

Application of mathematical models for predicting the trihalomethanes' content in drinking water in the city of Tetova

**Arbana Durmishi^{1*}, Agim Shabani¹, Shemsedin Abduli¹, Arianit A. Reka¹,
Ahmed Jashari¹, Murtezan Ismaili¹, Bujar H. Durmishi¹**

^{1*} Department of Chemistry, Faculty of Natural Sciences and Mathematics, University of Tetova,
^{*}Corresponding Author: arbana.du@gmail.com

Abstract

Trihalomethanes (THM) as the main by-products of disinfection are formed when chlorine acts with organic matter contained in drinking water. THMs at high concentrations are very harmful and may be carcinogenic to the liver, pancreas, nervous system, developing organs, while in women they may cause abortion. Therefore, THMs have long disturbed the scientific and public opinion. Because of this, THMs should be monitored continuously. THMs are mainly determined with the method of gas chromatography, which is a difficult and very costly procedure. To avoid this, the mathematical models used to predict THMs in drinking water have been used in recent years. By quickly measuring the values of some simple parameters of drinking water quality and replacing them in mathematical models, THMs content can be predicted. The purpose of this article is to predict the content of THMs in the drinking water of the city of Tetova for the spring season 2016 at the three sites T1, T2 and T3. The measured parameters and their average standard deviation values were: water temperature (9.81 ± 1.12 °C), residual chlorine (0.13 ± 0.01 mg/L), pH (7.47 ± 0.23), electrical conductivity (259.54 ± 24.89 µS/cm), chemical oxygen demand (3.30 ± 0.53 mg/L), total dissolved solids (452.88 ± 50.67) and chlorides (2.32 ± 0.66 mg/L) respectively. The average values are then placed in mathematical models and by calculation, the content of THMs in drinking water is predicted. Ten mathematical models were used for the prediction and their average value of the THMs with standard deviation was 17.75 ± 6.96 µg/L. This result was very close to the one experimentally measured in the spring of 2011 (20.06 ± 9.72 µg/L). From the result, we can conclude that the models used for THMs prediction have yielded successful results and this content of THMs does not pose a health risk to the population.

Keywords: THMs, physico-chemical parameters, drinking water, models for THMs prediction, health.

1. Introduction

Disinfection by-products (DBPs) are a class of chemicals that are formed when disinfectants react with organic compounds of drinking water. Some of the DBPs may be carcinogenic and some are suspected of causing acute 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) (Krasner *et al.*, 1989). So, a special class of DBPs are THMs, which in addition to carbon contain chlorine and bromine.

THMS were discovered in 1974 by Rook (Netherlands) and Bellar (USA). They first identified chloroform (CHCl₃), which is the main THMs in disinfected drinking water and is usually present at higher concentrations. Studies have found that THMs in chlorinated drinking water are in trace concentrations (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 water and since 1980 they have raised great concern due to the fact that they cause side effects in human health, cancer and reproductive disorders (Graves *et al.*, 2002).

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 plant, Netherlands (Rook, 1974). THM as synthetic organic compounds are created by the replacement of three hydrogen atoms in the methane molecule with the atoms of the halogen elements. Chloroform or trichloromethane (CHCl_3), bromochloromethane (CHBrCl_2), dibromochloromethane (CHBr_2Cl) 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 the 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 parameter and with their help predict (calculate) the concentration of THMs in drinking water. models can also use a simple worker in the drinking water plants to assess the concentration of THMs in every moment. These models can also use a simpler worker in the drinking water plant to estimate the concentration of THM at any moment.

A number of models have been developed to predict mathematically the total trihalomethanes (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 chlorophyll a, pH, bromine concentration, season, temperature, and chlorine concentration (Golfinopoulos *et al.*, 1998). The model showed that the concentration of TTHMs increases with the concentration of chlorophyll 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. Rodriguez and Serodes developed a model for predicting TTHMs in finished water in three plants and TTHMs producing at distribution system points (Rodriguez and Serodes, 2001). In two plants it was found that the temperature was the only significant variable and TTHMs concentration increased with the temperature. For the third plant the temperature, pH and flow rate were important variables. It was noted that the concentration of TTHMs increases with the temperature, and decrease with pH and flow. Villanova *et al.* developed a model in two Torres river water treatment plants in the city of Salamanca, Spain (Villanueva *et al.*, 2006). 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 you 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 studied 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 can not be used to predict THMs in drinking water of different locations with different characteristics and qualities.

Thus Elshorbagy has modeled the formation of different THMs under strictly extreme conditions of chlorine concentration, temperature and bromine ion concentration (Elshorbagy, 2000). 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) (Clark and Mano, 1998). Montgomery Watson Consulting Engineering modeled the THMs formation associated with TOC, pH, temperature, chlorine concentration, bromine ion concentration and contact time (Montgomery, 1993). Some other researchers such as Clark *et al.* studied the effect of the bromine ion concentration on THMs formation (Clark *et al.*, 1996). Other researchers studying the effect of other factors in THMs formation. Karimi and Singer reported a strong correlation between algae productivity and THM formation potential (THMPF) (Karimi and Singer, 1991). Canale *et al.* link THMPF with chlorophyll, zooplankton, water depth, dissolved oxygen and total phosphorus (Canale *et al.*, 1997).

2. Materials and Methods

2.1. Sampling stations, periods and sampling

Sampling stations for sampling drinking water in the city of Tetova are appropriately selected. They were: T1 - Teleferiku; T2 - Faculty of Mathematical and Natural Sciences and T3 - Faculty of Arts. From the mentioned stations, drinking water samples were taken every two weeks in March, April, May and June 2016 (spring season) to determine

the values of some of the most necessary parameters of drinking water quality. Parameters have been needed to predict THMs concentration with mathematical models. The method of sampling has a major impact on the obtained results of the analysis. Their acquisition was made after the careful determination of the stations and according to the recommendations of the State Drinking Water Regulation of the Republic of Macedonia (Government of the Republic of Macedonia, 2004), which is harmonized with WHO (WHO, 2005) and EU recommendations. Drinking water samples were taken in polyethylene and glass bottles with a volume of 1 L, they are rinsed 2-3 times with water sample and are filled up cap space and without air bubbles in the sample.

2.2. Measured parameters, reagents and instruments

The experimental part of the research was carried out on the field using relevant portable instruments, while the parameters chemical oxygen demand (COD) and chlorides were measured in the laboratories of the University of Tetova. In this research, in the spring season is carried out monitoring of seven key parameters of drinking water: water temperature (WT), residual chlorine (RC), pH, electrical conductivity (EC), the total dissolved solids (TDS), COD, and chlorides.

For parameters determination, the following reagents were used: tetra-methyl-benzidine as a reagent for RC; buffer solutions with pH 4, 7 and 9 for pH-meter calibration; standard solution of KCl for calibration of conductometer; for COD determination were used: solution of H_2SO_4 (1:3), KMnO_4 solution with $c = 0.002 \text{ mol/dm}^3$ and solution of oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$) with $c = 0.002 \text{ mol/dm}^3$; 10% K_2CrO_4 solution as indicator for chlorides determination; whereas as standard reagent for chlorides titration, AgNO_3 solution was used with $c = 0.0281 \text{ mol/dm}^3$.

The following instruments were used for the determination of the drinking water parameters at the stations: for WT measurement, a thermometer (integral part of the conductometer) was used, the portable conductometer WTW LF 320 was used for EC and TDS measurement; pH measurement is done with portable pH-meter 330i, WTW; RC is measured colorimetrically with a comparator; COD is determined with standard procedure using oxidant reagents KMnO_4 and $\text{H}_2\text{C}_2\text{O}_4$; chlorides are determined by argentometric titration.

3. Results and Discussion

Presentation of measurement results are given in the Figure 1 and Tables 1 – 3.

3.1. Water Temperature (WT)

WT plays a decisive role in the physical-chemical and biological behavior of the aquatic system (Dwivedi and Santoshi, 2004). WT is a critical parameter for aquatic life and has an impact on other water quality parameters such as dissolved oxygen concentration and bacterial activity in water. Chemical reactions depend on the WT and it controls the metabolic and reproductive processes of aquatic species. Some factors may have an impact on WT, such as vegetation, water flow rate, soil surface, thermal discharges, groundwater, etc.

The drinking water of the analyzed samples of the city of Tetova have had varying temperatures. The temperature range was 7.6 - 13.8 °C. The lowest WT was found in May at T1 station, while the highest WT was ascertained in June at T3 station. The average values of WT in March, April, May and June were 8.43, 9.62, 10.02 and 11.15 °C, respectively. The lowest average WT was at T1 station in March at 7.8 °C, while the highest average WT was 13.3 °C in June at T3 station. The average seasonal value with standard deviation of WT was 9.81 ± 1.12 °C. The values of this parameter were within the state regulations for drinking water, with minor exceptions (Fig. 1a).

3.2. Residual chlorine (RC)

RC has great importance in eliminating microorganisms in drinking water. His presence in drinking water shows that a sufficient amount of chlorine is first added to water to inactivate bacteria and some viruses that cause diarrhea and also water is protected from re-contamination during storage. The presence of free residual chlorine in drinking water is correlated with the absence of disease-causing organisms, and thus is a measure of water potability.

The range for KR has been 0.00 to 0.25 mg/L. The lowest value was measured at T3 in April and June, while the highest value was measured at T1 in May and June. The average values in March, April, May and June were 0.13, 0.11, 0.13 and 0.13 mg/L, respectively. The lowest mean of 0.05 mg/L was T3 (April and June), while the station with the highest mean 0.25 mg/L was T1 in June (Figure 1b). The average seasonal value with standard deviation of RC was 0.13 ± 0.01 mg/L and it was lower than the recommended value of the state regulation (Fig. 1b).

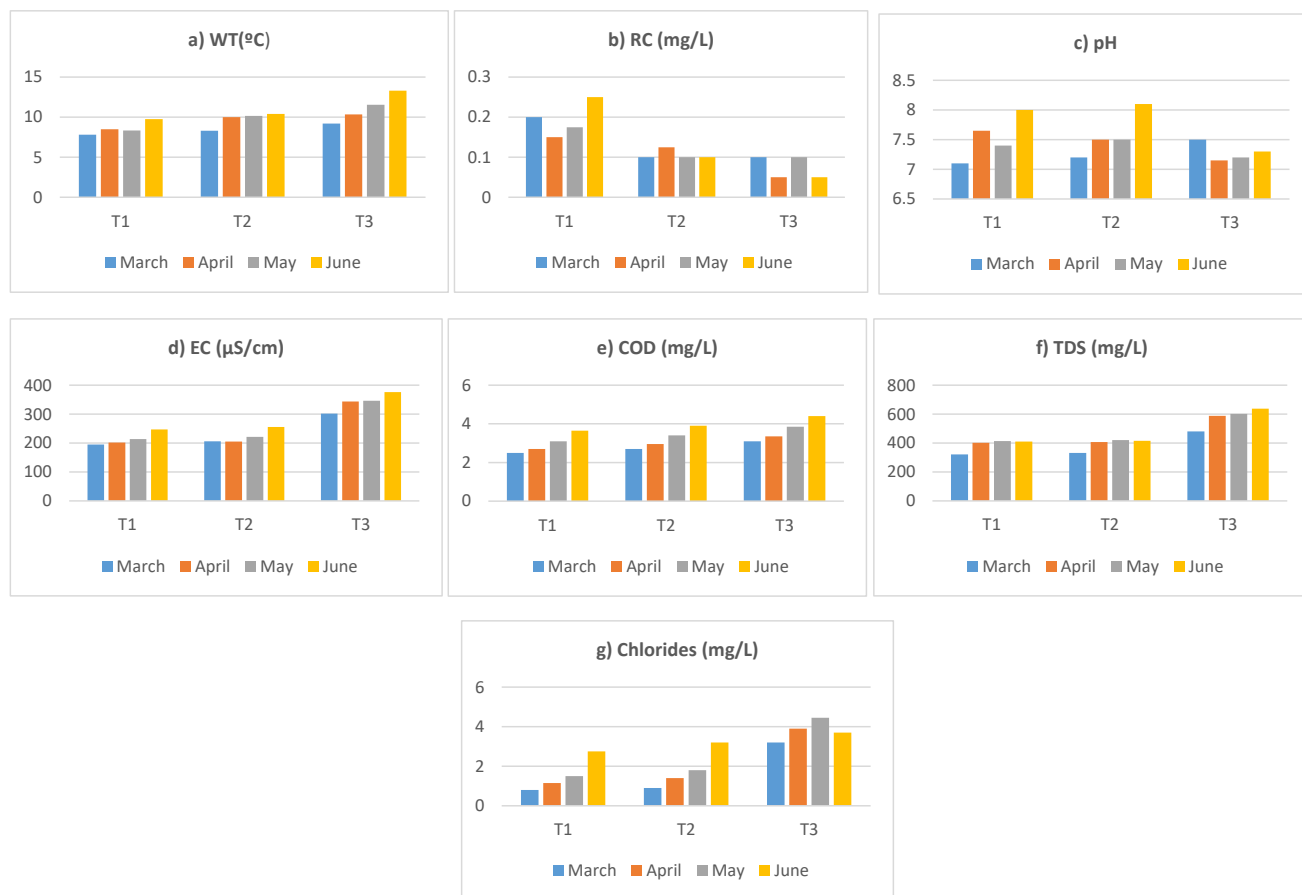


Fig. 1. Spatial and temporal variation of the parameters measured in drinking water.

3.3. pH value

The pH value of aquatic ecosystems depends on the chemical and biological activity of water. Natural waters usually have a pH value higher than 7. Natural waters usually have pH value higher than 7. It is derived from CO₂ from the atmosphere and those who liberated from the decomposition of organic substances as well as by human activity. CO₂ dissolves in water and create carbonic acid (H₂CO₃). This acid reacts with CaCO₃ of surface water and forms calcium bicarbonate (CaHCO₃) and consequently natural waters have a pH value > 7.

Samples of the analyzed waters had different pH values, with a range of 7.10-8.30. The lowest value was in March at T1 (March), T2 (April) and T3 (May), while the highest value of pH was measured in June at T2. The average values in March, April, May and June were 7.27, 7.43, 7.37 and 7.80, respectively. The lowest average value was 7.10 in T1 (March), while the highest 8.10 at T2 (June) see Fig. 1c. Seasonal mean value with standard deviation of pH was 7.47 ± 0.23 and it was within state regulation (Fig. 1c).

3.4. Electrical conductivity (PE)

Clean chemically water has high resistance. The greater the conductivity of natural water is the most polluted it will be. In natural waters resemble mineralization reactions and productivity. Natural water will have fewer or more mineral substances depending on when these two processes dominate. Water conductivity indicates the general presence of chemical compounds and is an indicator of water pollution.

This parameter at three stations has been different but not too pronounced. The slightly higher values are recorded at T3 station. Thus the EC values have been extended from 191 to 391 $\mu\text{S/cm}$. The lowest value was measured in April at T1, and the highest value in June at T3. The average values in March, April, May and June were 234.33, 250.00, 260.67 and 293.17 $\mu\text{S/cm}$, respectively (Fig. 1d). The average seasonal value of PE with standard deviation was $259.54 \pm 24.89 \mu\text{S/cm}$ and it was within the allowed state rule values (Fig. 1d).

3.5. Chemical Oxygen Demand (COD)

COD is commonly used for indirect measurement of the amount of organic compounds in water. The primary application of COD is to determine the amount of organic pollutants found in surface waters or sewage, making COD a useful measure of water quality. COD is the amount of oxygen required to carry out oxidation of organic pollution using strong oxidizing agents. Investigations related to organic contamination of drinking water and liver cancer have shown that mortality due to liver cancer is in a positive correlation with COD of drinking water.

The COD measurements have changed monthly with a range of 2.50 - 4.70 mg/L. So the lowest value was at T1 station in March, while the highest value was at T3 station in June. Average values during March, April, May and June were 2.77, 3.00, 3.45 and 3.98 mg/L, respectively. The station with the lowest average 2.50 mg/L was T1 (March), while the station with the highest average 4.40 mg/L was T3 in June (Fig. 1e). The seasonal mean value with standard deviation of COD was $3.30 \pm 0.53 \text{ mg/L}$, which is within the allowed state rule values (Fig. 1e).

3.6. The total dissolved solids (TDS)

TDS is the term used for residual waste in a vessel for measuring the mass after the sample has passed through a standard glass fiber filter and dries in constant mass at 103 to 105 °C or 179 to 181 °C. Many substances dissolved in water are undesirable. Dissolved minerals, gases and organic ingredients can produce the color, taste and aesthetically undesirable odor. High TDS content often has a laxative effect and sometimes adverse effect on individuals whose bodies do not fit in with them. TDS is mainly composed of Ca²⁺, Mg²⁺, bicarbonates, carbonates, sulphates, chlorides, nitrates and other substances. The high concentration of TDS around 3000 mg/L can also cause animal concern.

This parameter in three stations has been different but not too pronounced. Thus the values are from 321 to 653 mg/L. The lowest value was measured in March at T1, while the highest value was in June at T3. The lowest average 321 mg/L station was T1 (March), while the station with the highest average 638 mg/L was T3 in June (Fig. 1f). Average values during March, April, May and June were 378.00, 466.50, 479.33 and 487.67 mg/L, respectively. The seasonal mean value with standard deviation of the TDS was $452.88 \pm 50.67 \text{ mg/L}$ and it was within the allowed state rule values (Fig. 1f).

3.7. Chlorides

Chlorides are the least dangerous pollutants of drinking water. According to the allowed standards, their content in drinking water is quite high. Chloride ions found naturally in groundwater and surface water. Concentrations of chlorides higher than normal in freshwater are detrimental to water quality.

The results of the chlorides in the drinking water of the city of Tetova in the spring season are shown in Figures 1f. Their concentration ranges from 0.80 to 4.3 mg/L. The lowest value was measured at T1 in March, while the highest value measured in May was at T3. Average values during March, April, May and June were 1.63, 2.15, 2.28 and 3.22

mg/L, respectively. The lowest mean station of 0.80 mg/L was T1 (March), while the highest mean station of 4.45 mg/L was T3 (May). Seasonal mean value with standard deviation was 2.32 ± 0.66 mg/L and it was within the allowed state rule values (Fig. 1g).

3.8. Calculation of THM content prediction in drinking water of the city of Tetova by mathematical models

THMs prediction models are implemented based on routine measurements of some drinking water parameters and 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 (Babaei *et al*, 2015). For the THMs prediction in the drinking water of Tetova, we have used the equations of the ten mathematical models developed by (Durmishi, 2013). Mathematical models and their statistical performance are given in Table 1, while mathematical model equations and the calculation of THMs content estimation are in Table 2. In order to obtain a more reliable result for the prediction of THMs content for the spring season we have obtain the average value with standard deviation 17.75 ± 6.96 µg/L (Table 2 and 3). This result was very close to the seasonally average of THM (20.06 ± 9.72 µg/L) measured experimentally in 2011.

Table 1. Statistical characteristics of the used models.

Model	R	R Square	Adjusted R Square	Std. Error of the Estimate
1	0.715	0.511	0.491	5.56448330
2	0.705	0.497	0.487	5.58577520
3	0.728	0.529	0.510	0.10390448
4	0.728	0.529	0.510	0.10390448
5	0.668	0.446	0.443	0.11087405
6	0.691	0.478	0.471	0.10799000
7	0.703	0.494	0.484	0.10670865
8	0.717	0.514	0.501	0.10491394
9	0.726	0.527	0.512	0.10377630
10	0.726	0.527	0.512	0.10377630

Table 3. Calculation of the average value with standard deviation of the THMs content from ten models.

Model	Predicted content values of THMs content according to models (µg/L)
1	22.88
2	23.20
3	11.99
4	11.88
5	22.80
6	31.99
7	14.26
8	13.18
9	12.62
10	12.74
Average value:	17.75
Standard Deviation:	6.96
Content of THMs:	17.75 ± 6.96

Table 2. Mathematical model equations and calculation of THMs content prediction.

Model	Mathematical model equation and calculation of THMs content prediction
1	$THM = -10.925 + 0.688(WT) + 24.387(RC) + 0.461(pH) + 0.046(EC) + 2.076(COD) + 0.713(Chlorides)$ – Linear Model $THM = -10.925 + 0.688(9.81) + 24.387(0.13) + 0.461(7.47) + 0.046(259.54) + 2.076(3.30) + 0.713(2.32) =$ $= -10.925 + 6.749 + 3.170 + 3.444 + 11.939 + 6.851 + 1.654 = -10.925 + 33.807 = 22.88 \mu\text{g/L}$
2	$THM = 0.889 + 0.822(Chlorides) + 0.068(EC) + 21.205(RC)$ – Linear Model $THM = 0.889 + 0.822(2.32) + 0.068(259.54) + 21.205(0.13) = 0.889 + 1.907 + 17.649 + 2.757 = 23.20 \mu\text{g/L}$
3	$\log(THM) = 0.152 + 1.147\log(WT) + 0.158\log(RC) + 0.458\log(EC) - 0.557\log(TDS) + 0.252\log(Chlorides) + 0.240\log(pH)$ – Logarithmic Model $\log(THM) = 0.152 + 1.147\log(9.81) + 0.158\log(0.13) + 0.458\log(259.54) - 0.557\log(452.88) + 0.252\log(2.32) + 0.240\log(7.47) = 0.152 + 1.147 \times 0.992 + 0.158(-0.886) + 0.458 \times 2.414 - 0.557 \times 2.656 + 0.252 \times 0.365 + 0.240 \times 0.873 = 0.152 + 1.138 - 0.140 + 1.106 - 1.479 + 0.092 + 0.210 = 1.079 = 10^{1.079} = 11.99 \mu\text{g/L}$ After transformation, the exponential model was acquired: $THM = 10^{0.152} \cdot (WT)^{1.147} \cdot (RC)^{0.158} \cdot (EC)^{0.458} \cdot (Chlorides)^{0.252} \cdot (pH)^{0.240} / (TDS)^{0.557} = THM = 10^{0.152} \cdot (9.81)^{1.147} \cdot (0.13)^{0.158} \cdot (259.54)^{0.458} \cdot (2.32)^{0.252} \cdot (7.47)^{0.240} / (452.88)^{0.557} = 1.419 \cdot 13.723 \cdot 0.724 \cdot 12.756 \cdot 1.236 \cdot 1.620 / 30.157 = 360.096 / 30.157 = 11.94 \mu\text{g/L}$
4	$THM = 1.419(WT)^{1.147} \cdot (RC)^{0.158} \cdot (EC)^{0.458} \cdot (Chlorides)^{0.252} \cdot (pH)^{0.240} \cdot (TDS)^{-0.557}$ – Exponential Model $THM = 1.419(9.81)^{1.147} \cdot (0.13)^{0.158} \cdot (259.54)^{0.458} \cdot (2.32)^{0.252} \cdot (7.47)^{0.240} \cdot (452.88)^{-0.557} = 1.419 \cdot 13.723 \cdot 0.724 \cdot 12.756 \cdot 1.236 \cdot 1.620 \cdot 0.033 = 11.88 \mu\text{g/L}$
5	$\log(THM) = 1.254 + 0.286\log(Chlorides)$ – Stepwise Model $\log(THM) = 1.254 + 0.286\log(2.32) = 1.254 + 0.286 \times 0.365 = 1.254 + 0.104 = 1.358 = 10^{1.358} = 22.80 \mu\text{g/L}$
6	$\log(THM) = 0.113 + 0.256\log(Chlorides) + 1.31\log(WT)$ – Stepwise Model $\log(THM) = 0.113 + 0.256\log(2.32) + 1.31\log(9.81) = 0.113 + 0.256 \times 0.365 + 1.31 \times 0.992 = 0.113 + 0.093 + 1.299 = 1.505 = 10^{1.505} = 31.99 \mu\text{g/L}$
7	$\log(THM) = 0.364 + 0.282\log(Chlorides) + 1.689\log(WT) - 0.372\log(TDS)$ – Stepwise Model $\log(THM) = 0.364 + 0.282\log(2.32) + 1.689\log(9.81) - 0.372\log(452.88) = 0.364 + 0.282 \times 0.365 + 1.689 \times 0.992 - 0.372 \times 2.656 = 0.364 + 0.103 + 1.675 - 0.988 = 1.154 = 10^{1.154} = 14.26 \mu\text{g/L}$
8	$\log(THM) = 0.154 + 0.267\log(Chlorides) + 1.252\log(WT) - 0.532\log(TDS) + 0.431\log(EC)$ – Stepwise Model $\log(THM) = 0.154 + 0.267\log(2.32) + 1.252\log(9.81) - 0.532\log(452.88) + 0.431\log(259.54) = 0.154 + 0.267 \times 0.365 + 1.252 \times 0.992 - 0.532 \times 2.656 + 0.431 \times 2.414 = 0.154 + 0.097 + 1.242 - 1.413 + 1.040 = 1.120 = 10^{1.12} = 13.18 \mu\text{g/L}$
9	$\log(THM) = 0.340 + 0.258\log(Chlorides) + 1.030\log(WT) - 0.516\log(TDS) + 0.477\log(EC) + 0.153\log(RC)$ – Stepwise Model $\log(THM) = 0.340 + 0.258\log(2.32) + 1.030\log(9.81) - 0.516\log(452.88) + 0.477\log(259.54) + 0.153\log(0.13) = 0.340 + 0.258 \times 0.365 + 1.030 \times 0.992 - 0.516 \times 2.656 + 0.477 \times 2.414 + 0.153 \times (-0.886) = 0.340 + 0.094 + 1.022 - 1.370 + 1.151 - 0.136 = 1.101 = 10^{1.101} = 12.62 \mu\text{g/L}$
10	$THM = 2.188(Chlorides)^{0.258} \cdot (WT)^{1.030} \cdot (EC)^{0.477} \cdot (RC)^{0.153} \cdot (TDS)^{-0.516}$ – Exponential Model $THM = 2.188(2.32)^{0.258} \cdot (9.81)^{1.030} \cdot (259.54)^{0.477} \cdot (0.13)^{0.153} \cdot (452.88)^{-0.516} = 2.188 \cdot 1.242 \cdot 10.506 \cdot 14.177 \cdot 0.732 \cdot 0.043 = 12.74 \mu\text{g/L}$

4. Conclusions

From the results obtained during the analysis of the physical-chemical parameters, namely the THM forecast at the three sampling stations of Tetova, we can conclude that:

- The values of all parameters in the three measuring stations have been consistent and within the recommended values of the State Regulation and they meet the standards for drinking water quality (except residual chlorine that has been seasonally averaged lower than 0.2 mg/L).
- We appeal to the Tetova water utility to undertake preventive measures to maintain residual chlorine in drinking water within the recommended value (0.2 - 0.3 mg/L).
- According to the content of inorganic and organic materials, drinking water from the city of Tetova is of good quality and can be used for drinking without causing health problems.
- Models used for THMs prediction have yielded successful results.
- The prediction content of THMs for the spring season 2016 was $17.75 \pm 6.96 \mu\text{g/L}$ and was very close to the THMs seasonal average of 2011 experimentally measured ($20.06 \pm 9.72 \mu\text{g/L}$).
- The prediction results of THMs content have been within the state regulation and for the research period do not pose a risk to the health of the population.
- Because long-term consumption of drinking water with THMs can cause health problems, we recommend the relevant authorities to undertake preventive steps to keep THMs under control because it is known that during the hottest months of the year the variation in their content is much higher.
- We also recommend that in the future continuous monitoring of the physical-chemical and the THMs prediction in the drinking water of the city of Tetova must be done to have a clearer picture of their impact on the health of the population.

References

- [1]. Ali Akbar Babaei, Leila Atari, Mehdi Ahmadi, Kambiz Ahmadiangali, Mirzaman Zamanzadeh and Nadali Alavi, 2015. Trihalomethanes formation in Iranian water supply systems: predicting and modeling, *Journal of Water and Health*, 13(3), 859 – 869
- [2]. Bujar H. Durmishi, 2013. The study of the trihalomethanes (THMs) content variation with advanced analytical methods in the drinking water in the city of Tetova, Ph.D. Disertation, *University of Tirana*, Republic of Albania, 100-131.
- [3]. Canale, R., Chapara, C., Amy, G., and Edwards, M., 1997. Trihalomethane Precursor Model for Lake Youngs. *Washington Journal of Environmental Engineering, ASCE*, 123 (5), 259-265.
- [4]. Clark, R. M., and Sivaganesan Mano, 1998. Predicting Chlorine Residuals and Formation of TTHMs in Drinking Water. *J. Environ. Engrg.*, 124 (12), 1203-1210.
- [5]. Clark, R. M., Pourmoghaddas, H., Wymer, L., and Dressman, R., 1996. Modeling the Kinetics of Chlorination By-products Formation: The Effects of bromide. *J. SRT-aqua*, 45(3), 112-119.
- [6]. Dwivedi Padmanabh and Sonar Santoshi, 2004. Evaluation of physical-chemical and biological parameters in water reservoir around hills, Doimukh (District Papum Pare) Arunachal Pradesh. *Poll. Res.* 23(1), 101-104.
- [7]. Elshorbagy, W., 2000. Kinetics of THM Species in Finished Water. *J. Water Resour. Plng. and Mgmt., ASCE*, 126 (1), 21-28.
- [8]. Golfinopoulos, Spyros K, Nikos K. Xilourgidis, Maria N. Kostopoulou, and Themistokles D. Lekkas, 1998. Use of a multiple regression model for predicting trihalomethane formation . *Water Resources*, 32, Number 9, 2821-2829.
- [9]. Government of the Republic of Macedonia, 2004. State Drinking Water Regulation, Official Gazette No. 57/2004. *Government of the Republic of Macedonia*, Skopje.
- [10]. Graves, C. G., Matanoski, G. M., Tardiff, R. G., 2002. Weight of evidence for an association between adverse reproductive and developmental effects and exposures to disinfection by-products: A critical review. *Regul Toxicol Pharmacol*, 34, 103 –124.
- [11]. Karimi, A., and Singer, P., 1991. Trihalomethane Formation in Open Reservoirs. *J. AWWA*, 83(3), 84-88.

- [12]. Krasner, S. W., McGuire, M. J., Jacangelo, J. G., Patania, N. L., Reagan, K. M., and Aieta, M. E., 1989. The Occurrence of Disinfection By-products in US Drinking Water. *Journal of American Water Works Association*, 81, (8), 41-53.
- [13]. Montgomery, W., 1993. Mathematical modelling of the formation of THMs and HAAs in chlorinated natural waters. Denver, Colorado, AWW.
- [14]. Rodriguez, M. J., and Serodes, J. B., 2001. Spatial and temporal evolution of trihalomethanes in three water distribution systems. *Water Research*, 35, (6), 1572 –1586.
- [15]. Rook, J. J., 1974. Formation of haloforms during chlorination of natural water. *Water Treat. Exam.* 23, 234-240.
- [16]. Villanueva C. M., Cantor K. P., Grimalt J. O., Castaño-Vinyals G., Malats N., Silverman D., 2006. Assessment of lifetime exposure to trihalomethanes through different routes. *Occup Environ Med*, 63, 273–7.
- [17]. WHO, 2005. Trihalomethanes in drinking-water: background document for development of who guidelines for drinking-water quality; *WHO/SDE/WSH/05.08/64*. Geneva: WHO.