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# Assessment of groundwater, soil and some fruits and vegetables in Medias Town

## -Ph.D. Thesis abstract-

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**<u>Key words</u>: drinking water sources quality, soil quality, metal pollution index, quality index, transfer factors, fruits and vegetables, health risk assessment, Mediaş Town**

*„ We forget that water and life have the same circle*

*(Jacques-Yves Cousteau).”*

# INTRODUCTION

The indispensability and limitation of water recourses indicate the importance and significance of the natural resource, of water. The priceless accessibility to water limits the consciousness at the possible adverse effects, due to consumption of contaminated water with various chemical compounds or pathogens. Although the water supply system is the most common drinking water source, private well waters and public springs are used as well as drinking water sources; the inhabitants from the study area, from Medias Town use all three types of source. Recent studies and chemical analysis results, analysis conducted by the Public Health Department from Sibiu, show that the drinking water resources, specifically private well waters and public springs are characterized by higher nitrate, nitrite, ammonium and lead concentrations as the maximum allowable concentrations, according to the Romanian legislation.

The **aim** of the thesis was to develop an integrate model of the drinking water sources (public spring and private well waters) assessment, using metal pollution index and water quality index methods. This model was applied in a particulate way for the drinking water sources from Medias Town, Sibiu County.

The **major objectives** of the research activities, which were conducted, were:

***1.*** Information Review regarding the drinking water sources, the metal pollution index, the quality index and the metal transfer factors from soil to fruit and vegetable samples.

***2.*** Application of the developed pollution and quality index model with the aim of determining the quality status of drinking water (private well water and public spring) from Medias Town.

***3.*** Health risk assessment of nitrogen compounds ($NO_2^-$ and $NO_3^-$) and some metals (As, Cd, Cr, Cu, Ni, Pb and Zn).

To achieve the proposed aim, **specific objectives** were defined, such as:

***1.*** Documentary research regarding the sources, the quality and the national and international law about water quality, groundwater and soil quality.
***2.*** Documentary research regarding the anthropogenic pollution and drinking water sources from Medias Town.
***3.*** Definitions and methodology of metal pollution index and quality index methods for water.
***4.*** Definitions and methodology for the transfer factors.
***5.*** Quality determination of the drinking water sources, soil and some fruits and vegetables from Medias Town.
***6.*** Metal transfer from soil to plants with the application of the transfer factors.
***7.*** Health risk assessment at chemical compounds, such as nitrites, nitrates from water samples and at metals from soil samples, due to the transfer from soil to fruits and vegetables.

The research thesis is divided into two main parts: *theoretical*, in which **the thesis issues** are underlined, and *experimental*, which presents the **original contributions**. First part of the thesis is structured into three chapters, such as:

**Chapter I – Drinking water**, chapter in which a documentary research has been carried out, regarding the quality, pollution and legislation concerning the drinking water, groundwater and soil quality.

**Chapter II – Drinking water sources from Medias Town**, describing the study area, from a geographically point of view, and the anthropogenic pollution sources.

**Chapter III – The Metal Pollution index and the water quality index methods. The Transfer factors**, it is a documentary research about the metal pollution index, water and soil quality index, transfer factors and health risk index methods.

Original contributions are presented in the second part of the thesis, *experimental*, and it is structured into four chapters:

**Chapter IV – The research methodology**. The thesis objectives, the sampling plan, the water, soil and fruits and vegetables sampling and the analytical methods are presented. With the help of the analytical methods, a physico-chemical characterization of the samples was realized.

**Chapter V – The water quality from Medias Town**. This chapter indicates the original contributions of the thesis, the quality of the drinking water sources (private well waters and public springs) respectively, which is given by the results of the physico-chemical analyses (pH, electrical conductivity (EC), total hardness, chemical oxygen demand measured with the permanganate index method, $HCO_3^-$, $CO_3^{2-}$, $NO_2^-$, $NO_3^-$, $Cl^-$, $F^-$, $SO_4^{2-}$, $NH_4^+$, Ca, Mg, Na, K, As, Cd, Cr, Cu, Fe, Mn, Ni, Zn ) and the results of the metal pollution index and the quality index methods. Also, the potential risks at $NO_2^-$ and $NO_3^-$ index are exposed.

**Chapter VI – The soil quality from Medias Town. The metal transfer from soil to fruits and vegetables**. In Chapter six, the soil analyses results (pH, metals and ions content) and the metal pollution index results are detailed. Obtained data were used for metal assessment from some fruits and vegetables (tomato, pepper, peach, quince fruits, carrot root, onion bulb and lettuce leaves), as well as for the transfer factors methodology and risk assessment at metals.

**Chapter VII – General conclusions**, last chapter of the thesis presents the resulted conclusions of the undertaken study, obtained on the recorded results and the Ph.D. student's contributions.

# CHAPTER I – THE DRINKING WATER

The water represents an open and versatile system; as the most abundant molecule on Earth (Singh & Jain., 2013). Drinking water has a significant importance as it is essential for life support (Dean, 2005, WHO, 2011). The direct and available drinking water sources are represented by the surface waters (rivers, streams, lakes), groundwater (deep and shallow aquifers) and glaciers. The high amount of chemical substances (with natural or anthropogenic sources) characterizes the status/water quality (contamination or pollution).

The contamination is defined as *the presence of high amount of substances in the environment, water respectively, amount of chemical which exceeds the background* (Sciortino J.A. & Ravikumar R., 1999). On the other hand, according to Sciortino & Ravikumar (1999) and the Law 278 (2013), water and soil pollution represents the introduction of chemicals in the natural environment (water, air, soil), as a result of the anthropogenic activities, which altering the quality of the natural resources, with potential negative health effects on creatures (Sciortino J.A. & Ravikumar R., 1999, Law 278, 2013).

In Romania, the industrial activities influenced the quality of the natural factors, especially in the 90’. The nonferrous metallurgical industry (*Sometra* facility) was a metal pollution source (Cu, Zn, Pb, Sn). The main chemical and petrochemical facilities were localized at Râmnicu Vâlcea, Năvodari, Băile Govora, Turnu Măgurele, Copşa Mică and were sources for diverse chemical compounds.

## CHAPTER II – DRINKING WATER SOURCES FROM MEDIAS TOWN

Medias Town belongs to Sibiu County; it is the second largest urban area in the county. Medias is situated in the Tarnavelor Plateau, which is part of the Hartibaciu Plateau and Transilvanian Basin (Oancea et al., 1987). It is localized in the north of the part of the county and situated in the centre of the country.

The drinking water sources from Medias Town are Tarnava Mare river and aquifer sources. Tarnava Mare is part of the Mures hydrographical basin, which is situated in west and central part of the country. There are almost 5900 million $m^3$/year of water resources in the hydrographical basin (88.9% represented by surface and groundwater) from which 1100 million $m^3$/year are used (Oancea et al., 1987). Aquifers represent significant resources used mainly for household activities and are classified in two large categories:

1. **unconfined aquifers**, as a direct spring supply for the river system. They are localized at shallow depths and are under the direct influence of the climatic conditions; characterized by a depth of 0.0-0.5 m in the minor bed, 4.0-5.0 m in the major bed and 10 m on the slopes (Oancea et al., 1987).
2. **confined aquifers,** those are relatively independent of the climatic conditions. Confined aquifers do not supply rivers. In the study area, confined aquifers are localized only in the sedimentary at 250-300 m depth (Oancea et al., 1987).

Medias has a considerable history regarding the development and variety of industrial activities, but, today almost 90% of the industry does not exist anymore. Likewise, the agricultural activities were reduced and even stopped. Simultaneous with the industry development in Medias Town, metallurgical and chemical industry from Copsa Mica Town grew as well. Copsa Mica Town is situated near (almost 15 km) Medias; the area is known at the global level, due to the industrial activities (metals and carbon black processing) conducted in two industrial facilities, *Sometra* and *Carbosim* (Lăcătuşu & Lăcătuşu, 2010). At the European level, Copsa Mica was considered a „pollution hot spot" in Europe (Muntean et al., 2013).

## CHAPTER III – THE METAL POLLUTION INDEX AND THE WATER QUALITY INDEX METHODS. THE TRANSFER FACTORS

The metal pollution index methods are quality methods or mathematical tools, which help assessing the metal pollution status of the drinking water. In this thesis, three metal pollution indexes were applied for the water samples, namely: ♦the Degree of Contamination- *CD* ♦the Heavy Metal Evaluation Index- *HEI* ♦the Heavy Metal Pollution Index- *HPI* (Prasad & Bose, 2001, Bhuiyan et al., 2010, Mohan et al., 1996). The calculation methodology and the quality status indicated by the metal pollution index results are presented in *Table III.1.*, as it follows:

***Table III.1.*** *The metal pollution index methods used for water samples*

| Index | Calculation methods | The pollution status according to the index |
|---|---|---|
| the Degree of Contamination (***CD***)* | $CD = \sum_{i=1}^{n} C_f$<br>$C_f = \frac{C_{Ai}}{C_{Ni}} - 1$ | ♦ $CD < 1.0$ ⇨ low pollution level<br>♦ $CD = 1.0$ ⇨ medium pollution level<br>♦ $CD > 1.0$ ⇨ high pollution level |
| the Heavy Metal Pollution Index (***HPI***)* | $HPI = \frac{\sum_{i=1}^{n} W_i Q_i}{\sum_{i=1}^{n} W_i}$<br>$Q_i = \sum_{i=1}^{n} \frac{\{M_i(-)I_i\}}{S_i - I_i} \times 100$ | ♦ $HPI >$ **100** ⇒ the water is polluted |
| The Heavy Metal Evaluation Index (***HEI***)* | $HEI = \sum_{i=1}^{n} \frac{H_C}{H_{MAC}}$ | ♦ $HEI < 40$ low pollution level<br>♦ $HEI = 40\text{-}80$ medium pollution level<br>♦ $HEI > 80$ high pollution level |
| *according to Mohan et al., 1996; Prasad & Bose, 2001; Edet and Offiong, 2002; Bhuiyan et al., 2010 | | |

For the drinking water quality assessment the Water Quality Index (*WQI*) and the Drinking Water Quality Index (*DWQI*) were used, considering other chemical compounds as the metal content, such as nitrates, nitrites, ammonium, sulphates and total dissolved solids. The calculation methodology and the quality status are shown the *Table III.2*.

***Table III.2.*** *The quality index methods used for the drinking water quality assessment*

| Index | Calculation methods | The quality status according to the index |
|---|---|---|
| The Water Quality Index (***WQI***)* | $WQI = \left( \sum_{i=1}^{n} qW_i / \sum_{i=1}^{n} W_i \right)$ | ♦ $WQI < 25$ ⇨ excellent quality<br>♦ $WQI > 100$ ⇨ the water is not recommended for drinking |
| The Drinking Water Quality Index (***DWQI***)* | *DWQI* =<br>[aggregated index]+[ Min-Max oper.] | ♦ $DWQI < 60$ ⇨ good quality<br>♦ $DWQI > 100$ ⇨ poor quality |
| *according to Horton, 1965; Ravi Chandra Babu et al., 2006; Ramesh et al., 2010; Srinivas et al., 2011 | | |

Metal pollution index methods are used for risk exposure and pollution assessment; thereby soil samples are classified in quality classes. Among these index methods are the Degree of Contamination (*CD*), the Contamination factor ($C_f$), the Index of geo-accumulation ($I_{geo}$), the Pollution Load Index (*PLI*), the Risk factor and Risk index (*Ri*) (*Table III.3.).*

***Table III.3.*** *The metal pollution index methods used for soil pollution assessment*

| Index | Calculation methods | The pollution level status according to the index |
|---|---|---|
| The Degree of Contamination (***CD***) and the Contamination factor ($C_f$)* | $CD = \sum_{i=1}^{n} C_f$<br>$C_f = \frac{C_{Ai}}{C_{Ni}} - 1$ | ♦ $CD < 1.0$ ⇨ low pollution level<br>♦ $CD = 1.0$ ⇨ medium pollution level<br>♦ $CD > 1.0$ ⇨ high pollution level |
| The Index of geo-accumulation, ($I_{geo}$)* | $I_{geo} = \log_2 \left( \frac{C_m}{1{,}5 \times B_m} \right)$ | ♦ $I_{geo} \leq 0.0$ ⇨ unpolluted soil<br>♦ $2.0 < I_{geo} < 3.0$ ⇨moderately to strong polluted soil<br>♦ $I_{geo} > 5.0$ ⇨ extremely polluted soil |
| the Pollution Load Index (***PLI***)* | $PLI = \sqrt[n]{C_{f1} \times C_{f2} \times \ldots.. \times C_{fn}}$ | ♦ $PLI < 1.0$ ⇨ unpolluted soil<br>♦ $PLI = 1.0$ ⇨ soil with a normal background level<br>♦ $PLI > 1.0$ ⇨ polluted soil |
| The Risk factor ($E_r$) and the Risk index (***Ri***) | $Er = Tr \times C_f$<br>$Ri = \sum_{i=1}^{n} Er$ | ♦ $E_r \leq 40$ ⇨ low potential ecological risk<br>♦ $E_r \geq 320$ ⇨very high potential ecological risk<br>♦ $Ri < 150$ ⇨ low ecological risk<br>♦ $Ri \geq 600$ ⇨ very high ecological risk |
| *according to Muller, 1969; Hakanson, 1980; Tomlinson et al. 1980; Elnazer et al., 2015 | | |

The metal risk assessment due to the plants consume was determined by three index methods; so *EDEM* (the Estimated Daily Intake of Metals), *HQ* (the Hazard Quotient), and *HI* (the Hazard Index), according to the methodology described by Guerra et al. (2012) and Mahmood & Malik (2014) were used. In this study, the index methods were applied for the As, Cd, Cr, Cu, Ni, Pb and Zn contents.

## EXPERIMENTAL. ORGINAL CONTRIBUTIONS

## CHAPTER IV – THE RESEARCH METHODOLOGY

Three sampling campaigns were organized in the study area, Medias Town in order to achieve the thesis objectives. A number of 20 water samples (18 private well waters, F1-F18 and 2 public springs, I1 and I2) were sampled in the first sampling campaign in 21 March 2014. The second sampling campaign occur in the summer season, of 2014 from 21 to 22 August; 20 water samples from de same sampling points as in the first sampling campaign, 20 soil samples (S1-S20) and 18 fruit and vegetable samples (carrot root - *Daucus carota sativus*, tomato fruits - *Solanum lycopersicum*, onion bulb - *Allium cepa*, yellow bell pepper fruit - *Capsicum annuum*, lettuce leaves - *Lactuca sativa*, peach *Prunus persica* - and quince (*Cydonia oblonga*) fruits) were collected. Last of the sampling campaign took place in 11-12 August 2016, when a number of 26 well water samples (F1-F26), 3 public spring samples (I1-I3) and 29 soil samples (S1-S29) (*Figure IV.1.)* were collected.

*(a)* *(b)*

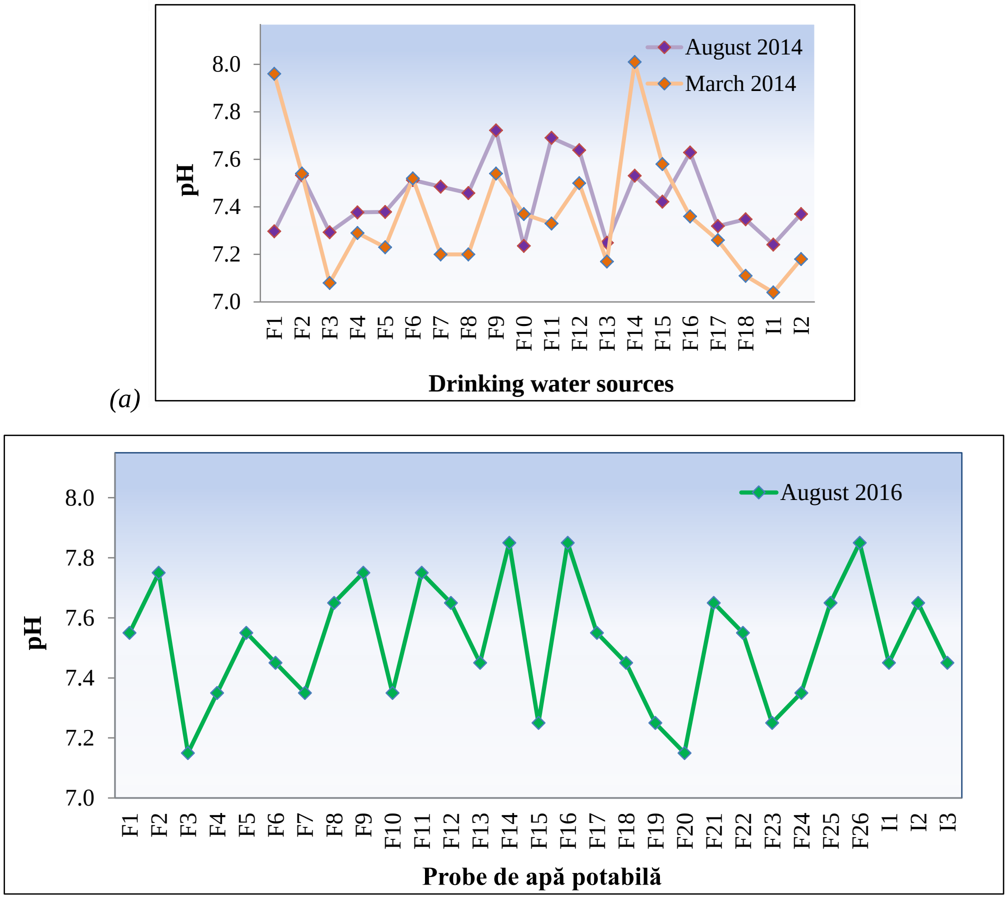
*(c)*

***Figure IV. 1.*** *Sampling points: a) private well water (F2),b) public spring (I1), c) soil samples (S3 and S17)*

Given the objectives of the thesis and the accuracy of results, the analytical techniques and methods were developed according to required reference standards. The quality control of the results was ensured by standard measurements with known chemical composition, reference materials and certified reference materials for the equipment calibration and methods validation. The chemical analyses were conducted at the Research Institute of Analytical Instrumentation, ICIA Cluj-Napoca laboratories. The laboratories are accredited by a member of group of experts of the European Commission for standardisation and conformity assessment, namely *RENAR* (certificate no. 352-L) *Accreditation Association*, which is the national accreditation organism. Furthermore, the laboratories methodologies follow the quality requirements of *SR EN ISO 9001:2008, regarding the quality management system* and the general requirements of *SR EN ISO/CEI 17025:2005, for the laboratory competence*.

# CHAPTER V - THE WATER QUALITY IN MEDIAS TOWN

The quality of drinking water sources (private well waters, F1-F26 and public springs, I1-I3) was assessed based on the results of the physico-chemical analyses, such as pH, electrical conductivity (EC), total dissolved solids (TDS), metals (Ca, Mg, Na, K, As, Fe, Cd, Co, Cr, Cu, Mn, Ni, Pb, Zn), ions ($Cl^-$, $NO_2^-$, $NO_3^-$, $SO_4^{2-}$, $F^-$) and $NH_4^+$, total hardness, total alkalinity, $HCO_3^-$, $CO_3^{2-}$, filterable residue dried at 105°C and the chemical oxygen demand. Results of the electrochemical analyses for the drinking water samples collected in all three sampling campaigns (March and August, 2014 and August 2016) show a pH between 7.0-8.0, which indicates and classifies the water samples as circumneutral (*Figure V.1*)



*(a)*

*(b)*

***Figure V.1.*** *The pH variation for the drinking water samples collected in March, August, 2014 (a) and August 2016 (b)*

Results regarding the As, Cr, Fe, Na, Ni and Zn contents do not exceed the maximum allowable concentrations (MACs), according to the *Romanian law*, compared with the Cd, Pb and Mn contents. Water sample F14 collected in August 2014 is characterized by the highest Pb concentration, exceeding the MAC (10 µg/L) with 20%. Water sample F16 is characterized with the highest Pb concentration in the third sampling campaign and the spring sample I1 has the highest Pb concentration in March, 2014. For the As and Cr contents, results are below the MACs (*Table V.1*).

According to the Romanian legislation, water sample F14 is polluted with Cd: the obtained results from August 2014 and 2016 exceed the MAC of 5.0 mg/L three and four times.

***Table V.1.*** *Maximum, minimum, mean values and MACs for As and Cr (Hoaghia et al., 2015c; Hoaghia et al., 2016a)*

| | Sample | Maximum | Sample | Minimum | Mean | Median | Standard deviation | MAC* |
|---|---|---|---|---|---|---|---|---|
| **March 2014** | *As (µg/L)* | | | | | | | |
| | F16 | 2.2 | F2-F4, F6-F13, F17, F18, I1 | **BQL | 0.7 | 0.4 | 0.7 | 10 |
| **August 2014** | F14 | 6.7 | F1-F4, F6-F13, F17, F18, I1; | BQL | 0.9 | 0.3 | 1.5 | |
| **August 2016** | I3 | 5.9 | F2-F4, F6-F13, F17-F26, I1, I2 | BQL | 0.8 | 0.3 | 1.4 | |
| **March 2014** | *Cr (µg/L)* | | | | | | | |
| | I1 | 7.9 | F2-F13, F15- F18, I2 | BQL | 1.0 | 0.5 | 1.8 | 50 |
| **August 2014** | I1 | 12.0 | F8 | 1,3 | 4.7 | 3.9 | 2.7 | |
| **August 2016** | F4 | 10.1 | F18 | BQL | 3.8 | 3.4 | 2.2 | |

*MAC, according to Romanian legislation (Law 311, 2014); **BQL (bellow the quantification limit of the method); 1.0 µg/L As and 1.0 µg/L Cr, as the quantification limits

Recent studies show $NO_2^-$, $NO_3^-$ and $NH_4^+$ pollution of groundwater used as drinking water source, in Medias Town (Roşu et al. 2014, Hoaghia et al., 2013). Analyses results for water samples collected in August 2014 and 2016 indicate a significant $NH_4^+$ pollution level; the maximum values are 48 mg/L (water sample F11) and 38 mg/L (water sample F12) (*Table V.2.*).

***Table V.2.*** *Statistical description for $NO_2^-$, $NO_3^-$, $NH_4^+$ in all drinking water samples from Medias Town (Hoaghia et al., 2015b; Hoaghia et al., 2015c)*

| Parameter | Minimum | Maximum | Mean | Standard deviation | Median | MAC* |
|---|---|---|---|---|---|---|
| **$NO_2^-$ (mg/L)** | ** BQL | 6.9 | 1.2 | 1.2 | 1.1 | 0.5 |
| **$NO_3^-$ (mg/L)** | BQL | 270 | 96 | 60 | 92 | 50 |
| **$NH_4^+$ (mg/L)** | BQL | 48 | 5.3 | 8.4 | 1.3 | 0.5 |

*MAC according to the Romanian legislation (Law 311, 2014) ** BQL (bellow the quantification limit of the method): QLM = 0.06 mg/L $NO_2^-$, 0.33 mg/L $NO_3^-$; 0.02 mg/L $NH_4^+$.

The $NO_2^-$ and $NO_3^-$ results exceed seven and fourteen times the MAC for $NO_2^-$ and five times for $NO_3^-$. In March, the maximum values are 6.9 mg/L $NO_2^-$ for water sample F7 and 250 mg/L $NO_3^-$ for F18 (Hoaghia et al., 2015b). Sample F17 is characterized by the highest $NO_2^-$ concentration (3.25 mg/L), while sample F10 has the highest $NO_3^-$ value (271 mg/L); the results were obtained in August 2014 (Hoaghia et al., 2015c). In August 2016, the results can be correlated with those obtained with two years earlier, sample F17 has the highest $NO_2^-$ content

(2.88 mg/L) and sample F10 the highest $NO_3^-$ content (211 mg/L). Possible sources for the nitrogen compounds pollution are the household and agricultural activities. Inhabitants use to rase animals and store the faecal wastes at very short distance from the drinking water sources. In addition, dry toilets and basin discharge are as well placed near the drinking water sources and could be another source for the $NO_2^-$, $NO_3^-$ and $NH_4^+$.

The $SO_4^{2-}$ concentrations range between 30 – 250 mg/L in March 2014 (Hoaghia et al., 2015b), 51-200 mg/L in August 2014 (Hoaghia et al. 2015c) and between 4.01 – 210 mg/L in the last sampling campaign from August 2016; the $Cl^-$ and $F^-$ contents are below the MAC of 250 mg/L for $Cl^-$ and 1.5 mg/L for $F^-$, according to Hoaghia et al. 2015a.

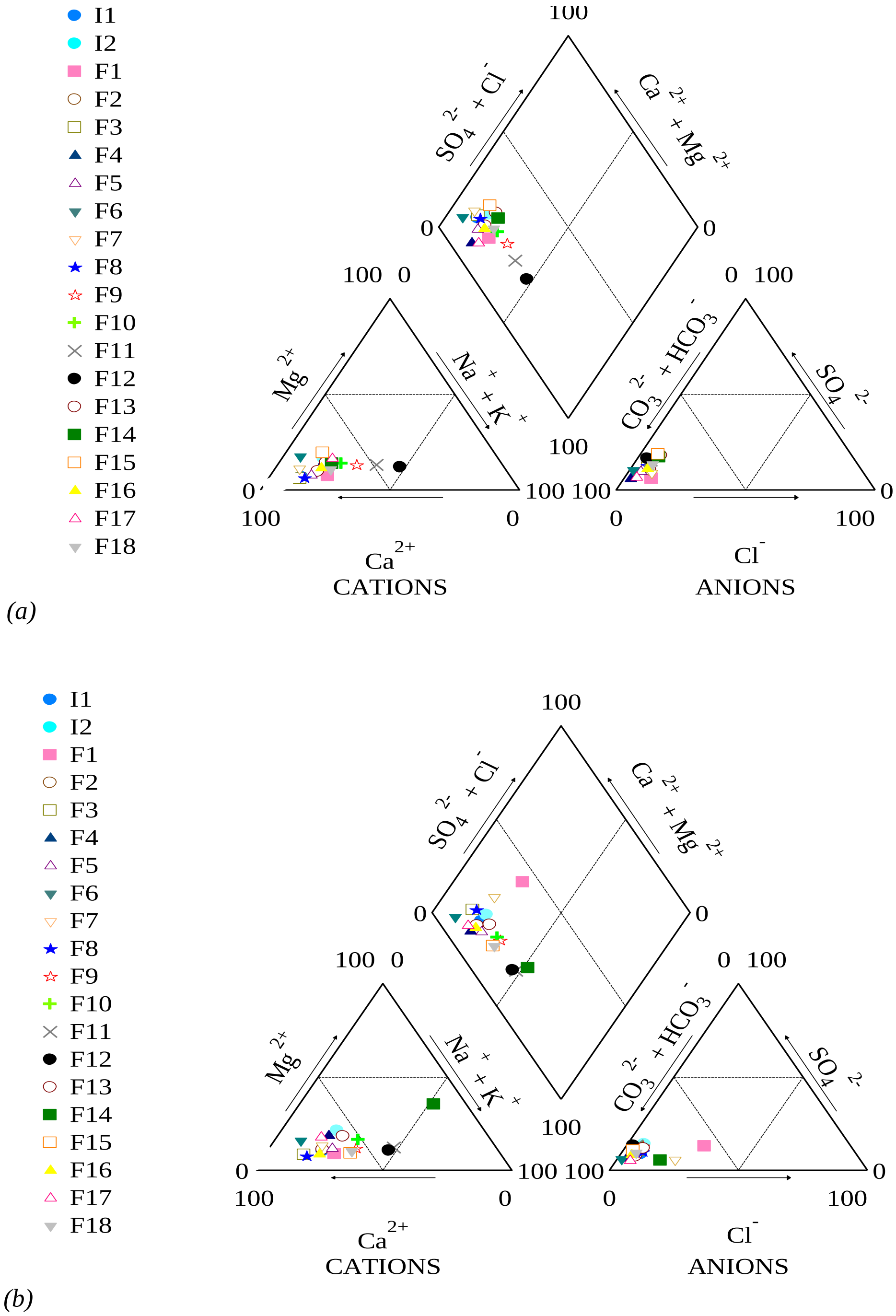
The total hardness results are higher as 5°d for all water samples. The MAC for the chemical oxygen demand is exceeding in all three sampling campaigns, with the maximum value of 33 $mgO_2/L$ (*Table V.3.).*

***Table V.3.*** *Statistical description for the total hardness, total alkalinity, $HCO_3$ and chemical oxygen demand for studied drinking water samples from Mediaş Town*

| | **Total hardness (°d)** | **$HCO_3^-$ (mg/L)** | **Total alkalinity (mmol/L)** | **CCO-Mn ($mgO_2/L$)** | **Filterable residue dried at 105°C (mg/L)** |
|---|---|---|---|---|---|
| **Minimum** | 15 | 201 | 3.3 | 0.9 | 0.24 |
| **Maximum** | 39 | 592 | 9.7 | 33 | 3.6 |
| **Mean** | 27 | 443 | 7.3 | 6.9 | 1.50 |
| **Standard deviation** | 6.4 | 80 | 1.3 | 7.5 | 0.67 |
| **Median** | 28 | 451 | 7.4 | 4.4 | 1.4 |
| **MAC*** | 5,0 | - | - | 5,0 | - |

*MAC according to the Romanian legislation (Law 311, 2014);

The groundwater typology can be determined by Piper and Stiff charts, which are composed with the help of the $SO_4^{2-}$, $Cl^-$, Na, Mg, K, $HCO_3^-$ and $CO_3^{2-}$ data. In the present study, the drinking water samples from Medias Town from the first two sampling campaigns, March and August 2014 are classified as Ca- $HCO_3^-$ types, except two samples, F11 and F12 which have high Na content, classifying the two samples into Na-$HCO_3^-$ types, according to *Figure V.2.(a) and (b)* (Hoaghia et al., 2015b).



(a)

(b)

***Figure V.2.*** *The typology of water samples collected in March (a) and August (b) 2014, according to the Piper chart (Hoaghia et al., 2015b)*

In the summer season of 2016, 76% of the water samples are classified as Ca- $HCO_3^-$ type, 17% are Na-$HCO_3^-$ type and rest of the 3% are Na-K-$HCO_3^-$ type, characterized by high Na and K contents (*Figure V.3.)*

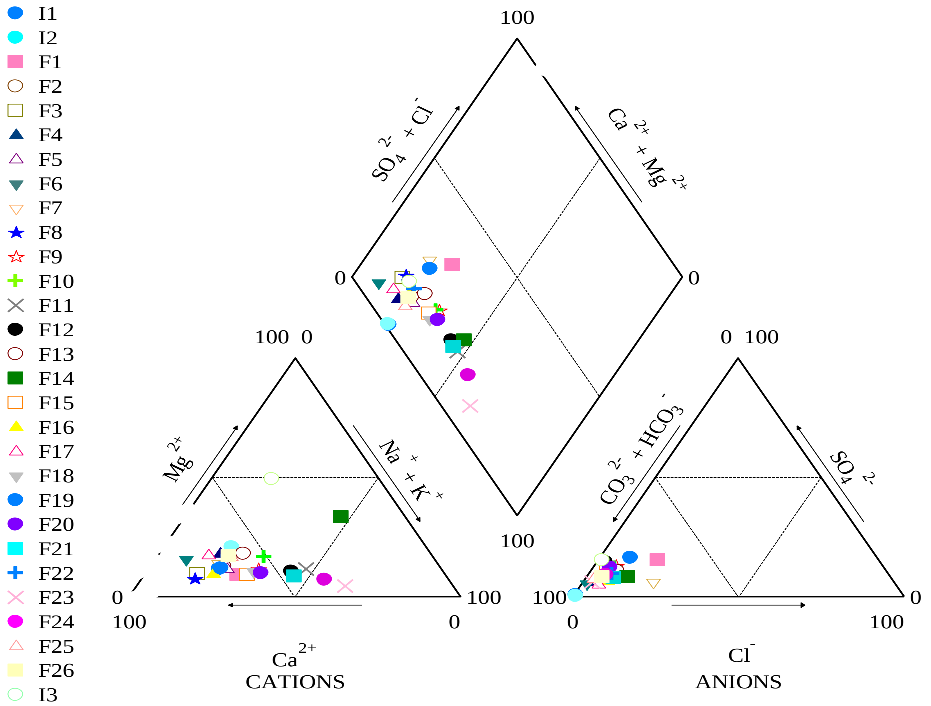


***Figure V.3.*** *The typology for drinking water samples studied in August, 2016, according to the Piper chart*

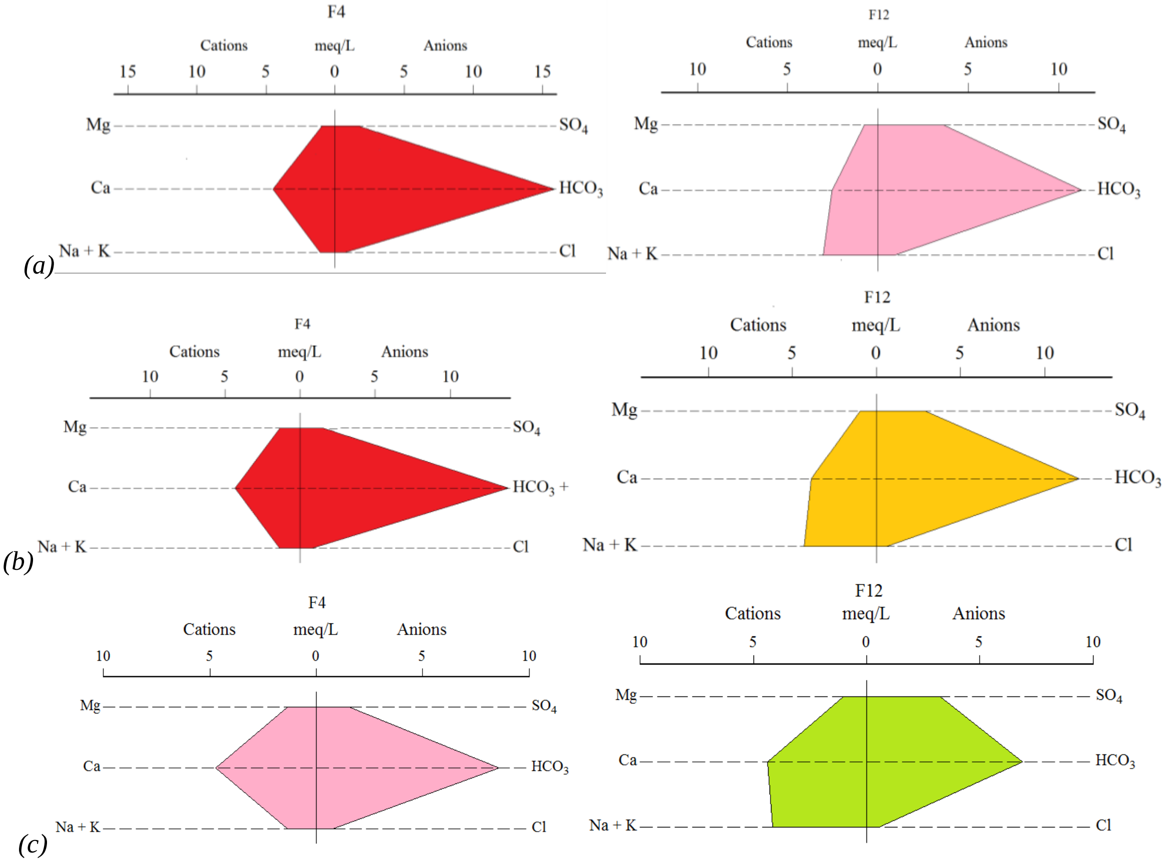


***Figure V.4.*** *The typology of water samples F4 and F12 collected in March 2014 (a), August 2014 (b) and August 2016 (c), according to the Stiff chart*

Using the Stiff chart, the predominant content of $HCO_3^-$ can be observed, which indicates the type of the water; for example water samples F4 and F12 are characterized in all three sampling champaings as $HCO_3^-$ type (*Figure V.4. a), b) and c)*).

The obtained results regarding the Degree of Contamination method, *CD*, are below the critical value of 1 (*CD* < 1), indicating the lack of metal pollution for all drinking water samples. Results range between -8.75 and -2.11 (*Figure V.5.).*

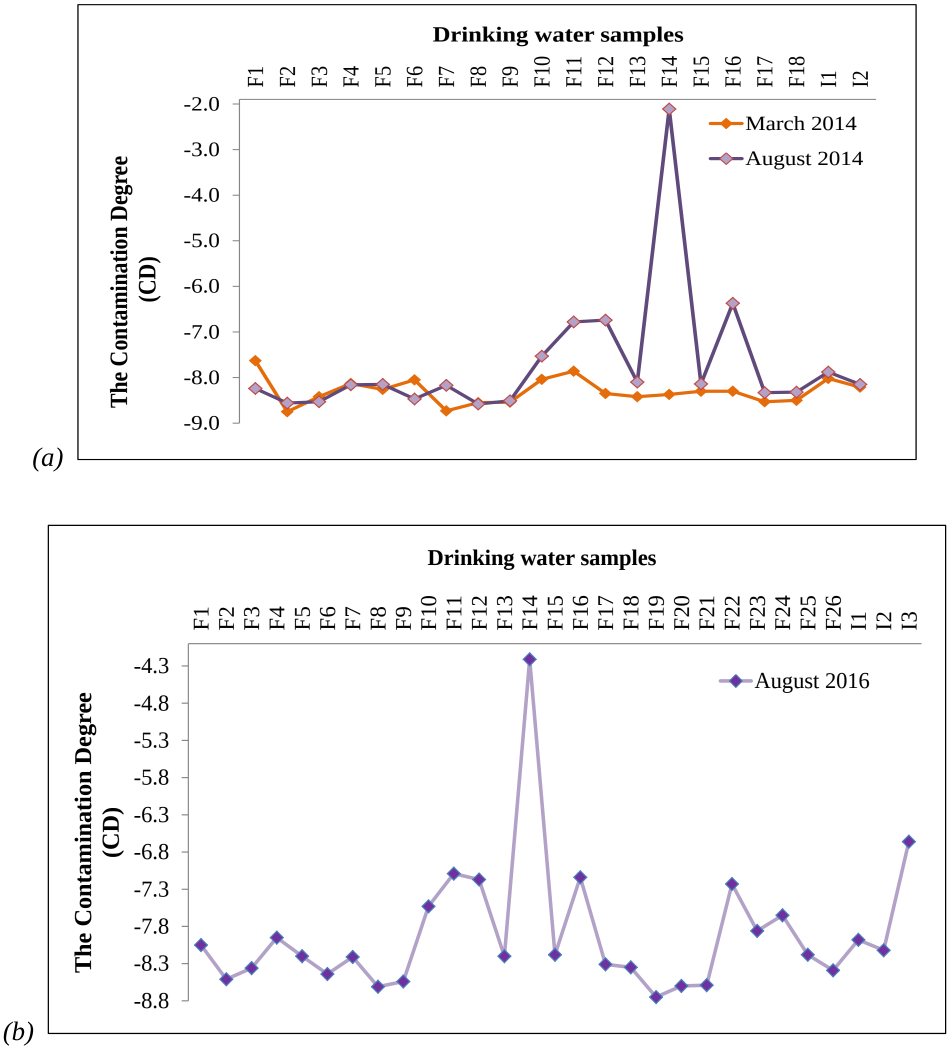


***Figure V.5.*** *The variation of the Contamination Degree (CD) results in March, August 2014 (a) and August 2016 (b)*

The *HPI* results are below the critical value of 100, except sample F14, which exceeds the critical value in both summer seasons (August 2014 and 2016) due to the high Cd concentration. In March 2014, the *HPI* values range between 1.45 and 12.10, with the maximum value obtained for water sample F4 and the minimum value for F7 (*Figure V.6.).* The *HEI* results are below the *high level of pollution* (*HEI* > 80); the results are even below *the low pollution level* (*HEI* < 40). Highest value was obtained for water sample F14, in both summer seasons, similar result as for *HPI*, which indicates a correlation between the two index methods and certifies the high pollution level for sample F14.

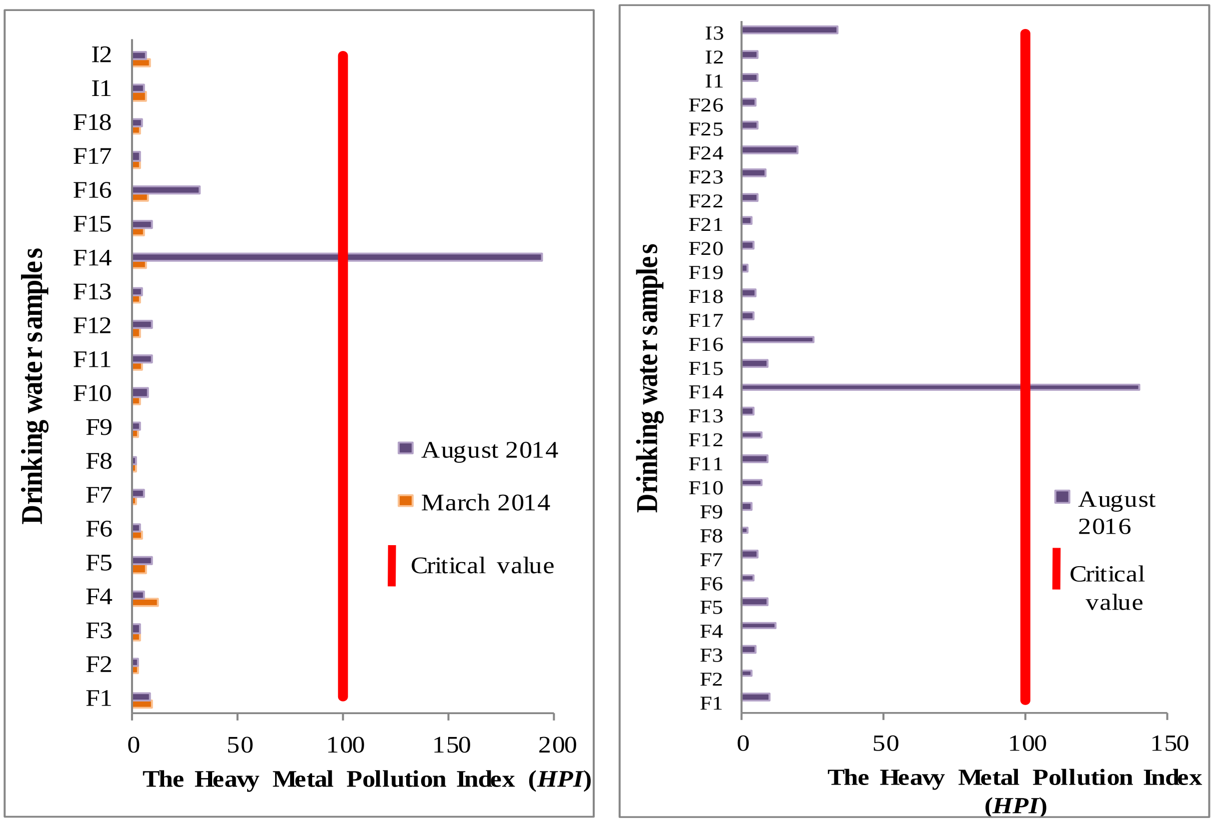


***Figure V.6.*** *Variations of the Heavy Metal Pollution Index (HPI) results for the drinking water samples*

The correlation matrix and hierarchical cluster analysis were used to correlate the metal content and the metal pollution index results. According to the correlation matrix, in March 2014 significant correlations can be observed, as follows: Cd-Cu, Cr-Fe, Cr-Pb, Cu-Zn, Cd-*HPI*, Cr-*CD*, Cr-*HEI*, Cu-*CD*, Fe-*CD*, Zn-*HPI*, Pb-*CD* and Pb-*HEI (Table V.10.).*

***Table V.10.*** *The correlations between metals and the metal pollution index results for the drinking waters sampled in March, 2014 (n=20)*

| **Var.** | **As** | **Cd** | **Cr** | **Cu** | **Mn** | **Ni** | **Fe** | **Zn** | **Pb** | ***CD*** | ***HPI*** | ***HEI*** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **As** | ***1** | -0.148 | 0.182 | 0.237 | -0.200 | 0.053 | 0.126 | -0.194 | 0.153 | 0.226 | 0.408 | 0.250 |
| **Cd** | -0.148 | **1** | 0.088 | **0.611** | 0.034 | 0.127 | -0.240 | **0.924** | -0.119 | 0.189 | **0.725** | 0.186 |
| **Cr** | 0.182 | -0.088 | **1** | 0.130 | -0.198 | -0.136 | **0.489** | -0.145 | **0.786** | **0.447** | 0.319 | **0.455** |
| **Cu** | 0.237 | **0.611** | 0.130 | **1** | -0.063 | 0.017 | 0.328 | **0.662** | 0.255 | **0.569** | **0.743** | **0.572** |

| **Var.** | **As** | **Cd** | **Cr** | **Cu** | **Mn** | **Ni** | **Fe** | **Zn** | **Pb** | ***CD*** | ***HPI*** | ***HEI*** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Mn** | -0.200 | 0.034 | -0.198 | -0.063 | **1** | -0.183 | -0.088 | 0.010 | -0.253 | 0.358 | 0.014 | 0.351 |
| **Ni** | 0.053 | 0.127 | -0.136 | 0.017 | -0.183 | **1** | 0.140 | 0.106 | -0.256 | 0.181 | 0.211 | 0.190 |
| **Fe** | 0.126 | -0.240 | **0.489** | 0.328 | -0.088 | 0.140 | **1** | -0.243 | **0.646** | **0.750** | 0.212 | **0.743** |
| **Zn** | -0.194 | **0.924** | -0.145 | **0.662** | 0.010 | 0.106 | -0.243 | **1** | -0.152 | 0.146 | **0.617** | 0.143 |
| **Pb** | 0.153 | -0.119 | **0.786** | 0.255 | -0.253 | -0.256 | **0.646** | -0.152 | **1** | **0.494** | 0.322 | **0.489** |
| ***CD*** | 0.226 | 0.189 | **0.447** | **0.569** | 0.358 | 0.181 | **0.750** | 0.146 | **0.494** | **1** | **0.653** | **0.998** |
| ***HPI*** | 0.408 | **0.725** | 0.319 | **0.743** | 0.014 | 0.211 | 0.212 | **0.617** | 0.322 | **0.653** | **1** | **0.660** |
| ***HEI*** | 0.250 | 0.186 | **0.455** | **0.572** | 0.351 | 0.190 | **0.743** | 0.143 | **0.489** | **0.998** | **0.660** | **1** |

*The bold values are different from 0 with a significant alpha level at 0.05

The hierarchical cluster analysis classifies the chemical compounds according to the similarities, so as to in March 2014 there are three cluster groups: *C1* – composed of Mn, As and Ni, *C2* – grouping Cu, Cd and Zn and *C3* – composed of Fe, Cr and Pb (*Figure V.7.)*

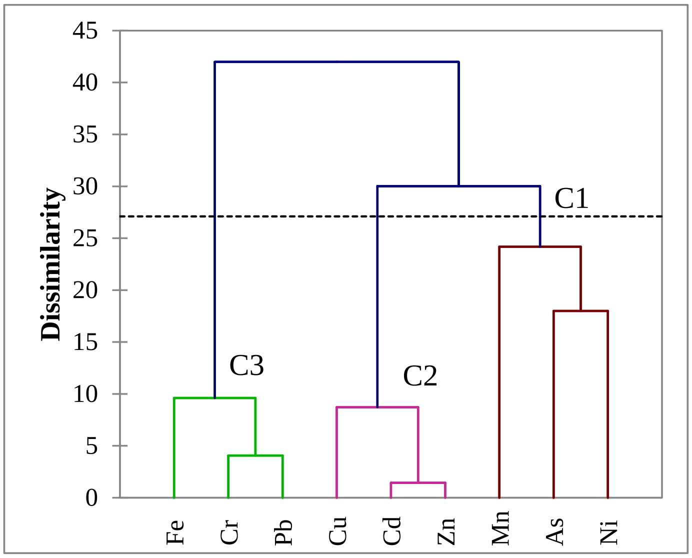


***Figure V.7.*** *The Hierarchical cluster analysis for the metal content (March, 2014)*

For the second sampling campaign, the dendrogram shows significant correlations between As-Cd, As-Ni, As-Pb, Cd-Ni, Cd-Pb, Cr-Fe, Cu-Mn, Cu-Zn, Mn-Cu, Mn-Zn, Ni-As, Ni-Cd. All three metal pollution index results present positive correlations with the studied metals, as follows: *CD* with As, Cd, Cu, Ni Zn and Pb, *HPI* with As, Cd, Ni and Pb, and *HEI* with As, Cd, Cu, Ni, Zn and Pb (*Table V.11.).*

***Table V.11.*** *The correlations between metals and the metal pollution index results for the drinking waters sampled in August, 2014 (n=20)*

| **Varb.** | **As** | **Cd** | **Cr** | **Cu** | **Mn** | **Ni** | **Fe** | **Zn** | **Pb** | ***CD*** | ***HPI*** | ***HEI*** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **As** | **1** | **0.898** | 0.029 | 0.258 | -0.055 | **0.664** | 0.047 | 0.294 | **0.836** | **0.862** | **0.929** | **0.862** |
| **Cd** | **0.898** | **1** | 0.110 | 0.239 | -0.057 | **0.728** | 0.070 | 0.365 | **0.742** | **0.901** | **0.990** | **0.901** |
| **Cr** | 0.029 | 0.110 | **1** | 0.257 | 0.016 | 0.033 | **0.616** | -0.039 | 0.122 | 0.176 | 0.117 | 0.176 |
| **Cu** | 0.258 | 0.239 | 0.257 | **1** | **0.552** | 0.105 | -0.061 | **0.718** | 0.101 | **0.450** | 0.255 | **0.450** |
| **Mn** | -0.055 | -0.057 | 0.016 | **0.552** | **1** | -0.187 | -0.284 | **0.533** | 0.127 | 0.342 | 0.013 | 0.342 |
| **Ni** | **0.664** | **0.728** | 0.033 | 0.105 | -0.187 | **1** | 0.058 | 0.112 | 0.371 | **0.575** | **0.695** | **0.575** |
| **Fe** | 0.047 | 0.070 | **0.616** | -0.061 | -0.284 | 0.058 | **1** | -0.308 | -0.012 | 0.008 | 0.050 | 0.008 |
| **Zn** | 0.294 | 0.365 | -0.039 | **0.718** | **0.533** | 0.112 | -0.308 | **1** | 0.231 | **0.539** | 0.376 | **0.539** |
| **Pb** | **0.836** | **0.742** | 0.122 | 0.101 | 0.127 | 0.371 | -0.012 | 0.231 | **1** | **0.833** | **0.822** | **0.833** |
| ***CD*** | **0.862** | **0.901** | 0.176 | **0.450** | 0.342 | **0.575** | 0.008 | **0.539** | **0.833** | **1** | **0.939** | **1.000** |
| ***HPI*** | **0.929** | **0.990** | 0.117 | 0.255 | 0.013 | **0.695** | 0.050 | 0.376 | **0.822** | **0.939** | **1** | **0.939** |
| ***HEI*** | **0.862** | **0.901** | 0.176 | **0.450** | 0.342 | **0.575** | 0.008 | **0.539** | **0.833** | **1.000** | **0.939** | **1** |

*The bold values are different from 0 with a significant alpha level at 0.05

According to the hierarchical cluster analysis, the data set obtained in August 2014 indicates three cluster groups: *C1* – comprises of Ni, Pb, As and Cd, *C2* – has close similarities between Cr and Fe, while *C3* – grouping Mn, Cu and Zn (*Figure V.8.).*

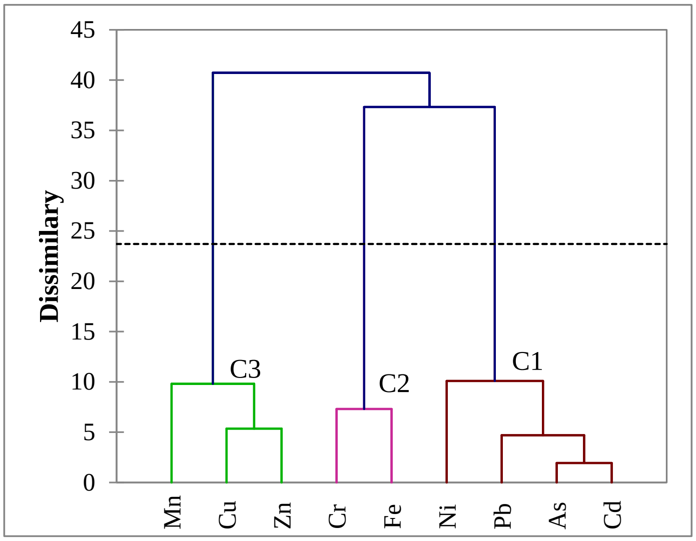


***Figure V.8.*** *The Hierarchical cluster analysis for the metal content (August, 2014)*

Significant correlations can be observed between the metal content and the metal pollution index results, in August 2016, as follows: As presents close similarities with Cd, Ni and Pb, Cd is correlated with Ni and Zn, while significant correlations are between Cr-Fe, Mn-Zn, and Ni-Fe; the metal pollution index results show positive correlations, such as: *CD* with As, *CD*, Mn, Ni and Zn, *HPI* with As, Cd, Ni and Zn, and *HEI* with As, Cd, Ni and Zn (*Table V.12.)*

***Table V.12.*** *The correlations between metals and the metal pollution index results for the drinking water sampled in August, 2016 (n=29)*

| **Varb.** | **As** | **Cd** | **Cr** | **Cu** | **Mn** | **Ni** | **Fe** | **Zn** | **Pb** | ***CD*** | ***HPI*** | ***HEI*** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **As** | **1** | **0.628** | 0.174 | 0.007 | -0.058 | **0.461** | 0.351 | 0.362 | **0.410** | **0.719** | **0.750** | **0.746** |
| **Cd** | **0.628** | **1** | 0.141 | 0.023 | -0.019 | **0.430** | 0.121 | **0.679** | -0.018 | **0.817** | **0.974** | **0.834** |
| **Cr** | 0.174 | 0.141 | **1** | 0.187 | -0.205 | 0.089 | **0.507** | -0.129 | 0.053 | 0.140 | 0.158 | 0.177 |
| **Cu** | 0.007 | 0.023 | 0.187 | **1** | -0.007 | -0.201 | -0.137 | 0.013 | 0.146 | 0.135 | 0.048 | 0.147 |
| **Mn** | -0.058 | -0.019 | -0.205 | -0.007 | **1** | -0.014 | -0.104 | **0.554** | -0.048 | **0.368** | 0.011 | 0.363 |
| **Ni** | **0.461** | **0.430** | 0.089 | -0.201 | -0.014 | **1** | **0.370** | 0.188 | -0.074 | **0.500** | **0.449** | **0.431** |
| **Fe** | 0.351 | 0.121 | **0.507** | -0.137 | -0.104 | **0.370** | **1** | -0.096 | 0.130 | 0.222 | 0.177 | 0.259 |
| **Zn** | 0.362 | **0.679** | -0.129 | 0.013 | **0.554** | 0.188 | -0.096 | **1** | -0.126 | **0.729** | **0.659** | **0.741** |
| **Pb** | **0.410** | -0.018 | 0.053 | 0.146 | -0.048 | -0.074 | 0.130 | -0.126 | **1** | 0.275 | 0.187 | 0.292 |
| ***CD*** | **0.719** | **0.817** | 0.140 | 0.135 | **0.368** | **0.500** | 0.222 | **0.729** | 0.275 | **1** | **0.888** | **0.980** |
| ***HPI*** | **0.750** | **0.974** | 0.158 | 0.048 | 0.011 | **0.449** | 0.177 | **0.659** | 0.187 | **0.888** | **1** | **0.907** |
| ***HEI*** | **0.746** | **0.834** | 0.177 | 0.147 | 0.363 | **0.431** | 0.259 | **0.741** | 0.292 | **0.980** | **0.907** | **1** |

* The bold values are different from 0 with a significant alpha level at 0.05

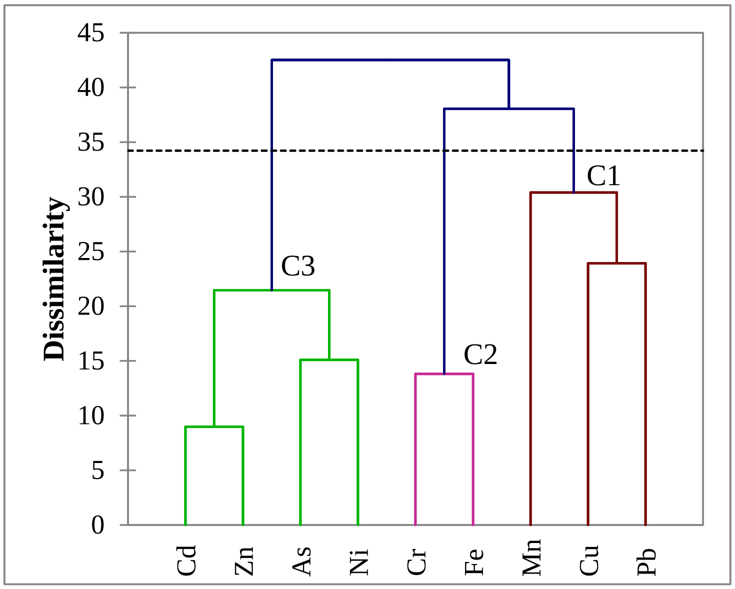


***Figure V.9.*** *The hierarchical cluster analysis for the metal content (August, 2016)*

The water samples collected in August 2016 are grouped in three cluster groups, giving to the hierarchical cluster analysis: *C1* – grouping Mn with Cu and Pb, *C2* – comprises of Cr and Fe, and *C3* – which shows close correlations between Cd, Zn, As and Ni (*Figure V.9.).*

The *WQI* method was applied with the help of the pH, CE, total alkalinity, total hardness, TDS, Ca Mg, Fe, $F^-$, $NO_3^-$, $Cl^-$ and $SO_4^{2-}$ results. Generally, the *WQI* results exceed the critical value of 100, which characterises the drinking water samples into *not recommended for drinking purpose*. In March 2014, *WQI* results range between 67 and 166, with the minimum value obtained for sample F12 and the maximum value for sample F15 (*Figure V.10.).*

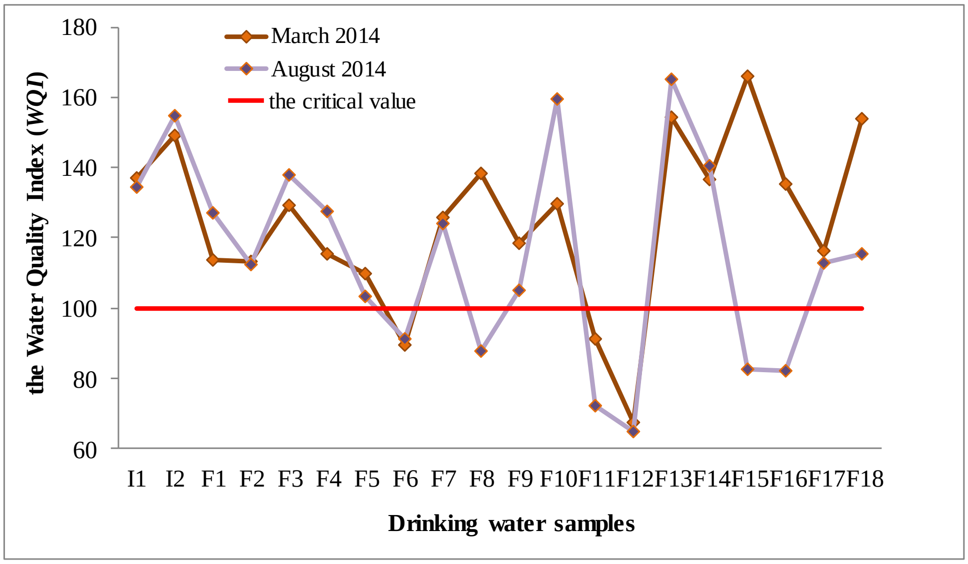


***Figure V.10.*** *The trend variation for Water Quality Index (WQI) obtained for water samples collected in 2014 (March and August)*

Data obtained in August 2014 is characterized by the minimum value of 65 (F12) and the maximum value of 165 (F13). Water sample F12 has the minimum values in both data sets, which confirms the *low quality status*. 95% of the drinking water samples from March 2014 are characterized as *not recommended for the drinking purpose*, and rest of the 5% are drinking waters with a *very poor quality status*. The water samples collected in August 2014 present similar quality status: 70% are water samples *not recommended for the drinking purpose*, 20% have a *very poor quality status* and the rest of the 10% are waters characterized with a *poor quality status* (*Figure V.11*).

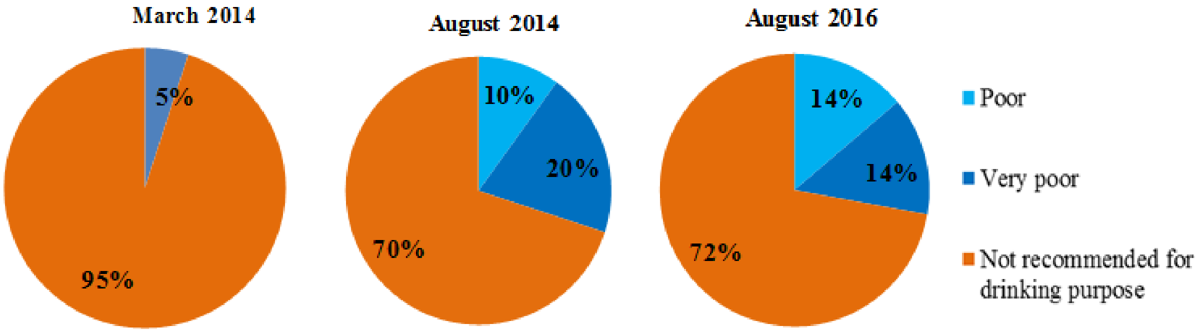


***Figure V.11.*** *Drinking water classes according to the quality status given by the Water Quality Index (WQI) results*

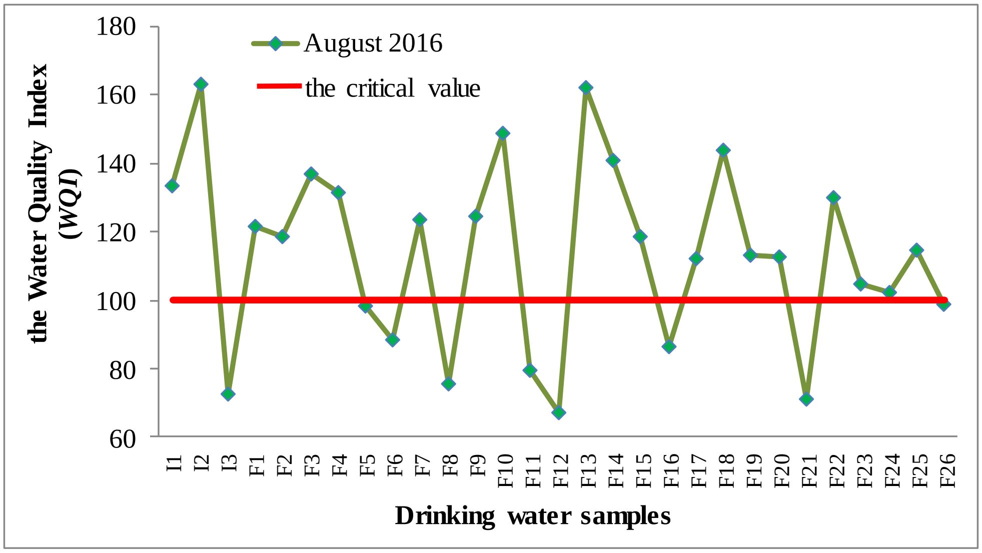


***Figure V.12.*** *The trend variation for Water Quality Index (WQI) results obtained for water samples collected in 2016 (August)*

The *WQI* results range between 67 and 163 in the summer season of 2016 (*Figure V.12.)*. The high $NO_3^-$ concentrations and $D_T$ values increase the *WQI* results, the $NO_3^-$ content exceeds twice and four times the MAC.

Also, the *DWQI* results classify the majority of the water samples into the *poor quality class*, as follows: in the rainy season of March 2014, 55% of samples have a *poor quality* and 25% of samples have a *very poor quality* (*Figure V.13.)*.

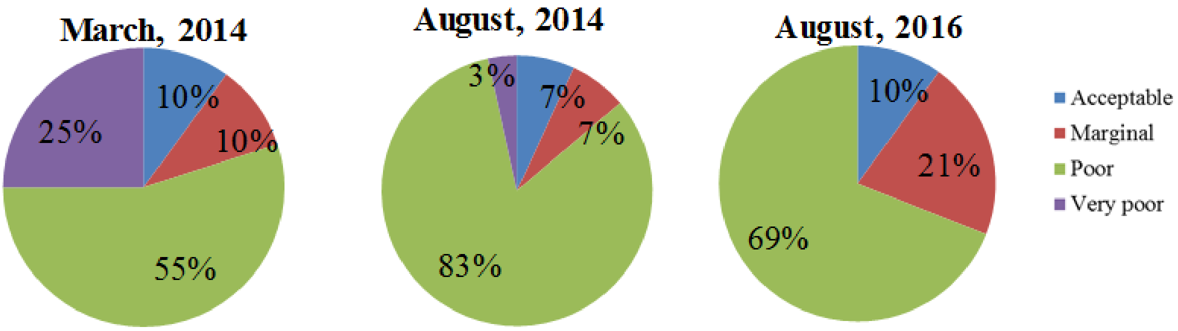
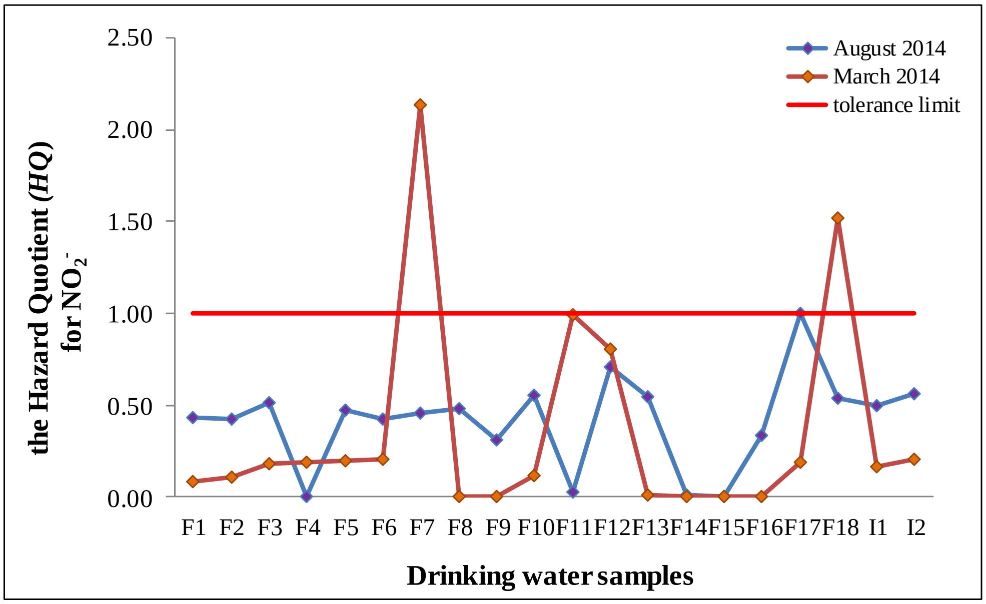


***Figure V.13.*** *The quality of the drinking water, according to the DWQI results*

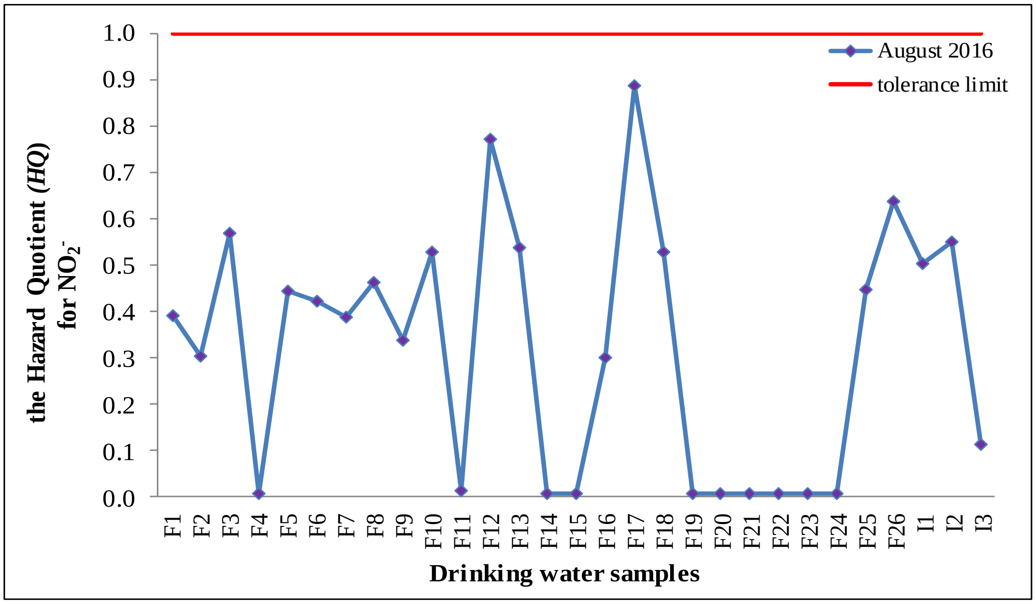
In the summer season of 2014, 83% of samples have a *poor quality* and 7% are characterized with an *acceptable quality*; the rest of the samples, 7% and 3% have a *marginal* and respectively a *very poor quality*. On the other hand, samples collected in August 2016 are classified in only two categories, namely in *poor* and *marginal quality* categories.

One of the specific objectives of the thesis was to assess the health risk at $NO_2^-$ and $NO_3^-$ with the help of three risk assessment index methods, namely the Chronic Daily Intake- *CDI*, the Hazard Quotient-*HQ* and the Hazard Index- *HI*. Generally, both parameters exceed two to four times the MACs (according to the legislative regulations). Results for the *CDI* calculated for the $NO_2^-$ content range between 0.003 and 0.029 mg/kg/day, and for the $NO_3^-$ content between 0.701 and 3.378 mg/kg/day, according to Hoaghia et al., 2016b.

In the current study the *CDI* varies in March 2014 from 0.00 to 0.213 mg/kg/day for $NO_2^-$ and from 0.74 to 7.75 mg/kg/day for the $NO_3^-$ content. The drinking water samples collected in the summer seasons of 2014 and 2016 are characterized by a *CDI* of $NO_2^-$ ranging from 0.00 to 0.10 mg/kg/day, and from 0.001 to 0.637 mg/kg/day respectively. Otherwise, for the $NO_3^-$ content, the *CDI* varies from 0.95 to 8.34 mg/kg/day in August 2014 and from 0.003 to 6.492 mg/kg/day for the water samples collected in the last sampling campaign of August 2016.



*(a)*



*(b)*

***Figure V.14.*** *The HQ variations for $NO_2^-$ in March and August, 2014 (a) and August, 2016 (b)*

The hazard quotient results, calculated for the $NO_2^-$ and $NO_3^-$ content, exceed the critical value of 1 ($HQ > 1.0$), which indicated a *potential pollution risk* at the respective nitrogen compounds. In the first sampling campaign, *HQ* for $NO_2^-$ ranges between 0.00 and 2.12 with three values higher as the extreme value, which indicates *possible non-carcinogenic risk* at the nitrogen compounds, and in August 2014 it ranges between 0.003 and 1.00. (*Figure V.14. (a)*). In 2016, the *HQ* results start from 0.006 until 0.89, according to *Figure V.14. (b)*), which shows a *no non-carcinogenic risk* at the nitrogen compounds.

Results for the *HQ* at $NO_3^-$ range between 0.15 – 4.85, in March 2014, 0.60 – 5.21 in August 2014 and between 0.003 – 4.058 in August 2016. The unity is exceeded for all data sets, due to the high $NO_3^-$ concentrations (*Figure V.15. (a),(b)*).

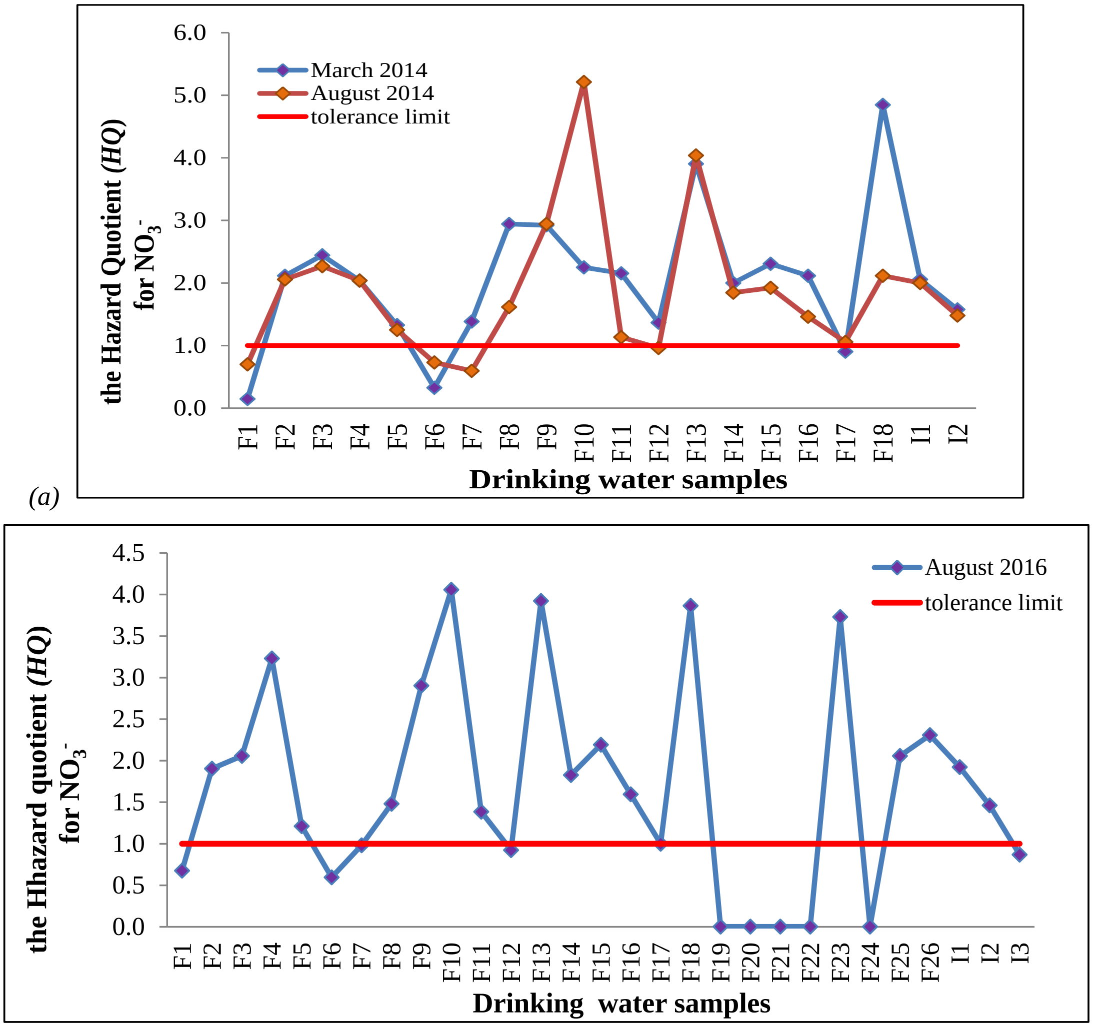


***Figure V.15.*** *The variations of the Hazard Quotient (HQ), for* $NO_3^-$*, in March, August, 2014 (a) and August, 2016 (b)*

85% of water samples collected in March and August, 2014 could present a *potential risk* at $NO_3^-$, according to the high results (*HQ* > 1.0), while in August 2016, 72% of samples have results higher as one (*HQ* > 1.0).

High nitrate content in the drinking water could be a predisposition for acute infant methemoglobinemia or ”blue baby” syndrome.

# CHAPTER VI – THE SOIL QUALITY FROM MEDIAS TOWN. THE METAL TRANSFER FROM SOIL TO FRUITS AND VEGETABLES

The soil samples were collected, prepared and analysed according to the quality standards; the methodology is described in *Chapter IV*.2 and *IV.3*. The parameters were analysed from soil leachate samples, namely the pH, EC and the ions content ($NO_2^-$, $NO_3^-$, $SO_4^{2-}$, $Cl^-$ $F^-$, $PO_4^{3-}$). Metal content was as well analyses from the extraction of dry matter samples, by *aqua regia*. The quality of the soil samples from Medias Town was determined, with respect to As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Zn.

***Table VI.1*** *Statistical description of the measured metal content for soil samples in 2014 and 2016 (Hoaghia et al., 2016c*)

| Variable | Min. | Max. | Code of the sample | Mean | Median | Standard deviation | Alert threshold * |
|---|---|---|---|---|---|---|---|
| As (mg/kg) | 1.0 | **24** | S23 | 8.0 | 8.0 | 1.67 | 15 |
| Cd (mg/kg) | 0.45 | **10.2** | S22 | 2.2 | 1.71 | 1.30 | 3 |
| Co (mg/kg) | 4.57 | 10.2 | S19 | 6.71 | 6.55 | 0.30 | 30 |
| Cr (mg/kg) | 12.0 | 63 | S7 | 27 | 25 | 0.23 | 100 |
| Cu (mg/kg) | 15 | **142** | S26 | 40 | 31 | 7.17 | 100 |
| Fe (mg/kg) | 1112 | 20412 | S21 | 12083 | 12621 | 66.4 | - |
| Mn (mg/kg) | 154 | 854 | S26 | 505 | 504 | 48.2 | 1500 |
| Ni (mg/kg) | 1.22 | 32 | S2 | 21 | 22 | 2.07 | 75 |
| Pb (mg/kg) | 14 | **174** | S29 | 75 | 74 | 6.62 | 50 |
| Zn (mg/kg) | 33 | 241 | S26 | 140 | 138 | 6.36 | 300 |

*Alert threshold/sensitive use, according to the Reg. 756, 1997; the bold values exceed the thresholds.

A high amount of metals characterizes the soil samples collected in the summer of 2014, with exceeding of the Cd and Pb alert thresholds (3 mg/kg Cd, 50 mg/kg Pb) (Hoaghia et al., 2016c). The alert threshold for Pb is twice exceeded for 80% of samples and, the intervention threshold, for 15% of soil samples (*Table VI.1.).*

The As content ranges between 3.98 – 10.9 mg/kg; for 90% of samples the background value if exceeded. For the Cr, Cu, Mn, Ni and Zn contents, the alert thresholds (100 mg/kg, Cr and Cu, 300 mg/kg Zn) are not exceeded and they range between 16 – 63 mg/kg Cr, 16-97 mg/kg Cu, 350 – 680 mg/kg Mn, 16 – 32 mg/kg Ni and 54 – 540 mg/kg Zn. On the other hand, the Pb intervention threshold (100 mg/kg) is twice exceeded, with the maximum value of 125 mg/kg.

According to *Regulation No. 756 from 1997*, the ionic content ($SO_4^{2-}$, $Cl^-$ şi $F^-$) does not exceed the thresholds.

The index of geo-accumulation ($I_{geo}$) was calculated for the Cr, Cu, Zn, As, Cd and Pb contents. Highest values were obtained for Cd, Cu and Pb; the results correlate with the highest amount of same metals. According to the $I_{geo}$ results, 5% of samples are *unpolluted to moderately pollute* with Cr; 30% of samples are *unpolluted to moderately pollute* with Cu, 45% are *moderately polluted* with Cu and rest of 20 % are *moderately to strong polluted* with Cu.

In August 2016, the soil samples are *unpolluted* with Cr for 10% of samples; 79% indicate an *unpolluted to moderately polluted* status, 7% indicate a *moderately pollution* with Cr, and the rest of 4% are characterized by a *strong pollution* with Cr (*Figure VI.1.).*

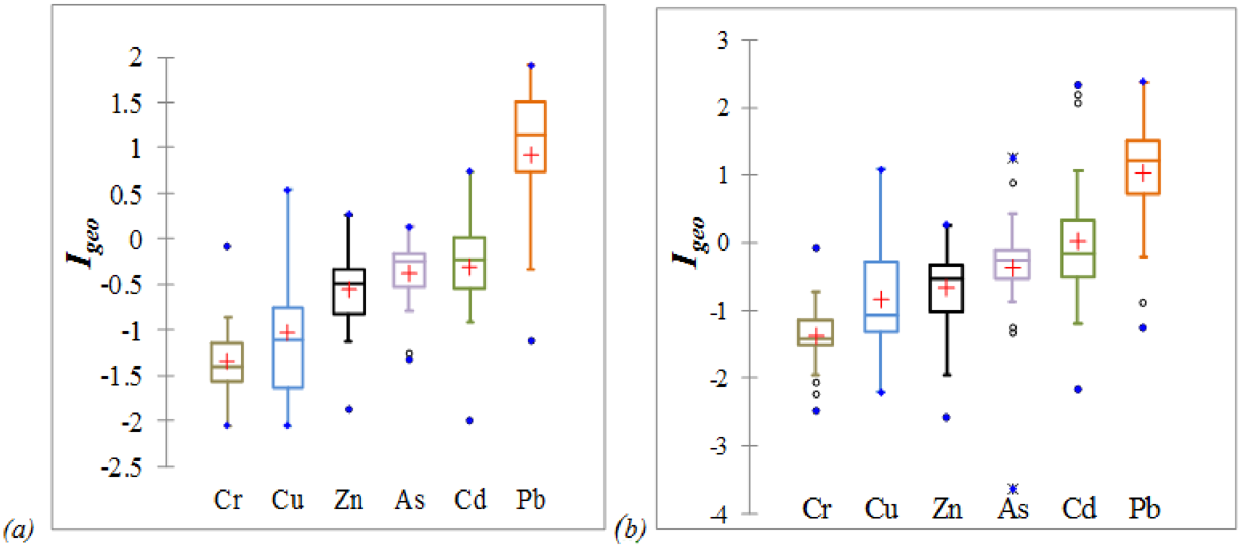


***Figure VI.1.*** *The index of geo-accumulation ($I_{geo}$) for soil samples collected in August, 2014 (a) and 2016 (b)*

The contamination factor ($C_f$) method classifies the soil samples into four pollution classes, namely *low*, *moderately*, *considerable* and *high pollution status*. The $C_f$ results show one case of *moderately pollution* with Cd and 25 cases of *moderately pollution* with Pb, in the first season of 2014. In 2016, *low pollution* with Cr and Zn, *considerable pollution* with Cd and Pb and *moderately pollution* with As and Cu can be observed (*Figure VI.2.).*

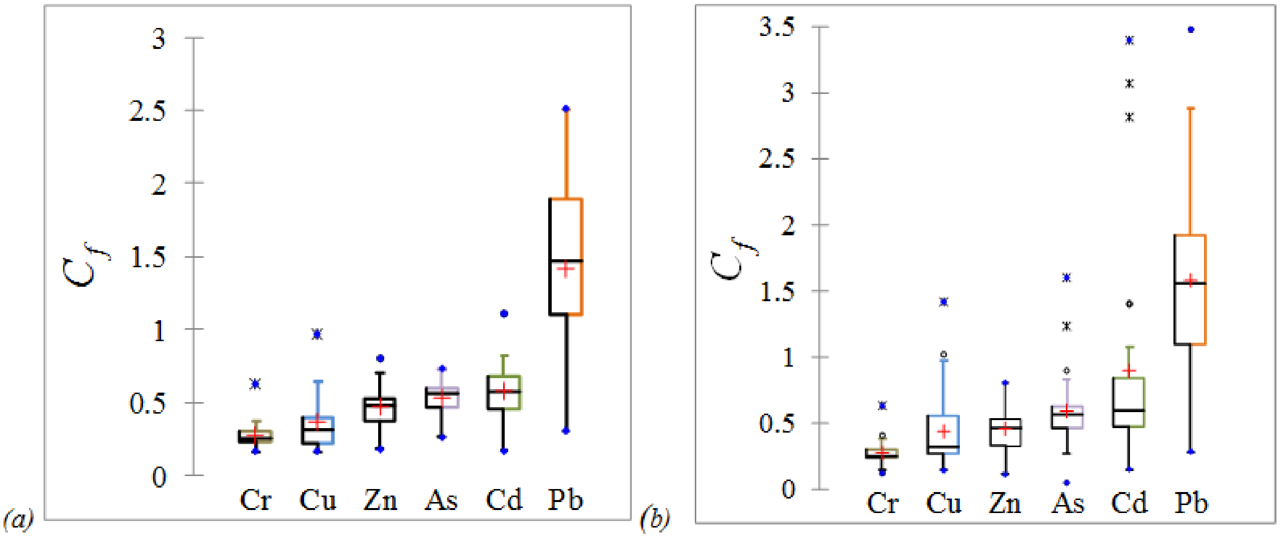


***Figure VI.2.*** *The contamination factor ($C_f$) results for soil samples collected in August, 2014 (a) and 2016 (b)*

According to the pollution index, *PLI*, in August 2014 no soil sample presents pollution; the *PLI* results range between 0.02 and 0.29, with a mean of 0.14. In 2016, there is no metal pollution as well (*Figure VI.3*).

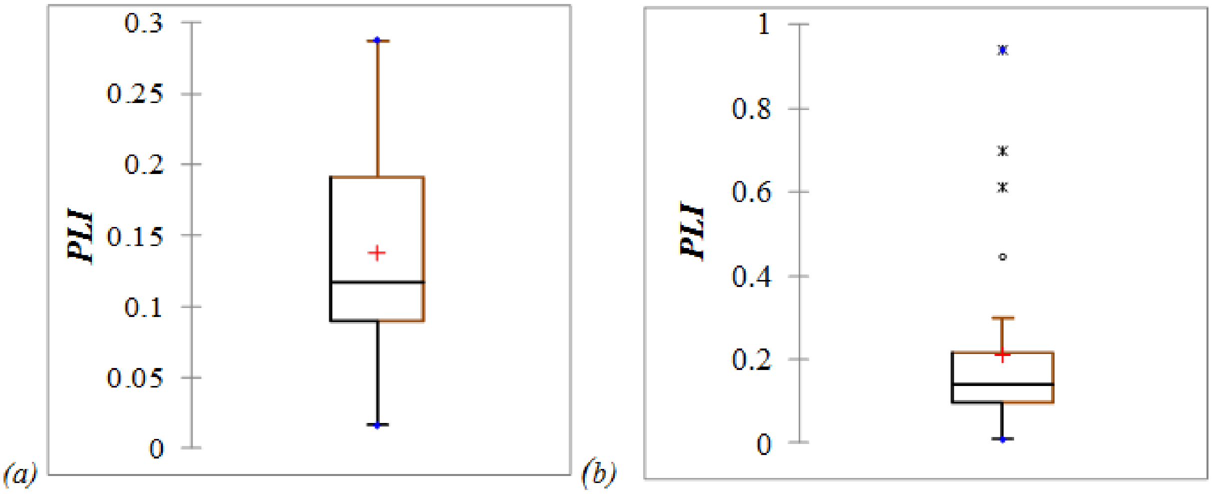


***Figure VI.3.*** *The pollution index (PLI) for soil samples collected in August, 2014 (a) and 2016)(b)*

The Risc factor method, *Er* indicates a *potential low ecological risk* at Cr, Cu, Zn, Cd, As and Pb. The highest *Er* values were obtained for Cd, Cu, As and Pb, as *Figure VI.4. a), b)* shows.

The cumulated risk with respect to all studied metals is specified by the Risk index, *Ri*. Low results classify the soil samples into *the low ecological risk status*.

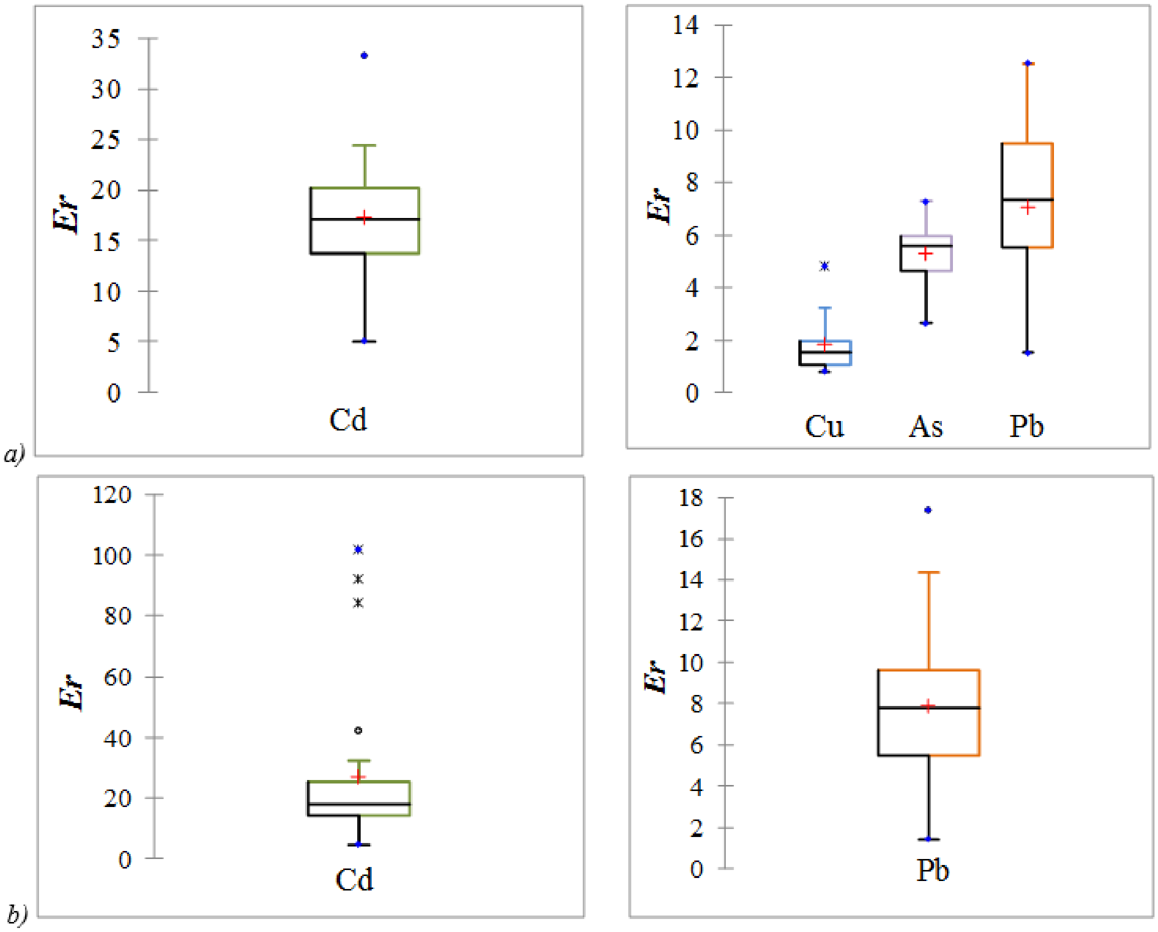


***Figure VI.4.*** *The risk factor, Er at Cd, Cu, As and Pb in August, 2014 (a) and 2016 (b)*

Eighteen vegetables and fruits samples (V1-V8) were collected in the summer of 2014. The sampling and sample preparation were done according to quality standards requirements. The fruit and vegetable samples are actually carrot roots, onion bulbs, lettuce leaves and tomato, pepper, quince, peach fruits.

Inductively coupled plasma mass spectrometry (ICP-MS) technique was used for the As, Cd, Co, Cr, Cu, Fe, Ni, Mn, Pb, Zn determinations. The results exceed the tolerance limits of As, Cd, Cu and Pb for the tomato, pepper fruits, carrot root and lettuce leaves samples (*Table VI.2*).

***Table VI.2.*** *The heavy metal content of vegetables and fruits*

| **Fruit, vegetable** | **Binomial nomenclature** | | **As (mg/kg)** | **Cd (mg/kg)** | **Cr (mg/kg)** | **Cu (mg/kg)** | **Ni (mg/kg)** | **Pb (mg/kg)** | **Zn (mg/kg)** |
|---|---|---|---|---|---|---|---|---|---|
| **tomato fruit** | *Solanum lycopersicum* | mean±SD* | 0.019±0.002 | 0.096±0.04 | 0.41±0.13 | 24.3±28.7 | 1.05±0.26 | 0.41±0.04 | 13.9±2.99 |
| | | range | 0.018-0.02 | 0.06-0.13 | 0.34-0.56 | 7.45-**57.4** | 0.79-1.31 | 0.38-**0.45** | 10.5-16.1 |
| **carrot root** | *Daucus carota sativus* | mean±SD | 0.05±0.05 | 0.27±0.13 | 0.03±0.08 | 3.31±0.77 | 1.34±0.54 | 0.35±0.21 | 10.4±1.74 |
| | | range | 0.01-**0.14**** | 0.04-**0.45** | 0.00-0.23 | 2.69-5.13 | 0.81-2.48 | 0.04-**0.75** | 8.26-13.2 |

| **Fruit, vegetable** | **Binomial nomenclature** | | **As (mg/kg)** | **Cd (mg/kg)** | **Cr (mg/kg)** | **Cu (mg/kg)** | **Ni (mg/kg)** | **Pb (mg/kg)** | **Zn (mg/kg)** |
|---|---|---|---|---|---|---|---|---|---|
| **onion bulb** | *Allium cepa* | mean±SD | 0.36±0.60 | 0.07±0.09 | 0.19±0.17 | 2.79±2.27 | 0.84±0.26 | 0.16±0.04 | 8.61±5.45 |
| | | range | 0.00-**1.05** | 0.0-0.17 | 0.0-0.30 | 0.87-5.29 | 0.0-0.30 | 0.12-0.20 | 3.06-13.9 |
| **pepper fruit** | *Capsicum annuum* | mean±SD | - | - | - | - | - | - | - |
| | | range | 0.04 | 0.09 | 0.5 | 3.60 | 1.07 | **0.81** | 13.3 |
| **lettuce leaves** | *Lactuca sativa* | mean±SD | - | - | - | - | - | - | - |
| | | range | 0.03 | **0.17** | 0.32 | 4.39 | 0.37 | 0.21 | 11.04 |
| **quince fruit** | *Cydonia oblonga* | mean±SD | - | - | - | - | - | - | - |
| | | range | 0.01 | 0.04 | 0.33 | 3.04 | 0.58 | 0.19 | 3.98 |
| **peach fruit** | *Prunus persica* | mean±SD | - | - | - | - | - | - | - |
| | | range | 0.02 | 0.13 | 0.38 | 4.67 | 0.70 | 0.12 | 13.43 |
| **FAO/WHO, 2011** | | | **0.10** | **0.20** | **2.3** | **40** | **66.9** | **0.30** | **20** |
| **Reg. No. 293, 2001 (vegetables)** | | | **0.5** | **0.1** | **-** | **5.0** | **-** | **0.5** | **15** |
| **Reg. No. 293, 2001 (fruits)** | | | **0.5** | **0.05** | **-** | **5.0** | **-** | **0.5** | **5.0** |

*SD (Standard Deviation); ** values in bold exceed the tolerance limits of metals (Reg. 293, 2001; FAO/WHO, 2011)

The trend of the metal content is As<Cd<Cr<Pb<Ni<Cu<Zn, with the highest values for the Cu, Ni and Zn concentrations.

The transfer factor, $T_f$ for As, Cd, Cr, Cu, Ni, Pb and Zn varies giving to the type of metal and the plants species. Highest $T_f$ values were obtained for Cu and Cd in tomato fruit and lettuce leaves samples, according to *Table VI.*3, with the following trend: Cu>Cd>Zn>Ni>Cr>Pb>As.

The tomato, peach, pepper fruits and onion bulb samples have the highest availability at Cr, and the carrot root samples at Ni. The carrot root samples are characterized by the highest availability at Pb, while the lowest availability, the lowest $T_f$ values respectively were obtained for the peach and quince fruit samples. The highest $T_f$ results were obtained for the carrot root samples at As, Cd, Cu, Pb and Zn.

***Table VI.3.*** *The transfer factor, ($T_f$) of metals form soil to fruits and vegetables (x10 $^{-3}$)*

| | **As** | **Cd** | **Cr** | **Cu** | **Ni** | **Pb** | **Zn** |
|---|---|---|---|---|---|---|---|
| Carrot *(Daucus carota sativus)* root | | | | | | | |
| **$T_f$** | 1.81-16.3 | 20.8-311.1 | 0.00-6.36 | 53.2-137.9 | 28.9-81.6 | 1.29-13.14 | 51.9-102.5 |
| Tomato *(Solanum lycopersicum)* fruit | | | | | | | |
| **$T_f$** | 1.65-2.63 | 25.0-73.8 | 9.23-26.2 | 152.6-1573 | 33.5-41.7 | 3.62-6.42 | 71.9-123.6 |
| Onion *(Allium cepa)* bulb | | | | | | | |
| **$T_f$** | 1.19-181.3 | 0.00-125.1 | 0.00-12.12 | 24.5-243 | 27.7-72.1 | 2.12-3.74 | 19.7-98.1 |
| Yellow bell pepper *(Capsicum annuum)* fruit | | | | | | | |
| **$T_f$** | 3.73 | 35.5 | 13.5 | 98.7 | 45.8 | 7.49 | 63.8 |
| Lettuce *(Lactuca sativa)* leaves | | | | | | | |
| **$T_f$** | 3.89 | 152.7 | 10.7 | 218.3 | 13.1 | 2.19 | 120.5 |
| Peach *(Prunus persica)* fruit | | | | | | | |
| **$T_f$** | 2.03 | 53.1 | 14.5 | 128.1 | 29.8 | 1.13 | 64.3 |
| Quince *(Cydonia oblonga)* fruit | | | | | | | |
| **$T_f$** | 1.40 | 38.0 | 10.9 | 151.3 | 20.6 | 2.01 | 43.5 |

For the risk assessment at metals, three assessment methods were used: *EDEM* (the Estimated Daily Intake of Metals), *HQ* (the Hazard Quotient) and *HI* (the Hazard Index). The *EDEM* results present the following trend: Cd<Cr<Pb<As<Ni<Zn<Cu. The tomato fruit samples present the highest *EDEM*, while the onion bulb has the highest *EDEM* results at As, and the carrot root, onion bulb and pepper, tomato, peach fruit samples present the highest *EDEM* values for the Zn content.

With regard to the hazard quotient, *HQ* results the highest values were obtained for Cu, As and Zn, exceeding the unity value (*HQ* > 1). The samples which could present a *potential risk* are the tomato fruit samples; for which the *HQ* exceeds with almost 200 times the critical value for the Cu content and two times for the Zn content; the root carrot samples are characterized with *HQ* results which exceed almost 9 times for the As content (*Table VI.4.)*. The lowest *HQ* results can be seen from the *HQ* values trend, as follows: Cr<Cd<As<Pb<Ni<Cu<Zn.

The hazard index (*HI*) ranges between 0.774 – 204.8, with the lowest values calculated for the quince fruit sample and the highest value for one of the tomato fruit samples.

One of the thesis objectives was developing a coherent and efficient quality assessing method/model regarding the drinking water quality sources, with the help of metal pollution index and quality index. The method is structured from six stapes, which finalizes with the evaluation of the drinking water quality sources (*Figure VI.5.)*.

***Table VI.4.*** The hazard quotient, *HQ* values obtained for *As, Cd, Cr, Cu, Ni, Pb and Zn*

| Metal | Min. | Sample | Max. | Sample | Mean | Standard deviation | Median |
|---|---|---|---|---|---|---|---|
| As (mg/kg) | $2.0 \times 10^{-4}$ | V16<br>*Allium cepa* | 8.97 | V7<br>*Allium cepa* | 0.52 | 2.11 | $3 \times 10^{-3}$ |
| Cd (mg/kg) | $1.0 \times 10^{-5}$ | V7<br>*Allium cepa* | 0.99 | V13<br>*Daucus carota sativus* | 0.22 | 0.28 | 0.08 |
| Cr (mg/kg) | $1.0 \times 10^{-5}$ | V3. V4. V8. V9. V12. V13.<br>*Daucus carota sativus*<br>V16. V17<br>*Allium cepa* | $5 \times 10^{-4}$ | V14<br>*Solanum lycopersicum* | $1.1 \times 10^{-4}$ | $1.3 \times 10^{-4}$ | $1.1 \times 10^{-4}$ |
| Cu (mg/kg) | $4.6 \times 10^{-2}$ | V7<br>*Allium cepa* | 203 | V10<br>*Solanum lycopersicum* | 12.32 | 47.5 | 0.69 |
| Ni (mg/kg) | $1.6 \times 10^{-2}$ | V5<br>*Lactuca sativa* | 0.76 | V2<br>*Daucus carota sativus* | 0.16 | 0.17 | 0.14 |
| Pb (mg/kg) | $9.8 \times 10^{-4}$ | V17<br>*Daucus carota sativus* | 0.40 | V18<br>*Capsicum annuum* | 0.09 | 0.11 | 0.05 |
| Zn (mg/kg) | $7.7 \times 10^{-2}$ | V7<br>*Allium cepa* | 2.13 | V14<br>*Solanum lycopersicum* | 1.03 | 0.56 | 0.95 |

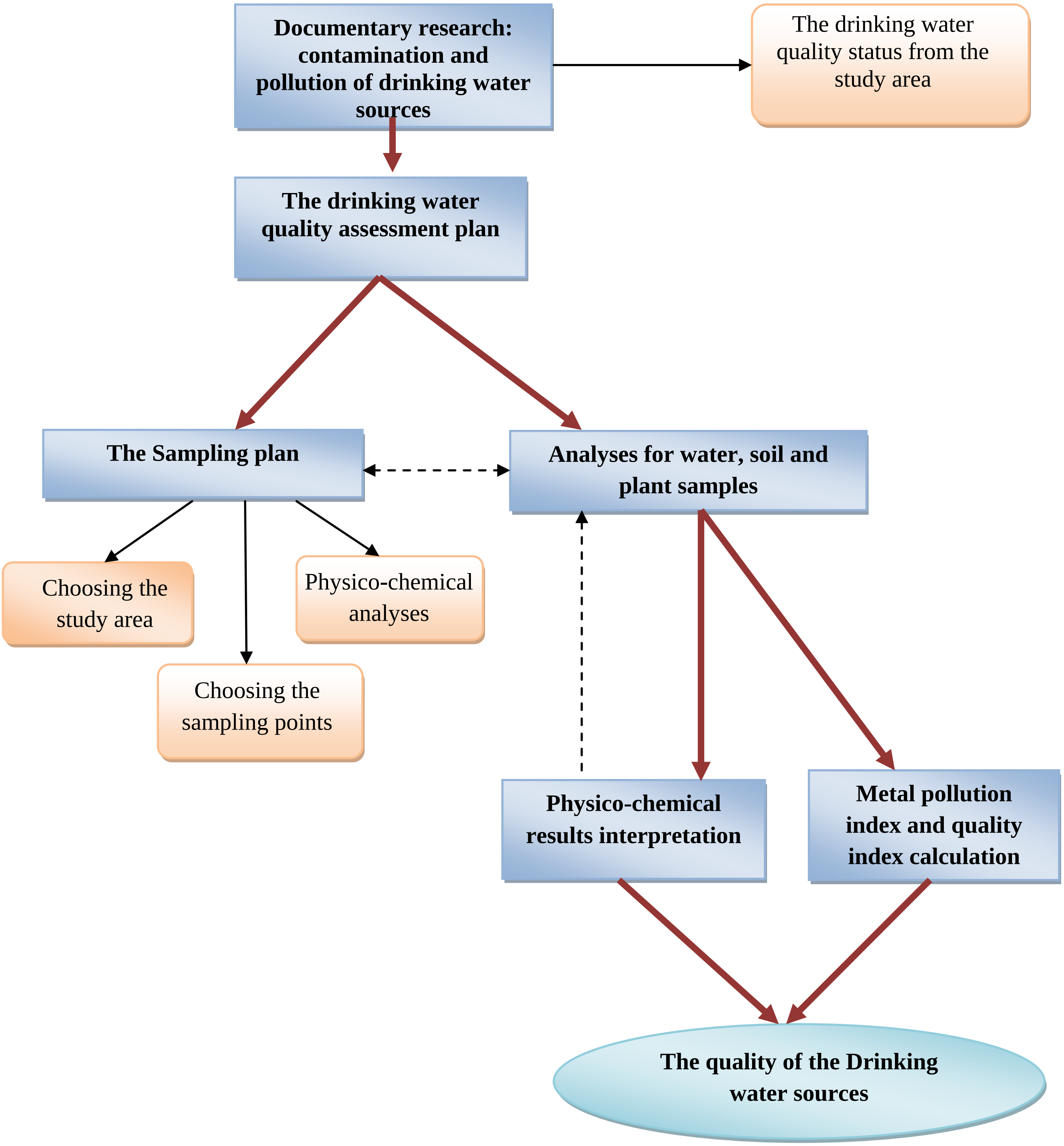


***Figure VI.5*** *The drinking water quality assessment method using metal pollution index and quality index methods*

# CHAPTER VII – GENERAL CONCLUSIONS

The drinking water quality is a very important parameter, due to the negative health effects on human and animals of the contamined water. Against the harmful health effects, prevention is an important step; which includes drinking water quality monitoring, physical-chemical assessment by analytical methods and application of mathematical tools, and finally, risk assessment at diverse chemical compounds.

The study area of Medias Town is localized near a large former nonferrous metallurgical facility. Agriculture, household activities and the limited access to drinking water sources (until 2009-2010 a part of the inhabitants had no water supply or sewage systems, using well waters as drinking water sources and collecting tanks as sewage system) could be potential pollution for the drinking water sources with possible negative health effects on human and animals.

The proposed specific objectives of the thesis were successfully reached; the documentary research and experimental results and conclusions are the following:

✓ According to the physico-chemical analyses, the drinking water sources are classified as circumneutral waters with pH values ranging between 7.0 and 8.0 in all three sampling campaigns (March, August 2014 and August 2016).

✓ Generally, the drinking water samples are polluted with $NO_2^-$, $NO_3^-$ and $NH_4^+$. The maximum admissible concentrations are exceeded until five times. The potential pollution sources are the agricultural activities (livestock, leachate from faecal waste deposits, nitrogen fertilizers) and household activities (rudimentary hygiene systems). The presence of microorganisms is justified by the high values of the chemical oxygen demand as well.

✓ The moderately salt amount is given by the electrical conductivity, filterable residue dried at 105°C and sulphate concentrations; positive correlations can be observed between the three indicators with the help of the Pearson correlation matrix. There are significant correlations between Ca, Mg, total hardness and total alkalinity. The relatively high values for the total hardness, Ca and Mg content are due to the geological structure, represented by the carbonate rocks, which characterizes the whole geological area.

✓ As the metal content, the Cd, Mn and Pb MACs are exceeded until four times, especially in the summer seasons, which indicates the increase of the chemical compounds of water due to the water level decrease.

✓ According to the Piper and Stiff charts, the groundwater types are generally Ca-$HCO_3^-$, followed by a lower percent of Na-$HCO_3^-$ and Na-K-$HCO_3^-$ types, which are characterized by relatively high Na and K amounts.

✓ The metal pollution index methods (the Contamination Degree, *CD* and the Heavy Metal Evaluation Index, *HEI* and the Heavy Metal Pollution Index, *HPI*) results are lower as the critical values, except for the sample with the highest Cd content which exceeds the MAC. Although, generally the *HPI* results show a certain metal pollution level, specifically with Cd.

✓ The Water Quality Index, *WQI* was calculated using the pH, TDS, EC, total hardness, Mg, Ca, total alkalinity, $SO_4^{2-}$, $F^-$, Fe, $NO_3^-$ and $Cl^-$ results. In the rainy season of March, 95% of the drinking water samples are classified as *not suitable for the drinking purpose* and 5% in the *very poor quality* class. In the summer seasons, 70% are *not suitable for the drinking purpose*, 20% have a *very poor quality* and 10% a *poor quality* status. The highest *WQI* results are correlated with the very high $NO_3^-$, $SO_4^{2-}$ concentrations and total hardness values.

✓ A number of 20 chemical parameters (pH, Mg, $Cl^-$, Pb, $SO_4^{2-}$, $A_T$, Fe, $D_T$, Ca, Ni, $F^-$, $NO_3^-$, $NO_2^-$, Cr, CE, Mn, Zn, Cu, Na, and Cd) were used in the *DWQI* methodology calculation. Results indicate *acceptable quality* for 20% of water samples and *poor* and *very poor quality* for rest of the samples collected in the spring season. In summer season, 7% of water samples have an *acceptable* and *marginal quality*, while rest of them are characterized by a *poor quality status*.

✓ The hazard quotient, *HQ* results for $NO_2^-$ are lower as one (*HQ* < 1.0), which indicated *safety* regarding the nitrites content from the drinking water, but the *HQ* results for $NO_3^-$ present a *potential risk* at $NO_3^-$, due to the high values (*HQ* > 1.0), for 85% and 72% of drinking water samples in both summer season.

✓ The soil samples from Medias Town are polluted with As, Ba, Cd, Cu and Pb, the metal content exceeding the alert thresholds for Cd and Pb, according to *Regulation No. 756 from 1997, according the environmental pollution assessment*. In summer season of 2014, the alert threshold for Pb is exceeded in 80% of the soil samples and for Cd in 5% for samples; furthermore the Pb intervention threshold is exceeded for 15% of soil samples. In the second sampling campaign of August 2016, two samples have the As and Cu alert thresholds exceeded, 30% of samples present higher Cd concentrations as the alert threshold and 80% of samples have higher Pb as the alert threshold. The Cd intervention threshold is exceeded for 10% of soil samples and 20% are characterized by high Pb content, which exceeds the intervention threshold. It can be concluded that the highest metal concentrations were measured at the soil samples collected from the western part of the town, which is the most vulnerable part of the town at metal pollution; the pollution source could be the former metallurgical facility from Copsa Mica.

✓ According to the index of geo-accumulation ($I_{geo}$) results, 60% of the soil samples present Pb pollution and 5% of soil samples are polluted with Cd, in August 2014. The soil samples collected in the second season are characterized, according to the $I_{geo}$ as *unpolluted to pollute* with Pb, Cd, Cu and Zn.

✓ The contamination factor ($C_f$) classifies the soil samples in the *pollution class*, pollution with Cu, Cd and Pb and according to the risk factor (*Er*) the soil samples present *potential ecological risk* at Cd and Pb.

✓ Metal determinations for fruits and vegetables samples show, higher concentrations as the As, Cd and Pb tolerance limits, namely for the pepper, tomato fruits, onion bulb, carrot root and lettuce leaves samples. The As content is very high in case of the 11% of the samples, and 28% of the samples indicate high values for the Cd content, while for 44% for the Pb content, with exceedance of the tolerance limits. Significant correlations are between Fe-Pb, Fe-Co and Co-Pb.

✓ As for the metal transfer factor from soil to samples, there were high results obtained for Cu, followed by Cd>Zn>Ni>Cr>Pb>As. The trend of the transfer type depends on the plant species and metals. Highest Cd and Cu availability were obtained in tomato fruit and lettuce leaves, and the carrot roots have high availability at Pb, Zn, As, Cu and Cd.

✓ The health risk assessment index methods indicate *potential risks* at the studied metals for the tomato fruits and carrot roots. The highest values were obtained for Cr, Cd and As.

The original contributions of the thesis are the applicability and use of the metal pollution index and drinking water quality index methods in Medias Town. It must be noted that although water and soil quality studies were conducted in the Copsa Mica and Medias region, the metal pollution and the drinking water quality index methods were applied for the first time in the research activities as part of this thesis. With the help of those index methods there was as well, a quality assessment model developed for the drinking water resources, through which the drinking water resources could be effectively classified in the corresponding quality classes; this represents a different original contribution.

This study opened new perspectives and opportunities, through which the community from Medias Town is conscious regarding the environmental protection and the necessity of health risks prevention at diverse risks.

Some of the future perspectives opened by this thesis are:

✓ widening the study area and application of the elaborated metal pollution and quality index methods for drinking water samples collected from possible polluted areas and from unpolluted/blank areas, for comparing data.

✓ nitrogen fertilizers determinations and data correlation between soil and water samples results.

✓ elaboration of feasible decontamination methods, from a technical and economically point of view, for drinking water sources (for nitrogen compounds specifically).

# LIST OF PUBLICATIONS

## Papers published in ISI Journals

1. M.A. HOAGHIA, C. ROMAN, E.A. LEVEI, D. RISTOIU, 2015, *Footprint and direct impact of anthropic activities on groundwaters from Medias area*, Studia Universitatis Babes-Bolyai, Chemia, LX (1), pp. 109-118, ISSN 1224-7154.
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11. L. SENILA, M. MICLEAN, O. CADAR, M. SENILA, M. KOVACS, M.A. HOAGHIA, 2016, *Validation of a method for determination of free glycerol in biodiesel*, Studia UBB Chemia, Nr. LXI (3, Tom II), dedicated to Professor Emil Cordos on the occasion of his 80th anniversary, pp. 333-345

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1. M.A. HOAGHIA, E. LEVEI, C. ROMAN, M. SENILA, C. TĂNĂSELIA, D. RISTOIU, 2015, *Assessment of inorganic contamination in well waters from nonferrous mining and urban areas in north-west and central Romania,* Food and Environment Safety – Journal of Faculty of Food Engineering. Stefan cel Mare University – Suceava, 14 (2), pp. 138-143.
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1. M.A. HOAGHIA, C. ROMAN, D. RISTOIU, *Observations on Groundwater Contamination with Nitrogen Compounds: A Case Study from Medias City, Sibiu County* – Bulletin of University of Agricultural Sciences and Veterinary Medicine Cluj-Napoca. Agriculture.
2. A. MOLDOVAN, M.A. HOAGHIA, O. CADAR, M. SENILA, C. ROMAN, *Removal of heavy metals from aqueous solutions using activated carbon* - Agriculture Science and Practice Journal.

**Scientific events**

1. „*Environmental Legislation, Safety* Engineering *and Disaster Management” – ELSEDIMA*, Cluj-Napoca, 2016, 26-28 of May. Participation with poster papers: M.A. HOAGHIA, E.

LEVEI, O. CADAR, C. ROMAN, M. SENILA, C. TANASELIA, D. RISTOIU, *Metal contamination and ecological risk assessment in the urban soils situated near a former non-ferrous metallurgical plant and* E. LEVEI, M.A. HOAGHIA, M. SENINA, C TANASELIA, M. MICLEAN, J. VIERS, J. CHMELEFF, *Multielemental fingerprinting of railings from nonferrous mining area*s.

2. *„Air and Water Components of the Environment Conference”,* 2015, 20-22 of March, Cluj-Napoca. Participation with poster papers: A. HOAGHIA, E. LEVEI, O. CADAR, D. RISTOIU, *Assessing of seasonal variation of water quality in Mosna River;* M. SENILA, M. SIMA, E. LEVEI, M. ROMAN, L. SENILA, A. HOAGHIA, D. MICU, O. CADAR, D. BALTEANU, *Drinking water quality in wells from an area affected by flood events: a case study of curvature Sub-Carpathians, Romania.*
3. *„Environmental Legislation, Safety Engineering and Disaster Management” – ELSEDIMA,* Cluj-Napoca, 2014, 18-19 of September. Participation with poster paper: M.A. HOAGHIA, C. ROMAN, M. PAUL, C. TĂNĂSELIA, M. URSU, D. RISTOIU, *Groundwater Chemistry Rendering using Durov, Piper and Ion Balance Diagrams. Study Case: the Northern Part of Sibiu County.*
4. *„The 13th International Symposium-Prospects for 3rd Millennium Agriculture”, Cluj-Napoca,* 2014, 25-27 of September. Participation with poster paper: M.A. HOAGHIA, C. ROMAN, D. RISTOIU, *Observations on Groundwater Contamination with Nitrogen Compounds: A Case Study from Medias City, Sibiu County.*
5. *„U.A.B. – B.EN.A.” Conference Environmental Engineering and Sustainable Development Alba Iulia, Romania,* 2013, 23-25 of May. Participation with poster paper: C.A. ROBA, G.E. POPIȚĂ, M.A. HOAGHIA, I. PIŞTEA, C.D. ROŞU, *Water Quality Index (WQI) for the assessment of wells water quality from Mediaş Town – Romania.*
6. *Environment and Progress,* 2013, Cluj-Napoca. Participation with poster paper: M.A. HOAGHIA, C. ROMAN, G. POPITA, C. TANASELIA, D. RISTOIU, *The importance of use ICP-MS method in environmental studies.*

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