.3617 dhe 2.0438 mg/L respectively. The average seasonal value with standard deviation was 2.2463±0.2459 mg/L, which is within the allowed values of the state regulation.

Total Dissolved Solids (TDS)

TDS is the term applied to the residue remaining in a mass measuring vessel after the sample has passed through a standard glass fiber filter and dried to constant mass at 103 - 105 °C or 179 - 181 °C. Water with high TDS content often has a laxative effect and sometimes the opposite effect on individuals whose bodies are not adapted to it. TDS mainly consists of Ca$^{2+}$, Mg$^{2+}$ ions, bicarbonates, carbonates, sulfates, chlorides, nitrates and other substances. High concentration of TDS around 3000 mg/L can also produce disturbance in animals. This parameter in four stations was different but not very pronounced. Thus, the values were brought from 123.00 - 375.00 mg/L. The lowest value was measured in March in K1, while the highest value measured in April was at K3. The average values during the months of March, April, May and June were 157.875, 261.75, 194.875 dhe 260.625 mg/L respectively. The average seasonal value with standard deviation was 218.7812 ± 51.2454 mg/L, which was lower than the recommended value of the state regulation.

Chlorides

Chlorides are less dangerous contaminants in drinking water. According to the permitted standards, their content in river waters is quite high. Chloride ions occur naturally in surface and groundwater. They are also found in high concentrations in seawater. Higher than normal chloride concentrations in freshwater are detrimental to water quality. The use of road salt for winter accident prevention is a major source of chlorides for the environment. Unfortunately, the chloride content has increased over time due to road widening and increased ground traffic. The results of our measurements of chlorides in the drinking water of the city of Kumanova for 4 months are shown in Fig. 1. Their concentration ranges from 2.83 - 5.67 mg/L. The lowest value was measured at K4 in March, while the highest value measured in April was at K3. The average values during the months of March, April, May and June were 4.2925, 4.8088, 4.3625 dhe 4.8136 mg/L respectively. The average seasonal value with standard deviation was 4.5659±0.2768 mg/L, which was within the allowed values of the state regulation.

Calculation of THM content prediction in drinking water of the city of Kumanova by mathematical models

THMs prediction models are implemented based on routine measurements of some drinking water parameters ad with their help, the concentration of THMs in drinking water is calculated. These predictive models contain different water quality parameters and individual models typically use three to eight parameters [16]. For the THMs prediction in the drinking water of Kumanova, we have used the equations of the ten mathematical models developed by [1]. Mathematical model equations and the calculation of THMs content are given below. In order to obtain a more reliable results for the prediction of THMs content for the spring season we have obtain the average value with standard deviation 26.9532 ± 10.03 μg/L (Table 1). Calculation by:

**Model 1:**

\[ THM = -10.925 + 0.688(WT) + 24.387(RC) + 0.461(pH) + 0.046(EC) + 2.076(COD) + 0.713(Chlorides) \]

**Model 2:**

\[ THM = -10.925 + 0.688(11.025) + 24.387(0.353125) + 0.461(7.3525) + 0.046(253.78125) + 2.076(2.24625) + 0.713(4.5659375) = 28.25 \ \mu g/L \]

\[ THM = 0.889 + 0.822(Chlorides) + 0.068(EC) + 21.205(RC) \]
THM = 0.889 + 0.822(4.5659375) + 0.068(253.78125) + 21.205(0.353125) = 29.38 μg/L

Model 3:
\[
\log(THM) = 0.152 + 1.147 \log(WT) + 0.158 \log(RC) + 0.458 \log(EC) - 0.557 \log(TDS) + 0.252 \log(Chlorides) + 0.240 \log(pH)
\]
\[
\log(THM) = 0.152 + 1.147 \log(11.025) + 0.158 \log(0.353125) + 0.458 \log(253.78125) - 0.557 \log(218.78125) + 0.252 \log(4.5659375) + 0.240 \log(7.3525) = 0.339 = 10^{0.339} = 2.182μg/L
\]

Model 4:
\[
THM = 1.419(WT)^{1.147} \cdot (RC)^{0.158} \cdot (PE)^{0.458} \cdot (Chlorides)^{0.252} \cdot (pH)^{0.240} \cdot (TDS)^{0.557}
\]

THM = 1.419(11.025)^{1.147} \cdot (0.353125)^{0.158} \cdot (253.78125)^{0.458} \cdot (4.5659375)^{0.252} \cdot (7.3525)^{0.240} \cdot (218.78125)^{-0.557} = 28.06 μg/L

In order to obtain a more reliable result for predicting the content of THMs for the spring season, we obtained the average value with standard deviation of THMs, as in the Table 1.

Table 1 Calculation of the mean value with standard deviation of THMs of ten models.

<table>
<thead>
<tr>
<th>Model</th>
<th>Values of THM content according to models (μg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>28.25</td>
</tr>
<tr>
<td>2</td>
<td>29.38</td>
</tr>
<tr>
<td>3</td>
<td>2.182</td>
</tr>
<tr>
<td>4</td>
<td>28.06</td>
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<td>5</td>
<td>27.54</td>
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<td>6</td>
<td>43.65</td>
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<td>7</td>
<td>27.54</td>
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<tr>
<td>8</td>
<td>26.30</td>
</tr>
<tr>
<td>9</td>
<td>28.18</td>
</tr>
<tr>
<td>10</td>
<td>28.45</td>
</tr>
</tbody>
</table>

Average 26.9532

Content of THMs 26.9532 ± 10.03 μg/L

IV. CONCLUSION

From the results obtained during the analysis of the physico-chemical parameters, namely the prediction of THMs in the city of Kumanova, we can conclude that:

- The parameter values were in accordance with the recommended values of the State Regulation on the quality of drinking water (except WT and RC);
- According to the content of inorganic and organic substances, the drinking water of the city of Kumanova is of good quality and can be used for drinking;
- The models used for the prediction of THMs have given successful results;
- The recommended value for THMs according to the National and European Regulation is 100 μg/L;
• The prediction of THMs content with the 10 models for the spring season of 2022 was $26.9532 \pm 10.03$ μg/L;
• So, for the research period THMs do not pose a risk to the health of the population;
• THMs reduction should be encouraged, but without compromising drinking water disinfection; and
• We recommend the relevant authorities to take preventive steps to keep THMs under control.

REFERENCES
Fig. 1 Spatial and temporat variation of the parameters values in drinking water.