

## Variation of Trihalomethanes Concentration In Tetova's Drinking Water in the Autumn Season

<sup>1</sup>Durmishi H. Bujar, <sup>2</sup>Daut Vezi, <sup>3</sup>Murtezan Ismaili, <sup>1</sup>Agim Shabani and <sup>1</sup>Arianit A. Reka

<sup>1</sup>Department of Chemistry, State University of Tetova,  
Ilindeni Street N.N., 1200 Tetova, Macedonia

<sup>2</sup>Department of Chemistry, University of Tirana, Avenue "ZOG I", Tirana, Albania

<sup>3</sup>Institute for Environment and Health, South East European University,  
Ilindeni Street N.N., 1200 Tetova, Macedonia

**Abstract:** The formation of carcinogenic trihalomethanes (THMs) in the process of water disinfection by chlorine has raised concerns in the scientific community as well as in the public opinion. This study aims to determine the concentration of THMs in Tetova's drinking water during the autumn season and compare it with the regulation in the Republic of Macedonia, the European Union and the World Health Organization. To this end, we have used the UV-VIS spectrophotometric method based on Fujiwara's reaction. The THMs concentration was measured in fifteen different locations in September, October and November 2011. The results indicate that the seasonal variation is below the critical values stipulated in the state, EU and WHO regulations (seasonal average  $22.22 \pm 12.06 \mu\text{g/L}$ ). This study is the first of its kind on THMs in the Republic of Macedonia. In conclusion, it can be inferred that the concentration of THMs in the drinking water of Tetova is not hazardous to human health.

**Key words:** Drinking water • Health • Trihalomethanes • UV-VIS Spectrophotometry

### INTRODUCTION

According to the World Health Organization (WHO), more than a billion people in the world have no access to potable water and more than three billion have a lack of adequate hygiene [1], therefore a very careful management of the drinking water is needed. In this respect, the monitoring of chemical parameters in the determination of organic compounds in the drinking water is very important, since these compounds are harmful to human health [2]. Of these, highly dangerous are the disinfection byproducts (DBPs) whose main subgroup are trihalomethanes (THMs) which have proved to be cancerous to people. Having this in consideration, the level of awareness of the public opinion in relation to the quality of the drinking water, especially to the THMs has increased lately [3].

The reaction between chlorine and organic compounds present in the drinking water always produces THMs, when the former is used as a

disinfectant in advance. The presence of THMs in the final stage of the drinking water was discovered for the first time by Rook [4] in the City of Rotterdam, whereas Bellar *et al.* [5] reported five months later that THMs had been found in the drinking water in the US.

Recently, the anxiety of healthcare authorities has been increasing due to the presence of the THMs in the drinking water, as a consequence of which harmful health effects emerge in consumers due to the constant and long-term exposure to the drinking water itself [6-8]. Waters that contain organic precursors (synthetic or natural) are especially considered to be the main source of THMs. In many cases, the humic substances soluble in water are THM precursors; however, other organic substances such as algae and their extracellular products can be key precursors [9].

The scientific interest in THMs has increased since the cancerous features of THMs were recorded [10-11]. Because of this, certain countries have set maximal limits and guidelines when it comes to the THMs, which vary

Table 1: Standards/Recommending guidelines for THMs (mg/L) in the world jurisdictions

| Compound              | WHO (1993)               | USEPA (2001) | Health Canada (2001) | Aus – NZ (2000) | UK (2000) | EU (2001) |
|-----------------------|--------------------------|--------------|----------------------|-----------------|-----------|-----------|
| Chloroform            | 0.200                    | 0.000*       | –                    | –               | –         | –         |
| Bromodichloromethane  | 0.060                    | 0.060*       | –                    | –               | –         | –         |
| Dibromochloromethane  | 0.100                    | 0.000*       | –                    | –               | –         | –         |
| Bromoform             | 0.100                    | 0.000*       | –                    | –               | –         | –         |
| Total Trihalomethanes | (THMs/WHO) $\leq 1^{**}$ | 0.080        | 0.100                | 0.250           | 0.100     | 0.100     |

\*The maximum target level of pollution

\*\*The sum of ratio of THMs levels guidance value should not exceed 1

from one state to another (Table 1) [12]. Total THMs are determined as a sum of concentrations of chloroform, bromoform, bromodichloromethane and dibromochloromethane.

The aim of the paper is to determine the variation of the THMs concentration and physical-chemical parameters in the drinking water in the city of Tetova during the autumn season 2011, in order to conclude the quality of the drinking water and its impact on the health of the population living in this region.

## MATERIALS AND METHODS

The city of Tetova is situated in the north-west part of Macedonia and has about 70 000 inhabitants. Even though it has sufficient water resources and permanent water flows, the lack of water is felt in this city. The expenditure per household has decreased from 2.5 million m<sup>3</sup> in 1998 to 2 million m<sup>3</sup> in 2008 [13]. The statistics show that the average amount of water per inhabitant is about 350-400 liters per day. The flow in the pipes of the reservoir is about 30 800 m<sup>3</sup>/day. The drinking water in Tetova is disinfected with gaseous chlorine without any kind of special treatment, whereas the Southeast European University (SEEU) utilizes the underground drinking water that is extracted from three personal wells and it is disinfected only by a UV radiation used as primary disinfectant.

The experimental part of the research was done in the laboratories of the State University of Tetova. Fifteen sample points were selected in the city of Tetova (T1 – T15) and during the months of September, October and November 2011 the drinking water samples were analyzed (Fig. 1). The samples were collected in polyethylene and glass bottles of 1.5 liters. Before collecting the water samples, a 1.5 mL solution of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> 10% was added in the glass bottles in order to remove the residual chlorine and to prevent the emergence of additional THMs.

The determined parameters were as follows: THMs, water temperature, turbidity, residual chlorine (RC), pH, electrical conductivity (EC), the total residue after of

evaporation (TRAЕ), total dissolved solids (TDS), chemical oxygen demand (COD), total organic carbon (TOC), dissolved organic carbon (DOC), ultraviolet absorbance in 254 nm (UV<sub>254</sub>), specific ultraviolet absorbance (SUVA), nitrates and chlorides. Various different chemicals with pro-analysis, suprapur and HPLC cleanness were used.

The following instruments were used in the study: Portable Conductivity Meter WTW LF 320; portable pH-meter 330i WTW, turbidimeter, spectrophotometer UV-Vis Ultrospec (Fig. 2), spectrophotometer UV-Vis HACH DR 2700, gas chromatograph Hewlett-Packard HP 5890 Series II ECD/FID and TOC Shimadzu analyzer.

The THMs in the drinking water are usually determined with the method of gas chromatography (GC). However, the majority of water management municipal services do not possess the adequate equipment, budget and professional cadres for this purpose. Therefore, the method of UV-VIS spectrophotometry was chosen for the quantitative determination of THMs, which requires instruments, freer reagents and shorter analysis time frame. In order to see the result accuracy of the UV-VIS spectrophotometric method, certain results were compared to the UV-VIS spectrophotometric method developed by the HACH Company and is called the THM plus Method and with GC, which are very sensitive and precise methods. In this respect, during the month of October, the THMs were determined in five sample points using the three measurement methods.

The determination of THMs using the method of UV-VIS spectrophotometry: Ten mL of pentane were added in a normal dish containing 1L of drinking water to be analyzed. The dish was shaken for about 3 minutes and then was left still until the two separate layers were visible. The pentane layer was then removed and was added to a test tube containing 2 mL of NaOH 50% and 3 mL of pyridine. The test tube was placed in a water bath at 45°C for 30 minutes in order to relieve the evaporation of pentane. Afterwards, the bath temperature was increased to 55°C for 45 minutes and later once more to 95°C for another 45 minutes [14]. After this, 2 mL of the



Fig. 1: The map of the study area



Fig. 2: The photo of UV-VIS Spectrophotometer Ultrospec 5300 pro, Amersham Biosciences

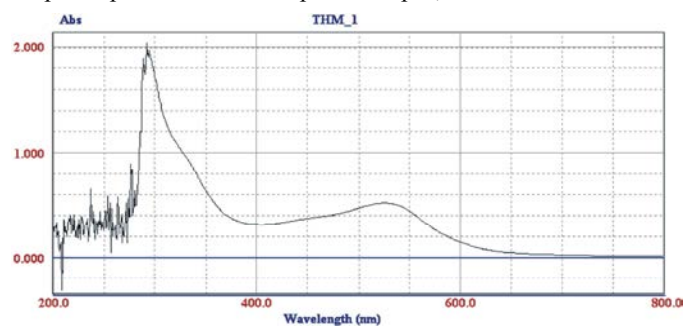


Fig. 3: THMs UV/VIS absorption spectrum,  $\gamma = 50 \mu\text{g/L}$

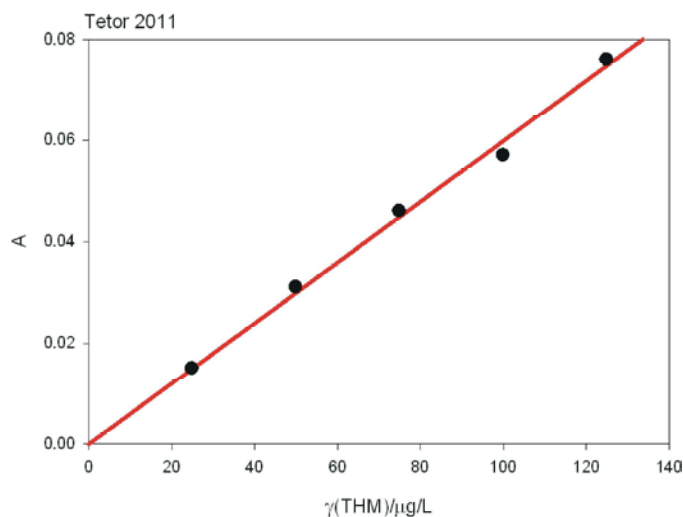


Fig. 4: Calibration curve for THMs determination, October 2011

pyridine layer (with a pink color) were removed and after the refrigeration was transferred to a 1 cm glass civet and the absorbance in 525 nm was measured (Fig. 3).

One mL of bromoform and 1 mL of chloroform were added in 1 000 mL of methanol with the purpose of the construction of calibration curve. The total THMs concentration for this solution was 4.37 mg/mL and this was the initial standard solution of THMs. The standard solutions for the calibration curve with concentrations of 25, 50, 70, 100 and 125  $\mu\text{g/L}$  were prepared by diluting the initial solution of THMs and each was diluted by using 1 L of distilled water (Fig. 4). These solutions were processed the same way as the samples of the drinking water were. This method is based on the Fujiwar's reaction.

The determination of THMs with the UV-VIS spectrophotometric method according to HACH, was carried out in accordance with the guidelines described in the literature [15], whereas the one using the GC method in accordance with literature guidelines described in [16].

## RESULT AND DISCUSSION

The experimental results have been presented in Tables 2-4 and Figures 3-7. The concentration of THMs on the sample points vary from one month to another at a low rate (Tables 2-4). Therefore, the average values of THM concentrations during the months of September, October and November were 27.71, 21.12 and 17.85  $\mu\text{g/L}$  respectively. Since the SEEU is supplied with underground water from wells and the water are disinfected only with UV radiation, during the period of measurements the residual chlorine was not detected and

as a consequence the concentration of THMs on the sample points T14 and T15 was 0.00  $\mu\text{g/L}$ . If we neglect these two points, then the T1 sample point in Noveber had the lowest value of 9.63  $\mu\text{g/L}$ , whereas the T10 sample point in September had the highest value of 45.50  $\mu\text{g/L}$ . In September, the lowest and highest values were respectively recorded on T5 and T10 sample points with 14.76  $\mu\text{g/L}$  and 45.50  $\mu\text{g/L}$  respectively. In October, the sample point T1 had the lowest value of 11.40  $\mu\text{g/L}$  and T10 had the greatest value of 32.26  $\mu\text{g/L}$ . In November, the sample point T1 had the lowest value of 9.63  $\mu\text{g/L}$  and T10 had the greatest value of 27.92  $\mu\text{g/L}$  (Fig. 5).

Of the monthly averages on the sample point, it was concluded that the lowest average value of THMs in autumn was detected on T1 with 12.41  $\mu\text{g/L}$ , whereas the highest value on T10 with 35.22  $\mu\text{g/L}$ . During the whole autumn season the range of THMs concentrations was 0.00 – 45.00  $\mu\text{g/L}$ , whereas the average value with a standard deviation was  $22.22 \pm 12.06$   $\mu\text{g/L}$ . This concentration of THMs in Tetova's drinking water is under the recommended values of the National Regulations for the drinking water (100  $\mu\text{g/L}$ ) [17], which is harmonized with the recommendations by the WHO and the EU.

The concentration variation of THMs in the autumn season was at its highest value in the month of September (27.71  $\mu\text{g/L}$ ) as a consequence of higher values of the following parameters: water temperature, pH, COD, TOC, DOC, residual chlorine, UV 254 and SUVA. The lower THMs values on T1, T5 and T6 refer to the shorter distance between the chlorination reservoir (short contact time), whereas the higher THMs values on T9, T10, T11 and T13 refer to the longer distance between the

Table 2: Results of measurements and statistics, September 2011

| Sample piont | Temperature | Turbidity | Residual chlorine | pH    | EC      | TRAE    | TDS     | COD   | TOC    | DOC   | UV <sub>254</sub> | SUVA    | Nitrates | Chlorides | THMs    |
|--------------|-------------|-----------|-------------------|-------|---------|---------|---------|-------|--------|-------|-------------------|---------|----------|-----------|---------|
| T1           | 10.50       | 1.30      | 0.1493            | 7.12  | 242.00  | 131.00  | 210.00  | 3.27  | 3.140  | 3.06  | 0.1040            | 0.03399 | 1.40     | 2.30      | 16.2120 |
| T2           | 10.60       | 0.30      | 0.2201            | 7.25  | 254.00  | 142.00  | 184.00  | 2.83  | 2.680  | 2.56  | 0.0870            | 0.03398 | 0.90     | 2.20      | 29.4860 |
| T3           | 10.80       | 0.20      | 0.2312            | 7.28  | 256.00  | 143.00  | 185.00  | 2.85  | 2.690  | 2.57  | 0.0880            | 0.03424 | 0.80     | 2.30      | 32.5360 |
| T4           | 10.70       | 0.40      | 0.2400            | 7.31  | 278.00  | 156.00  | 189.00  | 2.87  | 2.710  | 2.59  | 0.0890            | 0.03436 | 0.60     | 2.80      | 36.0360 |
| T5           | 10.60       | 0.30      | 0.2801            | 7.07  | 255.00  | 133.00  | 174.00  | 2.65  | 2.530  | 2.42  | 0.0840            | 0.03471 | 0.70     | 0.50      | 14.7560 |
| T6           | 10.90       | 0.70      | 0.2606            | 7.54  | 281.00  | 147.00  | 183.00  | 3.17  | 3.070  | 2.98  | 0.1000            | 0.03356 | 0.50     | 1.90      | 19.5720 |
| T7           | 10.70       | 0.50      | 0.2606            | 7.68  | 273.00  | 152.00  | 187.00  | 3.19  | 3.110  | 3.01  | 0.1020            | 0.03388 | 0.60     | 3.70      | 34.2720 |
| T8           | 10.90       | 0.60      | 0.2896            | 7.69  | 277.00  | 154.00  | 190.00  | 3.22  | 3.140  | 3.05  | 0.1030            | 0.03377 | 1.20     | 3.80      | 27.8600 |
| T9           | 10.60       | 1.10      | 0.3200            | 7.72  | 298.00  | 158.00  | 196.00  | 3.37  | 3.280  | 3.15  | 0.1070            | 0.03397 | 1.30     | 4.30      | 44.0480 |
| T10          | 10.70       | 1.30      | 0.3100            | 8.34  | 286.00  | 173.00  | 218.00  | 3.55  | 3.420  | 3.34  | 0.1130            | 0.03383 | 3.50     | 10.20     | 45.5000 |
| T11          | 10.90       | 1.40      | 0.3300            | 8.56  | 294.00  | 182.00  | 224.00  | 3.78  | 3.670  | 3.56  | 0.1210            | 0.03399 | 3.70     | 13.50     | 44.0480 |
| T12          | 11.40       | 1.20      | 0.2400            | 7.34  | 267.00  | 153.00  | 198.00  | 3.14  | 3.050  | 2.97  | 0.1000            | 0.03367 | 1.50     | 3.70      | 30.7680 |
| T13          | 10.80       | 1.50      | 0.2706            | 8.29  | 281.00  | 155.00  | 187.00  | 3.46  | 3.370  | 3.26  | 0.1100            | 0.03374 | 2.60     | 19.80     | 40.5440 |
| T14          | 11.30       | 1.20      | 0.0000            | 7.24  | 653.00  | 371.00  | 483.00  | 3.52  | 3.480  | 3.36  | 0.1140            | 0.03393 | 22.30    | 25.70     | 0.0000  |
| T15          | 11.30       | 1.20      | 0.0000            | 7.26  | 655.00  | 372.00  | 484.00  | 3.53  | 3.490  | 3.37  | 0.1140            | 0.03383 | 22.50    | 25.80     | 0.0000  |
| Min.         | 10.50       | 0.20      | 0.0000            | 7.07  | 242.00  | 131.00  | 174.00  | 2.65  | 2.530  | 2.42  | 0.0840            | 0.03356 | 0.50     | 0.50      | 0.0000  |
| Max.         | 11.40       | 1.50      | 0.3300            | 8.56  | 655.00  | 372.00  | 484.00  | 3.78  | 3.670  | 3.56  | 0.1210            | 0.03471 | 22.50    | 25.80     | 45.5000 |
| Median       | 10.80       | 1.10      | 0.2606            | 7.34  | 278.00  | 154.00  | 190.00  | 3.22  | 3.140  | 3.05  | 0.1030            | 0.03393 | 1.30     | 3.70      | 30.7680 |
| Average      | 10.85       | 0.88      | 0.2268            | 7.58  | 323.33  | 181.47  | 232.80  | 3.23  | 3.122  | 3.02  | 0.1024            | 0.03396 | 4.27     | 8.17      | 27.7092 |
| Stan. Dev.   | 0.28        | 0.4617    | 0.1023            | 0.471 | 135.145 | 78.263  | 102.69  | 0.32  | 0.343  | 0.346 | 0.0113            | 0.00029 | 7.4286   | 8.8296    | 14.7967 |
| Sum          | 162.7       | 13.20     | 3.4021            | 113.7 | 4850.00 | 2722.00 | 3492.00 | 48.40 | 46.830 | 45.25 | 1.5360            | 0.50945 | 64.10    | 122.50    | 415.638 |
| N            | 15          | 15        | 15                | 15    | 15      | 15      | 15      | 15    | 15     | 15    | 15                | 15      | 15       | 15        | 15      |

Sample points (with distance from the reservoir of chlorination) were: T1 – Faculty of Arts (4 km), T2 – Street 163 No. 11 (3.3 km), T3 – Butcher shop „Kadi ceshma“ (2.5 km), T4 – Primary school „Naim Frashëri“ (1.9 km), T5 – Teleferiku (0.8 km), T6 – Xhamia e larme (1.7 km), T7 – Eski xhamia (2.8 km), T8 – School of music (3.1 km), T9 – Xhamia tabhane (3.4 km), T10 – NT „Atlantida“ (4.1 km), T11 – Bus station (3.8 km), T12 – NT „Matica 2“ (3.5 km), T13 – SUT (State University of Tetova – Faculty of Natural and Mathematical Sciences) (2.9 km), T14 – UEJL 1 (Southeast European University - Institute for Environment and Health) and T15 – UEJL 2 (Southeast European University - Canteen) (4.3 km).

Table 3: Results of measurements and statistics, October 2011

| Sample piont | Temperature | Turbidity | Residual chlorine | pH    | EC      | TRAE    | TDS     | COD   | TOC    | DOC   | UV <sub>254</sub> | SUVA    | Nitrates | Chlorides | THMs    |
|--------------|-------------|-----------|-------------------|-------|---------|---------|---------|-------|--------|-------|-------------------|---------|----------|-----------|---------|
| T1           | 10.30       | 1.10      | 0.1207            | 7.43  | 241.00  | 131.00  | 186.00  | 3.45  | 3.370  | 3.26  | 0.1100            | 0.03374 | 1.54     | 1.20      | 11.3960 |
| T2           | 10.40       | 0.70      | 0.1570            | 7.62  | 244.00  | 135.00  | 165.00  | 2.46  | 2.340  | 2.28  | 0.0770            | 0.03377 | 0.60     | 2.40      | 23.2120 |
| T3           | 10.60       | 0.60      | 0.1801            | 7.68  | 248.00  | 137.00  | 166.00  | 2.48  | 2.350  | 2.29  | 0.0760            | 0.03319 | 0.80     | 2.50      | 24.8080 |
| T4           | 10.50       | 0.80      | 0.1801            | 7.85  | 253.00  | 139.00  | 168.00  | 2.56  | 2.430  | 2.37  | 0.0800            | 0.03376 | 1.30     | 2.60      | 29.6310 |
| T5           | 10.40       | 0.20      | 0.2501            | 7.24  | 194.00  | 125.00  | 159.00  | 2.41  | 2.290  | 2.26  | 0.0780            | 0.03451 | 0.70     | 1.70      | 14.6160 |
| T6           | 10.30       | 0.40      | 0.2801            | 7.48  | 215.00  | 136.00  | 167.00  | 2.59  | 2.480  | 2.34  | 0.0790            | 0.03376 | 1.30     | 2.30      | 18.1160 |
| T7           | 10.50       | 0.60      | 0.2801            | 7.14  | 236.00  | 147.00  | 172.00  | 2.67  | 2.550  | 2.43  | 0.0820            | 0.03374 | 1.50     | 2.60      | 24.8080 |
| T8           | 10.70       | 0.90      | 0.3107            | 6.87  | 239.00  | 150.00  | 176.00  | 2.68  | 2.560  | 2.44  | 0.0830            | 0.03402 | 1.60     | 2.90      | 23.2120 |
| T9           | 10.40       | 1.10      | 0.2715            | 6.82  | 241.00  | 155.00  | 173.00  | 2.74  | 2.620  | 2.56  | 0.0870            | 0.03398 | 1.90     | 3.30      | 29.9110 |
| T10          | 10.50       | 1.30      | 0.1801            | 7.67  | 264.00  | 173.00  | 186.00  | 3.68  | 3.560  | 3.49  | 0.1180            | 0.03381 | 3.60     | 5.80      | 32.2560 |
| T11          | 10.70       | 1.20      | 0.2104            | 7.85  | 258.00  | 183.00  | 188.00  | 3.86  | 3.720  | 3.64  | 0.1230            | 0.03379 | 3.80     | 12.50     | 29.9110 |
| T12          | 10.80       | 0.80      | 0.2014            | 7.52  | 217.00  | 141.00  | 163.00  | 2.57  | 2.610  | 2.53  | 0.0580            | 0.02292 | 2.50     | 3.60      | 26.5720 |
| T13          | 10.60       | 1.00      | 0.2400            | 7.88  | 249.00  | 164.00  | 178.00  | 2.94  | 2.780  | 2.63  | 0.0890            | 0.03384 | 3.70     | 5.20      | 28.3080 |
| T14          | 10.20       | 0.80      | 0.0000            | 7.13  | 678.00  | 381.00  | 491.00  | 1.92  | 1.770  | 1.58  | 0.0540            | 0.03417 | 17.60    | 25.10     | 0.0000  |
| T15          | 10.20       | 0.80      | 0.0000            | 7.15  | 679.00  | 382.00  | 492.00  | 1.93  | 1.760  | 1.59  | 0.0540            | 0.03396 | 17.80    | 25.20     | 0.0000  |
| Min.         | 10.20       | 0.20      | 0.0000            | 6.82  | 194.00  | 125.00  | 159.00  | 1.92  | 1.760  | 1.58  | 0.0540            | 0.02292 | 0.60     | 1.20      | 0.0000  |
| Max.         | 10.80       | 1.30      | 0.3107            | 7.88  | 679.00  | 382.00  | 492.00  | 3.86  | 3.720  | 3.64  | 0.1230            | 0.03451 | 17.80    | 25.20     | 32.2560 |
| Median       | 10.50       | 0.80      | 0.2014            | 7.48  | 244.00  | 147.00  | 173.00  | 2.59  | 2.550  | 2.43  | 0.0800            | 0.03379 | 1.60     | 2.90      | 24.8080 |
| Average      | 10.47       | 0.82      | 0.1908            | 7.42  | 297.07  | 178.60  | 215.33  | 2.73  | 2.613  | 2.51  | 0.0832            | 0.03313 | 4.02     | 6.59      | 21.1171 |
| Stan. Dev.   | 0.1831      | 0.2981    | 0.0935            | 0.348 | 155.893 | 83.897  | 112.463 | 0.558 | 0.565  | 0.583 | 0.0208            | 0.00284 | 5.6548   | 8.0058    | 10.3729 |
| Sum          | 157.1       | 12.30     | 2.8623            | 111.3 | 4456.00 | 2679.00 | 3230.00 | 40.94 | 39.190 | 37.69 | 1.2480            | 0.49696 | 60.24    | 98.90     | 316.757 |
| N            | 15          | 15        | 15                | 15    | 15      | 15      | 15      | 15    | 15     | 15    | 15                | 15      | 15       | 15        | 15      |

chlorination reservoir (long contact time). An additional factor for the emergence of higher values on the mentioned sample points can also be the organic pollution which can penetrate into the drinking water as a result of the outdated water supply system in the city, defects, frequent reparations as well as wastewaters.

Other parameters of the quality of the drinking water will not be discussed in this paper. They were measured

for purposes of extracting mathematical models in order to predict the THMs concentrations in the drinking water in Tetova and are not a subject of this article.

In order to verify the validity of the results, in October the THMs measurements were carried out with the three methods on sample points T4, T5, T8, T10 and T13 (Fig. 6). The figure shows that the results from the UV-VIS spectrophotometric method based on HACH and

Table 4: Results of measurements and statistics, November 2011

| Sample piont | Temperature | Turbidity | Residual chlorine | pH    | EC      | TRAE    | TDS     | COD   | TOC    | DOC   | UV <sub>254</sub> | SUVA    | Nitrates | Chlorides | THMs    |
|--------------|-------------|-----------|-------------------|-------|---------|---------|---------|-------|--------|-------|-------------------|---------|----------|-----------|---------|
| T1           | 9.40        | 1.50      | 0.0995            | 7.74  | 198.00  | 116.00  | 162.00  | 2.95  | 2.880  | 2.77  | 0.0940            | 0.02604 | 0.500    | 1.400     | 9.6320  |
| T2           | 9.50        | 0.20      | 0.1407            | 7.63  | 192.00  | 93.00   | 147.00  | 2.74  | 2.660  | 2.55  | 0.0860            | 0.03373 | 0.700    | 1.600     | 19.7680 |
| T3           | 9.70        | 0.30      | 0.1513            | 7.65  | 196.00  | 95.00   | 148.00  | 2.75  | 2.670  | 2.55  | 0.0870            | 0.03412 | 0.800    | 1.800     | 21.4200 |
| T4           | 9.60        | 0.30      | 0.1714            | 7.73  | 195.00  | 96.00   | 152.00  | 2.76  | 2.650  | 2.54  | 0.0860            | 0.03386 | 0.800    | 1.800     | 24.5280 |
| T5           | 9.70        | 0.20      | 0.2201            | 7.61  | 201.00  | 84.00   | 138.00  | 2.31  | 2.230  | 2.16  | 0.0730            | 0.03379 | 0.200    | 0.900     | 12.9640 |
| T6           | 9.50        | 0.40      | 0.2408            | 7.85  | 199.00  | 116.00  | 169.00  | 2.68  | 2.590  | 2.46  | 0.0830            | 0.03374 | 0.400    | 1.500     | 16.5480 |
| T7           | 9.90        | 0.40      | 0.2819            | 8.34  | 188.00  | 124.00  | 172.00  | 2.71  | 2.630  | 2.48  | 0.0840            | 0.03387 | 0.600    | 2.600     | 19.7680 |
| T8           | 9.70        | 0.60      | 0.2501            | 8.36  | 196.00  | 126.00  | 174.00  | 2.73  | 2.640  | 2.49  | 0.0850            | 0.03414 | 0.700    | 2.700     | 18.1160 |
| T9           | 9.60        | 1.10      | 0.2019            | 8.13  | 197.00  | 138.00  | 186.00  | 2.84  | 2.770  | 2.66  | 0.0900            | 0.03383 | 0.800    | 2.900     | 23.1560 |
| T10          | 9.70        | 1.20      | 0.1407            | 8.25  | 210.00  | 146.00  | 192.00  | 2.91  | 2.830  | 2.71  | 0.0920            | 0.03395 | 1.600    | 8.600     | 27.9160 |
| T11          | 9.70        | 1.30      | 0.1513            | 8.44  | 208.00  | 155.00  | 195.00  | 3.36  | 3.280  | 3.16  | 0.1070            | 0.03386 | 1.800    | 8.200     | 26.1800 |
| T12          | 9.70        | 0.90      | 0.1802            | 8.34  | 204.00  | 127.00  | 168.00  | 2.84  | 2.760  | 2.67  | 0.0910            | 0.03408 | 0.800    | 1.700     | 23.1560 |
| T13          | 9.90        | 1.30      | 0.2201            | 8.29  | 209.00  | 133.00  | 182.00  | 2.63  | 2.560  | 2.43  | 0.0820            | 0.03374 | 1.600    | 1.600     | 24.5280 |
| T14          | 9.70        | 1.30      | 0.0000            | 7.18  | 682.00  | 381.00  | 381.00  | 2.14  | 2.060  | 1.97  | 0.0670            | 0.03401 | 7.200    | 9.300     | 0.0000  |
| T15          | 9.70        | 1.30      | 0.0000            | 7.20  | 684.00  | 382.00  | 382.00  | 2.15  | 2.070  | 1.98  | 0.0680            | 0.03434 | 7.300    | 9.500     | 0.0000  |
| Min.         | 9.40        | 0.20      | 0.0000            | 7.18  | 188.00  | 84.00   | 138.00  | 2.14  | 2.060  | 1.97  | 0.0670            | 0.02604 | 0.200    | 0.900     | 0.0000  |
| Max.         | 9.90        | 1.50      | 0.2819            | 8.44  | 684.00  | 382.00  | 382.00  | 3.36  | 3.280  | 3.16  | 0.1070            | 0.03434 | 7.300    | 9.500     | 27.9160 |
| Median       | 9.70        | 0.90      | 0.1714            | 7.85  | 199.00  | 126.00  | 172.00  | 2.74  | 2.650  | 2.54  | 0.0860            | 0.03386 | 0.800    | 1.800     | 19.7680 |
| Average      | 9.67        | 0.82      | 0.1633            | 7.92  | 263.93  | 154.13  | 196.53  | 2.70  | 2.619  | 2.51  | 0.0850            | 0.03341 | 1.720    | 3.740     | 17.8453 |
| Stan. Dev.   | 0.135       | 0.4873    | 0.0822            | 0.422 | 170.254 | 94.507  | 76.934  | 0.312 | 0.313  | 0.303 | 0.0102            | 0.00205 | 2.2907   | 3.2743    | 8.72899 |
| Sum          | 145.0       | 12.30     | 2.4500            | 118.7 | 3959.00 | 2312.00 | 2948.00 | 40.50 | 39.280 | 37.58 | 1.2750            | 0.50110 | 25.80    | 56.100    | 267.680 |
| N            | 15          | 15        | 15                | 15    | 15      | 15      | 15      | 15    | 15     | 15    | 15                | 15      | 15       | 15        | 15      |

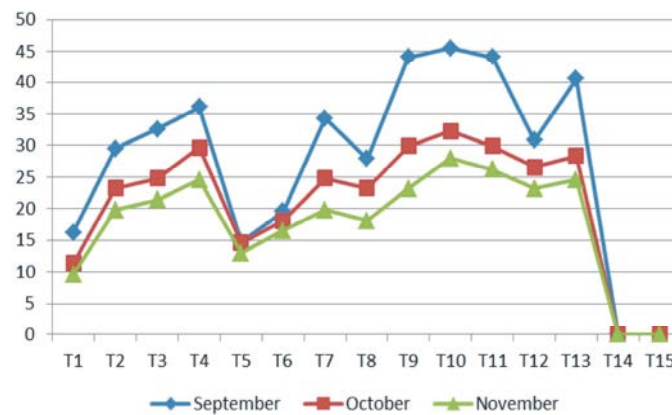


Fig. 5: Spatial and temporal variation of THMs concentration ( $\mu\text{g/L}$ ) in the autumn 2011

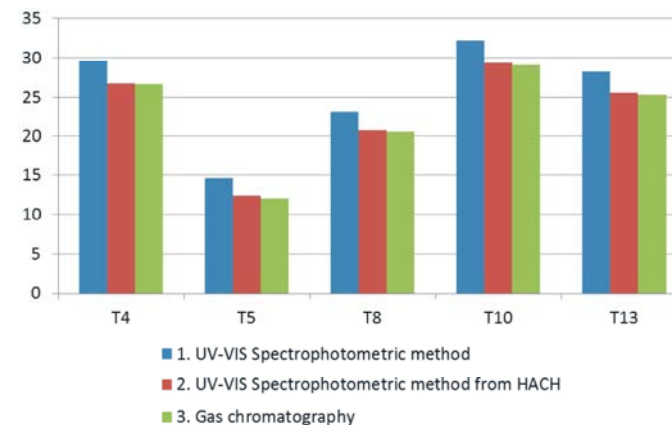


Fig. 6: Comparison of the THMs results with three determination methods, October 2011

the GC method show high compliance, whereas those from the UV-VIS spectrophotometric method slightly differ from the previous ones. In order to increase the sensitivity and accuracy of the results by using method

no. 1, we used reagents and solvents of HPLC cleanness. We can conclude that the UV-VIS spectrophotometric method can successfully be used in determining the THMs.

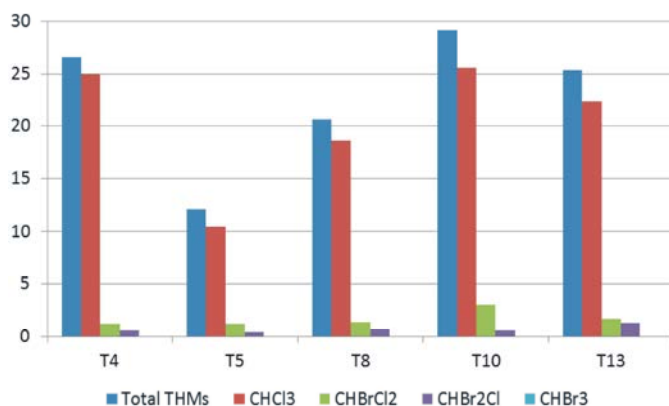


Fig. 7: Gas chromatography analysis results of THMs, October 2011

The GC method is quite suitable and was also used for specifying the THMs in the drinking water in Tetova (Fig. 7). For this purpose, in October, individual measurements of chloroform (CHCl<sub>3</sub>), bromodichloromethane (CHBrCl<sub>2</sub>), dibromochloromethane (CHBr<sub>2</sub>Cl) and bromoform (CHBr<sub>3</sub>) on T4, T5, T8, T10 and T13 were carried out. The results show that CHBr<sub>3</sub> were not detected on any of the sample points (0.00 µg/L), whereas CHCl<sub>3</sub> was the most represented species in the total THMs with a percentage from 86.71% on T5 to 93.54 % on T10. CHBrCl<sub>2</sub> appeared with a very low percentage of 4.32 % on T4 and 10.37 % on T10. CHBr<sub>2</sub>Cl appeared with a very low percentage of 1.86 % on T10 and 5.02 % on T13. These results are compatible with those of other researchers and show that the most represented species in the total THMs is chloroform.

### CONCLUSION

The presence of THMs in the drinking water in the last decades has caused great worries since these components can cause cancer in humans. The monitoring of the THMs formation is crucial in order to make sure that the drinking water remains at the acceptable security levels. Therefore, the actions to reduce the THMs should be encouraged and there should be no compromise when it comes to the water disinfection. The variation of the THMs level shows the effect of different factors on their formation under the conditions of water chlorination as well as the performance of enterprises that deal with water treatment and management.

The results of this study show that the level of THMs concentrations in the drinking water in the city of Tetova in the autumn 2011 amounting at 22.22±12.06 µg/L has been under the recommended values of the National

Regulation for the drinking water, the WHO and the EU and is currently safe for the population of this region. However, since the consumption of drinking water with THMs can cause health problems, we recommend to respective authorities to undertake preventive measures in keeping these values under control, especially when having in mind that during the hotter months the variation level of THMs can be very high. Based on the research results, we can also conclude that the UV-VIS spectrophotometric method can successfully be applied in determining the THMs and it can replace the UV-VIS spectrophotometric method based on HACH as well as the gas chromatographic method.

### REFERENCES

1. World Health Organization, 2001. Sustainability and optimization of Water supply and sanitation services. <[http://who.int/water\\_sanitation\\_health/wss/sustoptim.html](http://who.int/water_sanitation_health/wss/sustoptim.html)>, pp: 135-158.
2. Durmishi, B.H., M. Ismaili, A. Shabani and S.H. Abduli, 2012. Drinking Water Quality Assessment in Tetova Region. American Journal of Environmental Sciences, 8(2): 162-169.
3. Government of Newfoundland and Labrador, Department of Environment and Labour, Water Resources Management Division, 2000. Trihalomethane Levels in Public Water Supplies of Newfoundland and Labrador. Project, pp: 15-20.
4. Rook, J.J., 1974. Formation of Haloforms During Chlorination of Natural Waters. Journal of Water Treatment Examination, 23: 234-237.
5. Bellar, T.A. and J.J. Lichtenberg, 1974. Determining volatile organics at microgram-per-liter levels by gas chromatograph. J. Am. Water Works Assoc., 66: 739-744.

6. Sokeng, S.D., D. Lontsi, P.F. Moundipa, H.B. Jatsa, P. Watcho and P. Kamtchouing, 2007. Hypoglycemic Effect of *Anacardium occidentale* L. Methanol Extract and Fractions on Streptozotocin-induced Diabetic Rats, *Global Journal of Pharmacology*, 1(1): 01-05.
7. Prajapati Hetal Ritesh, Brahmshatriya Pathik Subhashchandra, Vaidya Hitesh Bharatbhai and V. Thakkar Dinesh, 2008. Avian Influenza (Bird Flu) in Humans: Recent Scenario, *Global Journal of Pharmacology*, 2(1): 01-05.
8. Bellar, T.A. and J.J. Ichenberg, 1974. Determining Volatile Organics at microgram-per-liter levels by gas chromatograph. *J. Am. Water Works Assoc.*, 66: 739-744.
9. Contu, A., M. Bordigoni, G. Sarritzu, G. Premazzi, M. Pudda and M. Schintu, 1990. Trihalomethanes in the Water Supplies of Sardinia, Italy. *Bull. Environ. Contam. Toxicol.*, 44: 805-812.
10. Hoehn, R.C., D.B. Barnes, B.C. Thompson, C.W. Randall, T.J. Grizzard and P.T.B. Shaffer, 1980. Algae as sources of trihalomethane precursors. *J. Amer Water Wks Assoc.*, 72: 344-350.
11. Symons, J.M., T.A. Bellar, J.K. Carswell, J. De Marco, K.L. Kropp, G.G. Robeck, D.R. Seeger, C.S. Slocum, B.L. Smith and A.A. Stevens, 1975. National organics reconnaissance survey for halogenated organics. *J. Am. Water Works Assoc.*, 67: 634-647.
12. Sadiq, R. and M.J. Rodriguez, 2004. Disinfection by-products (DBPs) in drinking water and predictive models for their occurrence: a review. *Science of the Total Environment*, 321: 21-46.
13. Jashari Nazif, 2010. Manual for drinking water, Tetova Water Supply, Tetova, pp: 14-18.
14. Huang, J., R. Smith and C. Gary, 1984. Spectrophotometric Determination of Total Trihalomethanes in Finished Waters. *Journal AWWA*, 76(4): 168-171.
15. HACH Company, 2007. Trihalomethanes THM Plus™ Method, Method 10132 - Water Bath Method, pp: 1-10.
16. Pauzi, M.A., C.H. Yew, M.S. Ramli and R. Ali, 2003. Trihalomethanes (THMs) in Malaysian Drinking Water. *Malaysian Journal of Chemistry*, 5(1): 056-066.
17. Government of the Republic of Macedonia, 2004. State Drinking water regulation, official gazette No. 57/2004, pp: 24.