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*Article*

# Groundwater chemistry, pollution and health risk assessment for nitrogen compounds. A case study in a suburban region of Romania

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## *Abstract*

*As groundwater is used as a source of drinking water, monitoring its quality is essential due to possible adverse effects on human health. Nitrogen compounds (nitrates, nitrites, ammonia) within certain concentration limits are natural components of the nitrogen cycle. Due to anthropogenic activities, high concentrations of nitrogen compounds are released into groundwater. The aim of this study was to evaluate the chemistry of groundwater in a suburban area in northeastern Romania, the sources of pollution with nitrogen compounds (nitrates, nitrites, ammonium), and the non-carcinogenic risk to human health associated with consumption in different groups age (women, men, and children) in the investigated region. The results showed that the concentration of nitrogen compounds varies from 5.12 to 98.3 mg/L for nitrates, from 0.008 to 85.2 mg/L for ammonium, and from 0.001 to 1.12 mg/L for nitrites. The maximum admissible concentrations have been exceeding 25%, 40% and respectively 10% of the total analyzed samples Bivariate graphs and Principal Component Analysis (PCA) were used to identify potential sources of nitrate, nitrites, and ammonium pollution of groundwater in the study area. The non-carcinogenic risk assessment for water consumption showed a hazard index (HItotal) for nitrogen compounds in groundwater in the investigated region, which ranged from 0.037 to 2.856 for men, between 0.054 and 3.427 for women, respectively between 0.080 and 6.145, for children. Spatial distribution maps using the Inverse Distance Weighting technique presented the geographical areas with the probability of groundwater contamination with nitrate, nitrite, and ammonium and the areas that pose a risk to human health by consuming groundwater in the study area for the three groups: men, women and children.*

***Keywords:*** *nitrogen compounds, pollution, groundwater chemistry, health risk assessment, principal component analysis, spatial distribution map*

## INTRODUCTION

Groundwater is an essential source of drinking water, supplying the hydrological systems used by the population to supports environmental ecosystems by providing water and nutrients. Humans use such groundwater sources for food production, energy, health and recreation [1].

Groundwater thus plays an important role in sustaining human life and activities, but is at risk by degrading water quality and exploitation. Climate change and population growth pose threats to groundwater, thus affecting water quantity and quality [2-5]. The risk assessment for groundwater in old industrial activities must take into account the interaction between pollutant loading and the underground natural environment. Agriculture, increasing the degree of urbanization and the potential of these activities to have a quantitative impact on groundwater increases the vulnerability to aquifer pollution. Aquifer dispersal spreads the pollutant over a wider area and may intersect with groundwater wells or springs, which makes water supply unsafe for humans and wildlife [6]. In areas with high contamination potential where the identification of sources has not been thoroughly tested, ammonium nitrate, derived from fertilizers, if not modified by biological activity (denitrification to $N_2$ gas), can produce biogenic $NO_3^-$ (by nitrification) with a composition different from that of synthetic nitrate. Synthetic nitrate migrates from the source, followed by $NH_4^-$, whose process is slow down by ion exchange in the solid phases of the aquifer, which, gradually oxidized can generate secondary and possibly more persistent $NO_3^-$ [7]. Agriculture is one of the biggest factors of pollution with forms of nitrogen in groundwater [8, 9]. Nitrate ($NO_3^-$) is a relatively stable component in the natural environment and has a high mobility and a high potential for loss from the unsaturated area by leaching. It exists mainly in combination with alkaline metal cations such as Na, K or Ca, all of which are easily soluble in water. The nitrite ion ($NO_2^-$) contains nitrogen in a relatively unstable oxidation state. Chemical and biological processes can further reduce nitrite to various compounds or oxidize it to nitrate [10].

Widespread use of fertilizers can be considered a major source of nitrogen that pollutes groundwater. Pollution sources, including septic tanks, broken sewer systems, contribute to nitrogen contamination of groundwater [11-13].

Degradation of groundwater quality can result in loss of drinking water supply, degradation of surface water systems, which can lead to high costs for cleaning or alternative water supply, and potential health problems [14, 15]. The pollution of groundwater with nitrogen and microbial organisms from agriculture has a major social significance from the perspective of drinking water supply for rural settlements in Romania.

Ammonium ($NH_4^+$) is present in groundwater naturally due to anaerobic degradation of organic matter and artificially due to the disposal of organic waste. Anthropogenic $NH_4^+$ is one of the major components dissolved in contaminated groundwater, therefore differentiating geogenic and anthropogenic sources and processes is crucial to ensure good groundwater management in this sensitive area where groundwater is used for agriculture, industry and supply people [16].

A higher level of nitrate concentration in drinking water of 50 mg/L presents a high risk, especially for infants. Epidemiological studies indicate negative effects on reproductive function, diabetes and thyroid disease due to ingestion of nitrates through drinking water, associated with an increased risk of certain cancers. Endogenous formation of N-nitroso compounds (NOCs) and other primary mechanisms by which nitrogen ingested from drinking water can have harmful effects on health. Ingestion of high doses of nitrates can inhibit the absorption of iodine with hypertrophic changes in the thyroid. Nitrite reacts with hemoglobin to form methemoglobin reducing the ability to carry oxygen in the blood [17].

About 5% of the ingested nitrate is converted to nitrite as a result of the absorbed nitrate which is secreted into saliva and then converted to nitrite in the mouth by bacteria (oral microbiome). The reaction of nitrite with other compounds in the acidic environment of the stomach may lead to the endogenous formation of NOCs [18].

In order to monitor the toxicity risk of nitrates and nitrites associated with drinking water, the World Health Organization (WHO) sets the maximum acceptable level of nitrates in drinking water of 50 mg/L and 3 mg/L, respectively for nitrites and 0.5 mg/L for ammonium [19, 20]. In Romanian legislation the maximum concentration allowed by the Romanian Law for drinking water quality is 50 mg/L for nitrates and 0.5 mg/L for nitrites and ammonium [21]. Harmful effects on human health due to exposure to contaminants in drinking water can be determined through a systematic approach to risk assessment. Risk assessment can help to identify them and decide on measures to reduce exposure levels and achieve acceptable levels of risk. The WHO confirmed that exposure to ammonium from environmental sources is insignificant compared to the endogenous synthesis of ammonia or urea in the human digestive system. They reported that ammonium in drinking water is not immediately relevant to human health. However, it has been observed that the presence of ammonium can decrease the efficiency of disinfection, lead to the formation of nitrites in water distribution systems, cause malfunctions of manganese removal filters and create odor in water [20].

Geographic information system (GIS) is one of the most powerful techniques used for the analysis and management of spatial information. GIS is used to delimit the spatial extent of sites affected by natural or anthropogenic contamination [22]. The spatial distribution map of groundwater quality parameters, health risk to contaminants and water quality assessment can be outlined using various spatial interpolation techniques.

The purpose of this study was to evaluate the chemistry of groundwater in a sub-urban area in north-eastern Romania, the sources of pollution with nitrogen compounds (nitrates, nitrites, ammonium) and the non-carcinogenic risk to human health associated with consumption at different ages and gender groups (men, women and children) in the investigated region.

## MATERIALS AND METHODS

### *Groundwater chemistry*

To evaluate the quality of groundwater in the study area, twenty samples were collected in September 2021 (sampling conditions: ambient temperature 16-23°C, <5% rainfall, cloudless) in high-density polyethylene bottles, pre-washed, sealed and covered, without air gaps. The sampling points are represented in figure 1. The samples were preserved at 4°C and transported to the analytical laboratory in order to perform water quality analysis. Analytical procedures in accordance with the Romanian Standard, Law no. 458/2002 for drinking water intended for human consumption were used [21].

pH and electrical conductivity (EC) were determined by electrochemical technique. Major ions: Sulphate ($SO_4^{2-}$) was determined turbidimetrically, chloride ($Cl^-$), bicarbonates ($HCO_3^-$), total hardness (TH) as $CaCO_3$ by volumetric technique, nitrate ($NO_3^-$), nitrite ($NO_2^-$), ammonium ($NH_4^+$) by spectrometric UV-Vis technique, $Ca^{2+}$, $Mg^{2+}$, $Na^+$, $K^+$ were determined by inductively coupled plasma optical emission spectrometry. Total dissolved solids (TDS) were determined by gravimetric technique. For accuracy, the analysis of each sample was checked for ionic balance, with the charge balance error (% CBE), as shown in formula (1) [23]:

$$\%CBE = \frac{(\sum Cations - \sum Anions)}{(\sum Cations + \sum Anions)} \text{ x } 100, \text{ meq/L} \qquad (1)$$

It is recommended that % CBE value to be ± 5%.

### *Descriptive statistics of chemical components in groundwater*

Descriptive analysis (including mean, minimum, maximum, standard deviation, coefficient of variation) is used to describe the basic characteristics of the data obtained in the study and to indirectly indicate the activity of the selected parameter in groundwater samples. The analysis of the correlation factors presents the interactions between the physical-chemical parameters of the groundwater samples that can reflect the sources of dissolved substances and the observation of the hydro chemical composition of the groundwater. The numerical degree of the relations between the physical-chemical parameters of the groundwater is given by the correlation coefficient ($p$ value), with values between -1 and +1. A higher correlation coefficient shows a strong positive / negative connection between two hydro chemical variables. A numerical value close to zero shows an unconnected relationship between the two-groundwater factors. A negative correlation coefficient expresses that the measurable factors develop in inverse ways. In this investigation, Number Cruncher Statistical System (NCSS) statistical software package was used to calculate the examination of correlation factors [24, 25].

### *Spatial distribution maps*

The location of the groundwater samples was manually marked using the Global Positioning System (GPS) and the geographical coordinates were imported into Geographic Information. The

GIS-based analysis of spatial-temporal behaviour of groundwater samples taken from the study area for nitrates, nitrites ammonium parameters and Hazard Index was prepared using ArcGIS version 10.5 [26, 27] with spatial statistical analyst module and Inverse Distance Weighting (IDW) technique [28]. In the IDW model, the effectiveness of the continuous variable is assumed to decrease with distance from the unknown point, therefore the distance is used as the weight of the known variable in estimating the unmeasured points. This method is called Inverse Distance Weighting, because as the distance from the unknown point increases, the weight decreases. The effect of the spatial dependence intensity of the data can be applied due to the increase of the inverse distance power. The square of the inverse distance is a popular choice for this purpose. The IDW method is widely used in the spatial interpolation of groundwater quality parameters [29-31]. The final groundwater quality map was created by overlapping all weighted value to delimit the groundwater quality in the study area [32].

The IDW technique was used to analyse the spatial distribution of groundwater quality in the Ramnicu Valcea city area and the health risk of $N\text{-}NH_4^+$, $N\text{-}NO_3^-$ and $N\text{-}NO_2^-$.

*Principal component analysis, PCA*

Principal component analysis (PCA) is a multivariate procedure used to reduce the size of a data set that contains a large number of correlated variables, remaining the same variables at the same time, transforming the original variables into uncorrelated (orthogonal) main components by diagonalizing the correlation matrix data. The main components (PCs) are expressed by equation (2):

$$Z_{ij} = a_{i1}x_{1j} + a_{i2}x_{2j} + a_{i3}x_{3j} + \cdots + a_{im}x_{mj} \tag{2}$$

where: *Z* is the component score; *a* is the loading of the components; *x* is the measured value of the variable; *i* is the component number; *j* is the sample number and *m* is the total number of variables [33].

In this study, thirteen groundwater quality parameters were used. Prior to the analysis, the data were first verified to meet the Kaiser-Mayer-Olkin (KMO) criteria applying. KMO test measures the adequacy of the sampling for each analyzed parameter and indicates the fit of the data for the analysis of the main components. KMO test was applied using NCSS software package. The minimum KMO value is 0.5 for the validity of PCA analysis application.

The main components (PCs) were selected based on the Kaiser test. Components with eigenvalues greater than 1.0 were taken into account. Eigenvalues indicate the significance of the PC, higher eigenvalues of PC were considered more significant [33]. The eigenvalues were extracted from the covariance matrix of the original variables. The first PC1 counted had the most significant variance of the data set followed by the second PC2. The extracted eigenvalues were rotated to make the factors interpretative without changing the original set of mathematical data. Varimax rotation can effectively reduce the contribution of less important variables in groundwater quality, as it simplifies tasks by rigidly rotating the PC axes for easier interpretation of results. In this study, Varimax orthogonal rotation was used to calculate the loads of rotational factors of different factors [34]. The rotation of the factor-loading matrix reflected how much a certain parameter was correlated with different factors. The higher the factor, the greater its influence. PCA and the KMO tests were processed using statistics software for multivariate analysis technique, compatible with Microsoft Excel, XLSTAT.

*Procedure for non-carcinogenic risk assessment*

The model for risk assessment for human health developed by the United States Environmental Protection Agency, USEPA [35] has been used in many studies [36-39]. This study assesses the health risk of three categories: women, men and children, due to behavior and physiology differences. In this study we selected to assess the non-carcinogenic risk to human health do to the following parameters: $NO_3^-$, $NO_2^-$ and $NH_4^+$. The model for drinking water intake or consumption is calculated according to (3), (4) and (5) formulas.

The chronic daily intake (CDI) expresses the amount of potential toxins absorbed in the body through drinking water and indicates the chronic daily intake of pollutant per unit weight [40]. CDI is calculated with the formula:

$$\mathrm{CDI} = \frac{\mathrm{C \times EF \times ED \times IR}}{\mathrm{ABW \times AET}} \tag{3}$$

$$\mathrm{HQ_{oral}} = \frac{\mathrm{CDI}}{\mathrm{RfD}} \tag{4}$$

$$\mathrm{HI_{total}} = \mathrm{HQ_{nitrate}} + \mathrm{HQ_{nitrite}} + \mathrm{HQ_{ammonium}} \tag{5}$$

where, in formula (3):
*C* is the average concentration of the pollutant in the water; *EF* is the frequency of exposure (days/year); *ED* is the duration of exposure (in a year); *IR* is the daily intake of groundwater (L/day); *ABW* is the average human body weight (kg) for men women and children and *AET* is the average exposure time (days).
In formula (4) the Hazard quotient is presented as HQ. RfD indicates the reference dose of the contaminant (mgN-$NO_3^-$/L, mgN-$NO_2^-$/L or mgN-$NH_4^+$/L).

The parameters selected for non-carinogenic risk assessment are presented in Table 1, [40, 41].

**Table 1.** Selected parameters for health exposure assessment in groundwater samples.

| Risk exposure factors | Men | Women | Children | Units |
|---|---|---|---|---|
| IR | 2.5 | 2.5 | 1 | L/day |
| ED | 76.89* | 82.82* | 12 | Years |
| EF | 365 | 365 | 365 | Days/year |
| ABW | 78 | 65 | 14.5 | kg |
| AET | 28065 | 30229 | 4380 | Days |
| C | Contaminant concentration | | | mg/L |

ABW: average body weight; C: concentration of contaminant; ED: exposure duration; EF: exposure frequency; AET: average time; IR: ingestion rate; *medium lifetime [41].

To evaluate the global potential for non-carcinogenic effects caused by nitrogen compounds, a Hazard Index ($HI_{total}$) approach was applied [35], the recommended limit being 1. The groundwater samples with $HI_{total}$ values greater than 1 may represent a low risk; the index between 1 and 2 indicate a medium risk and greater than 2, a high risk as result of contamination with nitrogen compounds.
In this study, according to the Toxicological Profile for Nitrates and Nitrites, the reference dose of RfD for nitrate was 1.6 mgN-$NO_3^-$/L, for nitrite 0.1 mgN-$NO_2^-$/L and for ammonium 0.9 mgN-$NH_4^+$/L [42, 43].

## RESULTS AND DISCUSSIONS

### *Study area description*

The study area is located geographically in 45.03304 - 45.0554 northern latitudes and 24.29244 - 24.30762 eastern latitudes 6.5km from Ramnicu Valcea (figure 1). The relief is characterized by fragmented rock formations in the form of EV - oriented strips, with a complex geological composition, from crystalline rocks to quaternary. Limestone exploited as a primal material by the Raureni Chemical Platform, clay, sand and stone, widely used in construction, are found in sedimentary, neogene and quaternary deposits, spread throughout the county. The agricultural area of the county represents 42.13% of its total area, 35.8% being represented by arable land [44]. The hydrographic network includes the middle and lower basin of the Olt River and numerous tributaries, as well as a variety of accumulation lakes. The climate is temperate-continental, specific to Romania, with temperatures between 11.3-35.8°C, with increasing precipitation compared to the amount of annual precipitation.

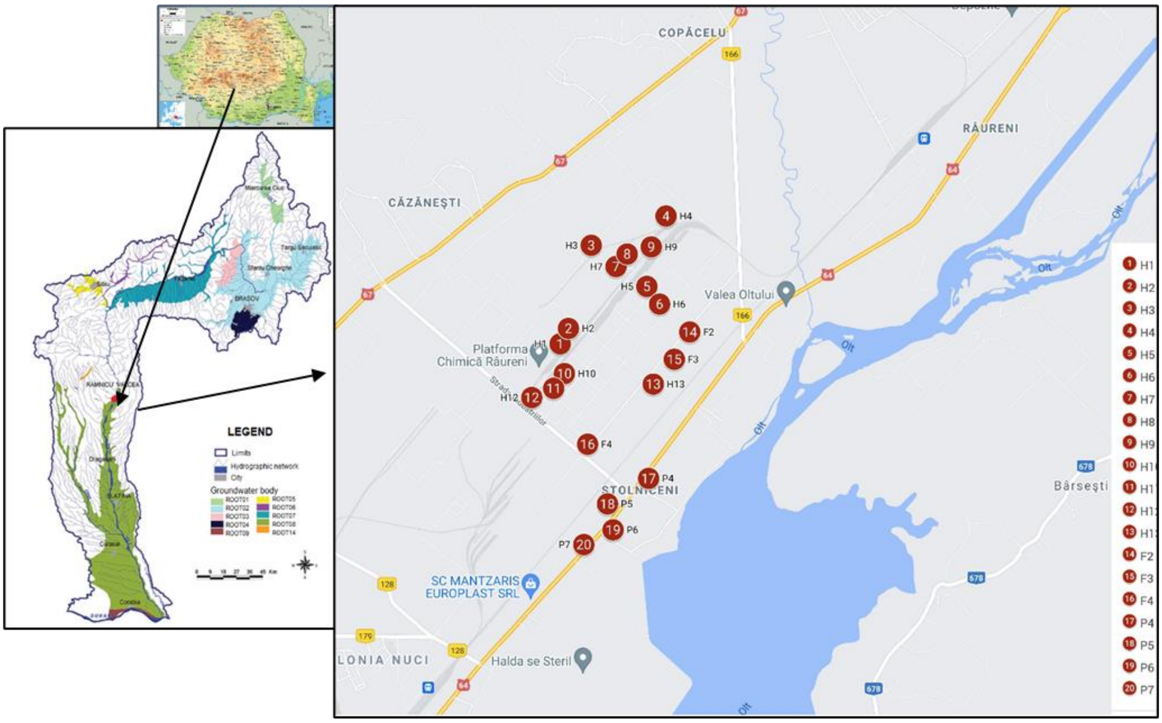

**Fig. 1.** Location of study area with groundwater samples points

*Physical-chemical characteristics of groundwater*

Statistical analysis of groundwater quality parameters in the sub-urban region of Ramnicu Valcea, Romania are described in Table 2. For the evaluation of groundwater quality intended for human consumption, the analysed physical-chemical parameters were presented compared to the maximum admissible limits according to WHO guidelines for drinking water quality [20] and Romanian Law 458/2002 [21].

**Table 2**. Statistical analysis of the physical-chemical parameters of the groundwater samples, comparison with the maximum admissible values (MAV) according to Romanian Law 458/2002 and WHO guidelines; percentage of samples exceeded MAV

| Parameters | Minimum | Maximum | Mean | SD | CV, % | Romanian Law [21] | WHO | Samples exceeded MAV,% |
|---|---|---|---|---|---|---|---|---|
| pH | 6.50 | 8.20 | 7.18 | 0.35 | 4.90 | 6.5-9.5 | 6.5-8.5 | 0 |
| $NH_4^+$ | 0.008 | 85.2 | 11.8 | 24.1 | 204 | 0.5 | 0.5 | 40 |
| $NO_3^-$ | 5.12 | 98.3 | 29.1 | 28.8 | 99.1 | 50 | 50.0 | 25 |
| $NO_2^-$ | 0.001 | 1.12 | 0.23 | 0.31 | 138 | 0.5 | 3.0 | 10* |
| $Ca^{2+}$ | 57.9 | 329 | 179 | 74.1 | 41.5 | - | 100 | 75 |
| $Na^+$ | 27.6 | 268 | 116 | 76.0 | 65.6 | 200 | 200 | 20 |
| $Mg^{2+}$ | 0.60 | 63.0 | 17.0 | 16.4 | 98.4 | - | 50 | 10 |
| $Cl^-$ | 11.3 | 467 | 168 | 126 | 74.9 | 250 | 250 | 25 |
| $SO_4^{2-}$ | 16.9 | 182 | 81.0 | 53.7 | 65.9 | 250 | 250 | 0 |
| $HCO_3^-$ | 265 | 921 | 537 | 203 | 378 | - | 350 | 70 |
| EC | 485 | 3205 | 1514 | 735 | 48.6 | 2500 | 400 | 15* |
| TH | 173 | 866 | 516 | 207 | 40.4 | - | 500 | 70 |
| TDS | 502 | 2698 | 1230 | 610 | 49.6 | - | 1000 | 50 |

The results of %CBE were situated within the acceptable range of ± 5% indicating that the correctness of the measurements in the study area was significantly good (minimum = -2.69; maximum = 3.81). The values of the standard deviation (SD) vary from 0.31 to 735. The SD variation could be due to various hydro-geochemical reactions or the huge difference in the distribution of salts in groundwater. High values of the coefficient of variation (CV, %) could be cause of variable distribution of physical-chemical parameters in groundwater or a result of anthropogenic contamination. In this study, the highest CV values were recorded for $NH_4^+$ (204%), followed by $NO_2^-$ (138%), $NO_3^-$ (99.1%), $Mg^{2+}$ (98.4%), $Cl^-$ (74.9%), $SO_4^{2-}$ ( 65.9%), $Na^+$ (65.6%), $K^+$ (39.41%), $HCO_3^-$ (37.8%) and pH (4.9%). These results indicate that $NH_4^+$, $NO_2^-$ and $NO_3^-$ could be the main key factors that control the chemistry of groundwater in the studied area.

All parameters are in mg/L, except EC (μS/cm) and pH (pH unit); SD: Standard deviation; CV: Coefficient of variation, %; *percentage of exceeded samples according to [21].

The pH range was observed between 6.5 and 8.2 (mean 7.18) indicating a neutral nature of groundwater in the studied region. All the values were situated within the allowable range of 6.5-8.5, table 2 [19].

Electrical conductivity (EC) is a measure of dissolved salts present in water. EC value less than 1500 μS/cm shows a reduced enrichment of salts in groundwater. EC value situated between 1500 μS/cm and 3000 μS/cm, indicate an medium enrichment of salts and finally, EC value higher than 3000 μS/cm a high enrichment of salts [45].

In the studied area, EC values ranged from 485 to 3205 μS/cm (mean 1514 μS/cm), Table 2. According to the EC classification, 85% of groundwater samples were situated below mean value, 10% of the samples had high enrichment of salts and 15% exceed the limit of the Romanian National Standards for drinking water. These results could be the results of the rock-water interaction processes, geochemical reactions and anthropogenic sources, as main factors that influence the chemistry of groundwater in the studied area.

Totally dissolved solids concentrations (TDS) ranged from 502 mg/L to 2698 mg/L with a mean value of 1230 mg/L (Table 2).

Based on the literature data for TDS value, groundwater could be classified as follows: suitable for drinking water intended from human consumption (value less than 500 mg/L); permissible for drinking (500 mg/L to 1000 mg/L); suitable only for irrigation (1000 mg/L to 3000 mg/L) and unsuitable for drinking and irrigation without treatment (value higher than 3000 mg/L) [46]. According to above classification, 40% of the groundwater samples were suitable for water intended for human consumption. 60% of the collected samples were above the maximum admissible value (1000 mg/L), the samples being suitable only for irrigation.

Dissolved calcium ($Ca^{2+}$) and magnesium ($Mg^{2+}$) can greatly contribute to the hardness of the groundwater. The total hardness (TH) content expressed as $CaCO_3$ varied from 173 mg/L to 866 mg/L (mean 516 mg/L), Table 2. Approximately 65% of the groundwater samples have exceeded a maximum limit of 500 mg/L for which the samples were not suitable for consumption in the investigated region [19].

The cationic dominance model was presented in the order $Na^+ > Ca^{2+} > Mg^{2+} > NH_4^+$ for 80% of the samples. Ten percentage of the samples follow the order: $Ca^{2+} > Na^+ > Mg^{2+} > NH_4^+$, the rest of 10% indicated an order of the cations which follows: $Ca^{2+} > Na^+ > NH_4^+ > Mg^{2+}$.

For 70% of the groundwater samples the anionic dominance model presented $HCO_3^- > Cl^- > SO_4^{2-} > NO_3^- > NO_2^-$ and for 30% of the samples the order was $HCO_3^- > SO_4^{2-} > Cl^- > NO_3^- > NO_2^-$. The $Ca^{2+}$ concentration was situated between 57.9 and 2329 mg/L (mean 179 mg/L), and higher than MAV (200 mg/L) in 75% of the total samples. The $Na^+$ concentration varied from 27.6 to 268 mg/L (mean 116 mg/L), with 20% of the samples above MAV according to WHO (200 mg/L). $Mg^{2+}$ varies from 0.6 to 62.6 mg/L (mean 16.7 mg/L). Only 10% of the total samples have concentrations above the maximum allowed limit [19].

In the study area, excessive levels of $Cl^-$ were detected, with a maximum of 467 mg/L (mean 168 mg/L). $SO_4^{2-}$concentration reached a maximum of 182 mg/L (mean 81.4 mg/L). The concentrations of $HCO_3^-$ in groundwater were situated in the range of 265 mg/L to 921 mg/L (mean 537 mg/L) (Table 2). High concentrations of bicarbonate in groundwater could be due to different types of aquifers located in sedimentary basins with carbonate rocks or could be associated with connections between groundwater and contaminated surface water [47].

*Distribution of nitrogen compounds and contamination process*

The concentration of $NO_3^-$ in groundwater varies between 5.12 mg/L and 98.3 mg/L (mean 29.1 mg/L); the values of $NH_4^+$ concentrations were situated between 0.008 mg/L and 85.2 mg/L (mean 11.8 mg/L), respectively the $NO_2^-$ values were ranged from 0.001 mg/L to 1.12 mg/L (mean 0.23 mg/L), Table 2 and Fig. 2. Compared to the MAV values, 25% of groundwater samples were not suitable for drinking water intended for human consumption (Table 2).

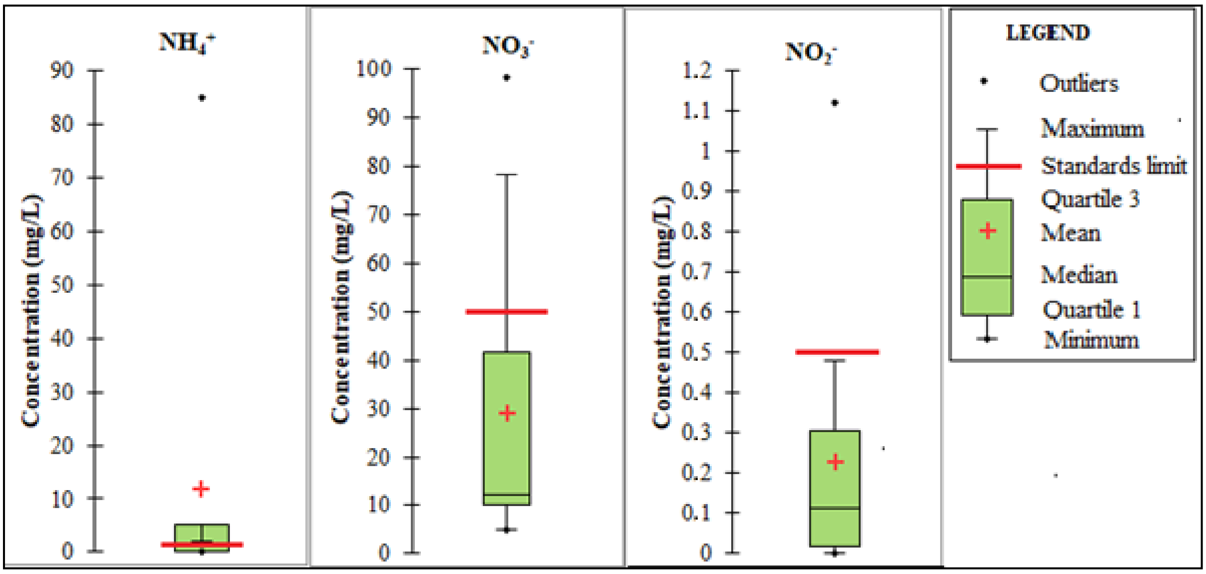

**Fig. 2**. Boxplots of the ammonium, nitrate and nitrite concentration from groundwater including the lower than determination limits of the methods and maximum admissible values imposed by the National Standard for drinking water quality

The spatial distribution map of nitrogen compound concentrations presented in Figure 3 indicated a number of five sampling points, which provide groundwater unsuitable for drinking purpose.

The most affected wells in terms of ammonium, nitrate and nitrite concentrations are located in the village of Stolniceni, corresponding to the sampling points 17 (P4), 18 (P5), 19 (P6) and 20 (P7). In addition, the nearest fountain to the village area, namely F4, sampling point 16 located in Ramnicu Valcea, is also affected by the pollution of the aquifer with nitrogen compounds.

Similar studies performed in rural areas in different regions of Romania with significant agricultural production have shown aquifer pollution with nitrogen compounds [48, 49]. Higher concentrations of nitrates and ammonium in the analysed groundwater samples most likely came from anthropogenic sources, irrigation, septic tanks, degradation of organic waste, nitrogen-based fertilizers for soil amendment, animal production, sewage or abandoned industrial landfills as was reported in literature data [50-52]. $NO_3^-$ is very soluble in water and can easily reach the groundwater. An oxidizing medium can cause the nitrification reaction that usually converts ammonia to nitrate, thus increasing the concentration of $NO_3^-$ and $NO_2^-$ [53].

Ammonium ($NH_4^+$) can be present in groundwater naturally due to anaerobic degradation of organic matter or artificially due to the disposal of organic waste. Anthropogenic $NH_4^+$ is one of the major components dissolved in some types of aquifer contaminated with waste leachate or agricultural practices. $NH_4^+$ from aquifers can have substantial effects on water-rock interactions and can be a substantial source of nitrogen in surface waters that receive surface groundwater. There are few studies documenting the transport and reaction processes of $NH_4^+$ in aquifers [16].

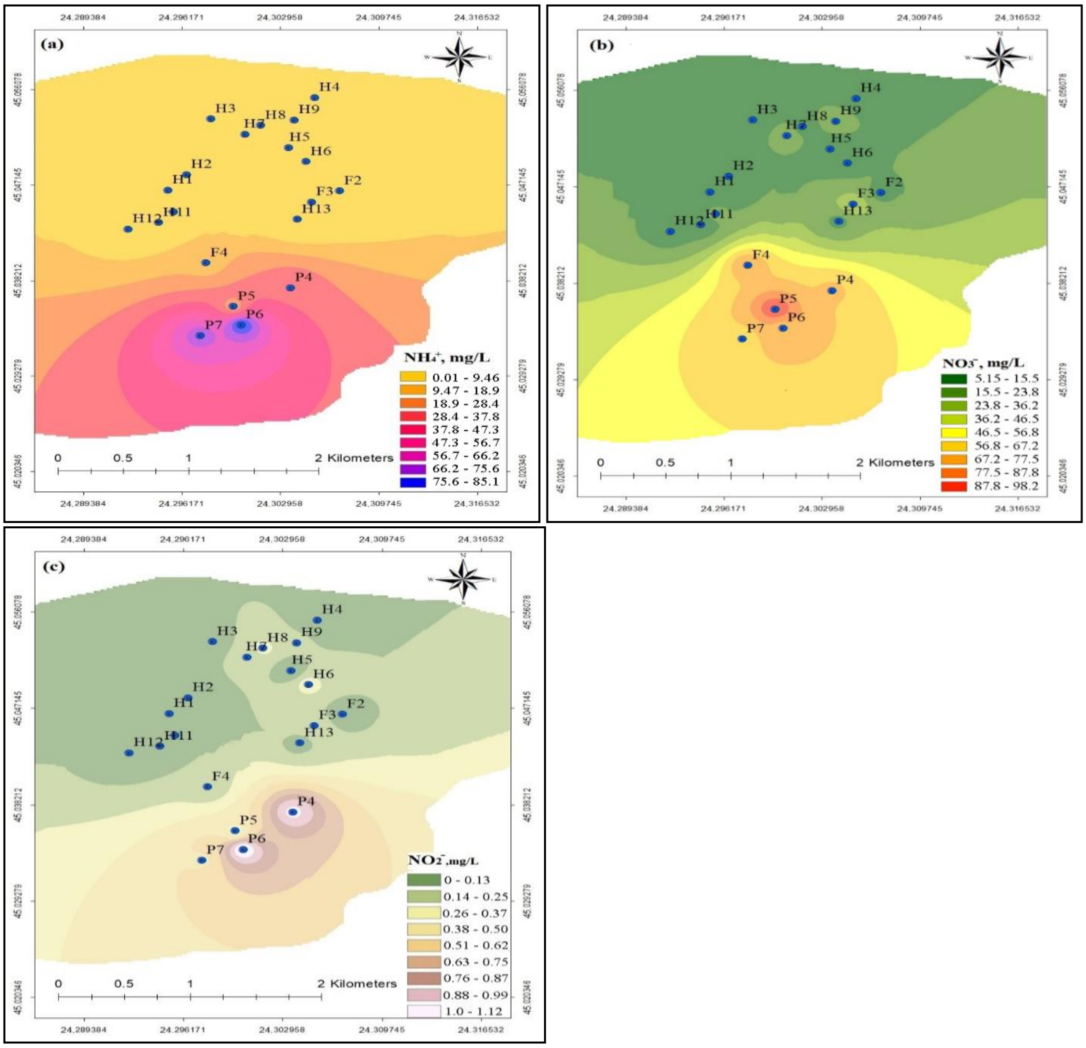

**Fig. 3.** The distribution map of groundwater ammonium concentration (a), nitrate concentration (b) and nitrite concentration (c) from study area, (mg/L)

*Correlation*

Pearson's correlation matrix analysis was performed in the study to reveal the linear correlations between two sets of parameters described in Table 3.

**Table 3.** Matrix correlation (Pearson)

| Variables | pH | $NH_4^+$ | $NO_3^-$ | $NO_2^-$ | $Ca^{2+}$ | $Na^+$ | $Mg^{2+}$ | $Cl^-$ | $SO_4^{2-}$ | $HCO_3^-$ | EC | TDS | TH |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| pH | 1 | | | | | | | | | | | | |
| $NH_4^+$ | -0.632** | 1 | | | | | | | | | | | |
| $NO^3$- | -0.381 | 0.717** | 1 | | | | | | | | | | |
| $NO^2$- | -0.467* | 0.819** | 0.673** | 1 | | | | | | | | | |
| $Ca^{2+}$ | -0.436 | 0.612** | 0.420 | 0.604** | 1 | | | | | | | | |
| $Na^+$ | 0.075 | 0.032 | -0.234 | -0.126 | -0.530* | 1 | | | | | | | |
| $Mg^{2+}$ | -0.012 | 0.037 | 0.535* | 0.312 | 0.154 | -0.354 | 1 | | | | | | |
| $Cl^-$ | -0.251 | 0.828** | 0.742** | 0.752** | 0.435 | 0.156 | 0.236 | 1 | | | | | |
| $SO_4^{2+}$ | 0.081 | 0.466 | 0.276 | 0.399 | 0.334 | 0.124 | -0.041 | 0.637** | 1 | | | | |
| $HCO_3^-$ | -0.332 | -0.068 | -0.412 | -0.067 | 0.431 | -0.119 | -0.187 | -0.393 | -0.285 | 1 | | | |
| EC | -0.565* | 0.787** | 0.652** | 0.678** | 0.612** | -0.120 | 0.160 | 0.533* | 0.408 | 0.144 | 1 | | |
| TDS | -0.606** | 0.836** | 0.683** | 0.668** | 0.620** | -0.108 | 0.140 | 0.572* | 0.344 | 0.113 | 0.970** | 1 | |
| TH | -0.393 | 0.559* | 0.552* | 0.643** | 0.946** | -0.590** | 0.468* | 0.467* | 0.285 | 0.324 | 0.600** | 0.601** | 1 |

* *p* value <0.001; ** *p* value <0.01

Very strong positive correlation between $NH_4^+$ and $NO_2^-$ (0.819), $NO_3^-$ and $NO_2^-$ (0.673) and respectively, between $NH_4^+$ and $NO_3^-$ (0.717) indicated an accumulation of inorganic nitrogen in the southwestern part of the studied region, possibly due to waste or fertilizers discharges into aquifer. Positive correlation coefficients between $NH_4^+$ and $Cl^-$ (0.828), or $NO_3^-$ and $Cl^-$ (0.742) and between $NO_2^-$ and $Cl^-$ (0.752) indicated anthropogenic external sources due to agricultural practices such as fertilization or leachate infiltration of organic wastes. Negative correlations between $Na^+$ and $Mg^{2+}$ (-0.354) and between $Ca^{2+}$ and $Na^+$ (-0.530) indicated ion exchange processes between $Na^+$, $Mg^{2+}$ and $Ca^{2+}$ in the water and aquifer matrix.

Typical bivariate graphs have been widely used to identify potential sources of pollution with nitrogen compounds [27]. Figure 4 shows positive correlations between nitrogen compounds and $Cl^-$ ions. $NO_3^-$ versus $Cl^-$ ($R^2 = 0.5509$); $NH_4{}^+$ versus $Cl^-$ ($R^2 = 0.6849$) respectively $NO_2^-$ versus $Cl^-$ ($R^2 = 0.5659$) suggesting that the presence of nitrogen compounds in concentrations exceeding the MAVs were presented due to non-point anthropogenic sources.

Low correlations between the other ions, such as: $NH_4{}^+$ versus $Na^+$, $Ca^{2+}$, $Mg^{2+}$, $SO_4^{2-}$, respectively pH ($R^2 = 0.001$; $R^2 = 0.3747$; $R^2 = 0.0013$, $R^2 = 0.2152$, $R^2 = 0.3993$), $NO_3^-$ versus $Na^+$, $Ca^{2+}$, $Mg^{2+}$, $SO_4^{2-}$, pH ($R^2 = 0.0548$; $R^2 = 0.1767$; $R^2 = 0.0548$, $R^2 = 0.0749$, $R^2 = 0.1455$), and $NO_2^-$ versus $Na^+$, $Ca^{2+}$, $Mg^{2+}$, $SO_4^{2-}$, pH ($R^2 = 0.0158$; $R^2 = 0.3651$; $R^2 = 0.0972$ , $R^2 = 0.1579$, $R^2 = 0.5659$), reflects the probability that the level of nitrogen compounds concentrations could be controlled by industrial polluted sources.

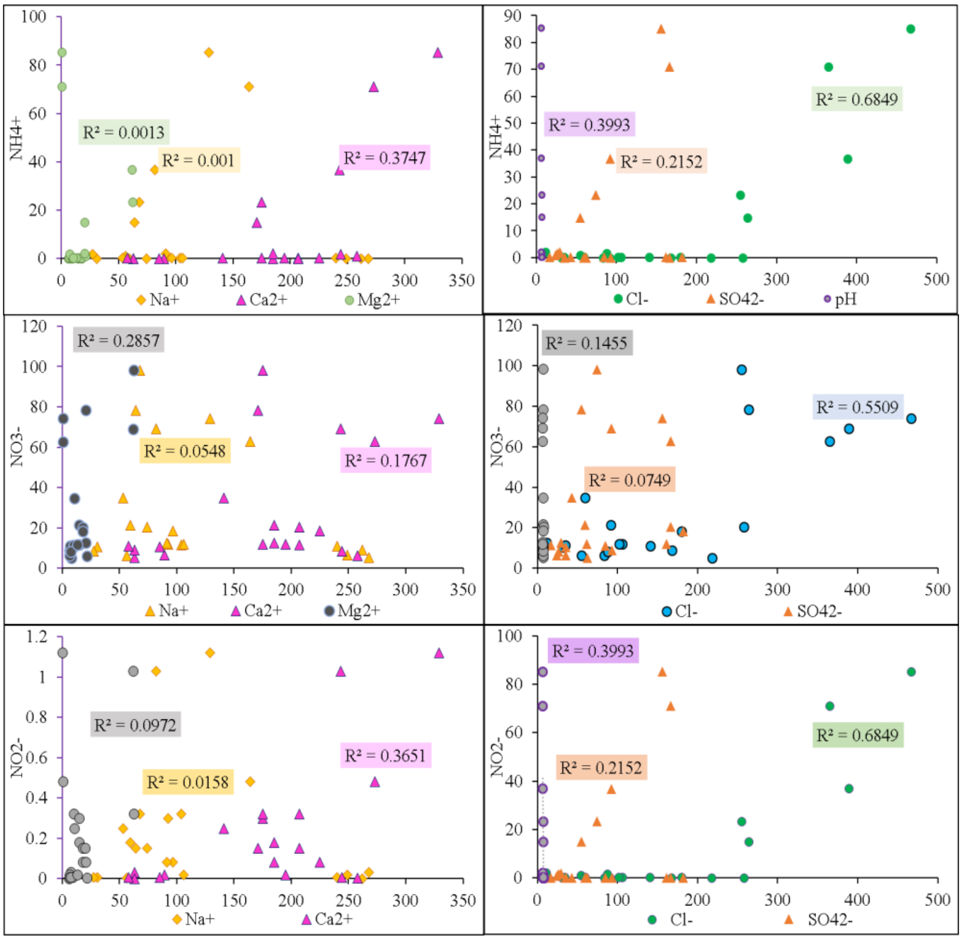

**Fig. 4.** Relationship between (a) $NH_4^+$ and $Cl^-$, $SO_4^{2-}$, pH; (b) $NH_4^+$ and $Na^+$, $Ca^{2+}$, $Mg^{2+}$; (c) $NO_3^-$ and $Cl^-$, $SO_4^{2-}$, pH; (d) $NO_3^-$ and $Mg^{2+}$, $Na^+$, $Ca^{2+}$; (e) $NO_2^-$ and $Cl^-$, $SO_4^{2-}$, pH; (f) $NO_2^-$ and $Na^+$, $Ca^{2+}$, $Mg^{2+}$ concentrations of the groundwater in study area.(mg/L except pH- unit pH)

*Analysis of principal components, PCA*

Following the application of the calculation process of the principal components, KMO value was equal to 0.525 confirming the validity of the PCA analysis implementation. According to the selection criteria, factors with eigenvalues exceeding 1.0 were considered in this study. Two principal components (PC1, PC2) were extracted from the groundwater quality parameters, representing 65.96% of the total variations. The variance percentages and cumulative percentages of each component after applying the Varimax rotation as well as the loads for the 2 PCs are presented in Table 4. Each principal component can be used to interpret specific hydro geochemical processes by examining their loads. PC1 represented 43.82% of the total variance, which was strongly weighted with $NH_4^+$, $NO_3^-$, $NO_2^-$, and $Cl^-$. About 25% of the total groundwater samples were located in the area affected by anthropogenic activities, with values of the parameters concentration that contribute to the loading of PC1 above the maximum allowed limits (Figure 5). The contribution of these ions to PC1 can be considered contamination of groundwater in the studied area due to the influence of external anthropogenic factors such as organic waste leachate infiltration, industrial or agricultural practices. PC2 represented 22.14% of the total variance, being weighted mainly with $Ca^{2+}$ and $HCO_3^-$ and TH. PC2 could be considered because of cation exchange processes at the soil-water interface with considerable influences on TH.

**Table 4.** Loadings of physical-chemical variables on two principal components for groundwater samples

| Parameter | PC1 | PC2 |
|---|---|---|
| pH | -0.418 | -0.511 |
| $NH_4^+$ | 0.914 | 0.178 |
| $NO_3^-$ | 0.848 | 0.078 |
| $NO_2^-$ | 0.840 | 0.235 |
| $Ca^{2+}$ | 0.527 | 0.748 |
| $Na^+$ | 0.013 | -0.652 |
| $Mg_2^+$ | 0.280 | 0.174 |
| $Cl^-$ | 0.926 | -0.178 |
| $SO_4^{2-}$ | 0.625 | -0.253 |
| $HCO_3^-$ | -0.316 | 0.765 |
| EC | 0.779 | 0.390 |
| TDS | 0.796 | 0.385 |
| TH | 0.564 | 0.726 |
| Variability (%) | 43.82 | 22.14 |
| Cumulative % | 43.82 | 65.96 |

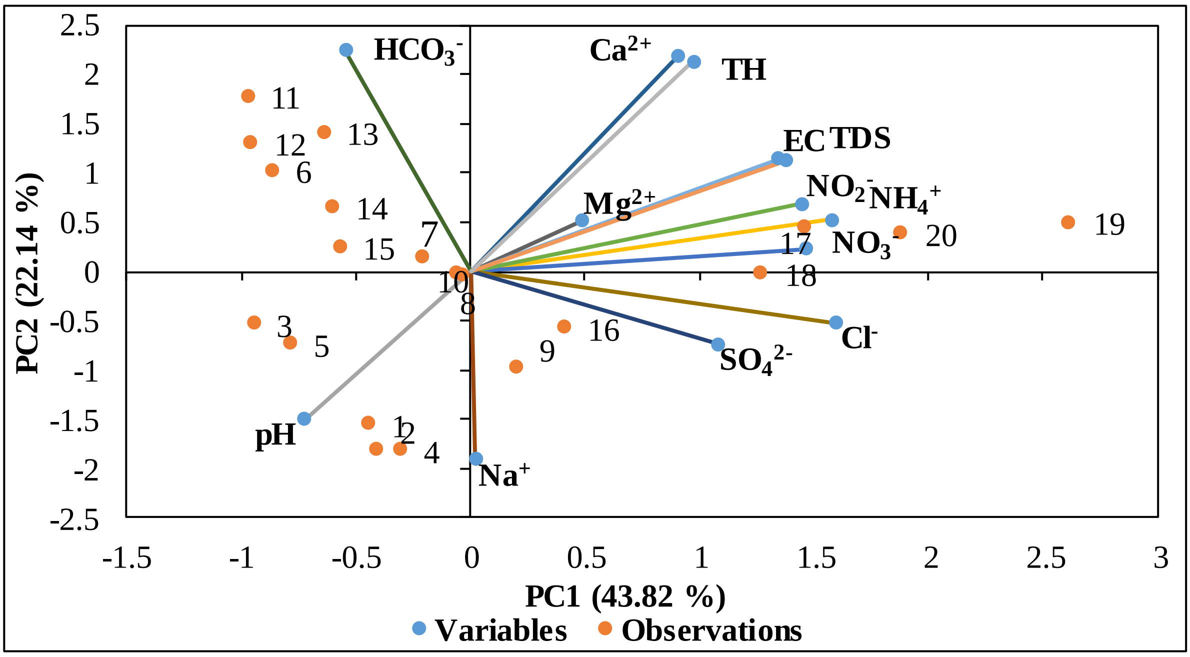

**Fig. 5.** Factor loadings (axes PC1 and PC2: 65.96% variability) after Varimax rotation.

*Non-carcinogenic risk assessment*

The spatial distribution maps of the non-carcinogenic risk (hazard index - $HI_{total}$) for male, female and children, using the IDW technique are described in figure 6. The Hazard quotient ($HQ_{nitrite}$) results for the three age groups considered showed very low minimum values (close to zero) for all groups, with maximum values of 0.0109 (men), 0.0131 (women) and 0.0235(children).

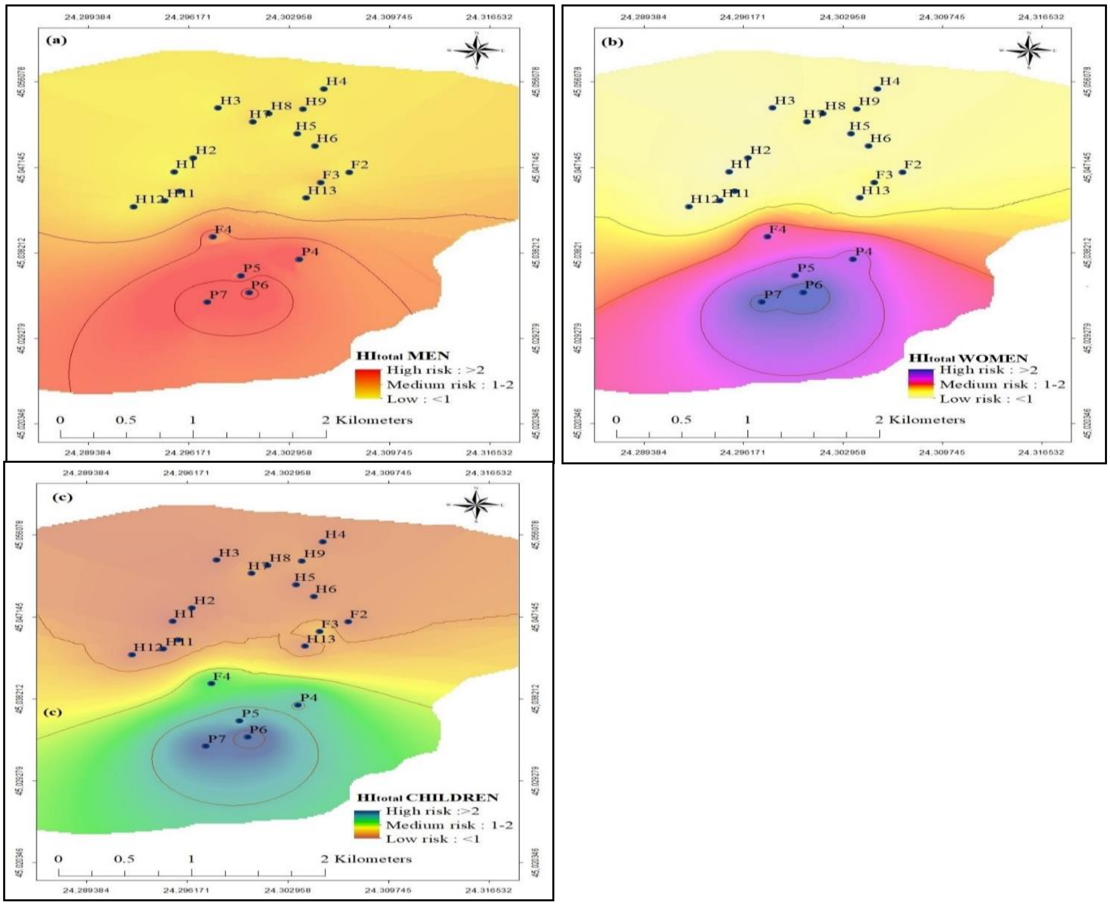

**Fig. 6**. Spatial distribution map of $HI_{total}$ for Men (a), Women (b) and Children (c) in study area

The results of the non-carcinogenic risk for men, women, and children through the intake of drinking water containing nitrates, nitrites, and ammonium are presented in table 5.

$HQ_{nitrate}$ results showed values between 0.0371 and 0.7117, 0.0445 and 0.8540, 0.0798 and 1.5313 for men, women and children, respectively. $HQ_{ammonium}$ results showed maximum values of 2.1334 in men group, 2.560 in women group and 4.5905 in children group (Table 5).

For the non-carcinogenic risk, the total $HI_{total}$ for nitrogen compounds in groundwater from the investigated region ranged from 0.037 to 2.856 for men, from 0.045 to 3.427 for women, and between 0.080 and 6.145 (mean 1.866), respectively for children. As was mentioned previously, $HI_{total}$ value greater than 1 indicate the probability of adverse risk to human health due to exposure to drinking water intake [35].

The results obtained indicate that out of twenty sampling points, five wells from which groundwater samples were collected have high levels of nitrates and ammonium and thus may lead to exposure of age groups (men, women and children) to risk increased harm to human health.

The spatial distribution of non-carcinogenic risk ($HI_{total}$) illustrates that men, women and children in the south-west of the study region present a relatively higher risk to health through groundwater consumption.

**Table 5.** Results of non-carcinogenic risk through drinking water intake

| **Samples** | **$HQ_{men}$** | | | **$HQ_{women}$** | | | **$HQ_{children}$** | | | **$HI_{total}$** | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | **$NH_4^+$** | **$NO_3^-$** | **$NO_2^-$** | **$NH_4^+$** | **$NO_3^-$** | **$NO_2^-$** | **$NH_4^+$** | **$NO_3^-$** | **$NO_2^-$** | **Men** | **Women** | **Children** |
| H1 | 0.0005 | 0.0371 | 0.0003 | 0.0006 | 0.0445 | 0.0004 | 0.0011 | 0.0798 | 0.0006 | 0.038 | 0.045 | 0.082 |
| H2 | 0.0004 | 0.0647 | 0.0001 | 0.0005 | 0.0776 | 0.0001 | 0.0008 | 0.1392 | 0.0001 | 0.065 | 0.078 | 0.140 |
| H3 | 0.0004 | 0.0461 | 0.0002 | 0.0004 | 0.0553 | 0.0002 | 0.0008 | 0.0991 | 0.0004 | 0.047 | 0.056 | 0.100 |
| H4 | 0.0043 | 0.0790 | 0.0001 | 0.0051 | 0.0947 | 0.0001 | 0.0092 | 0.1699 | 0.0001 | 0.083 | 0.100 | 0.179 |
| H5 | 0.0004 | 0.0761 | 0.0000 | 0.0004 | 0.0913 | 0.0001 | 0.0008 | 0.1637 | 0.0001 | 0.076 | 0.092 | 0.165 |
| H6 | 0.0045 | 0.0826 | 0.0031 | 0.0054 | 0.0991 | 0.0037 | 0.0097 | 0.1777 | 0.0067 | 0.090 | 0.108 | 0.194 |
| H7 | 0.0002 | 0.1550 | 0.0018 | 0.0002 | 0.1860 | 0.0021 | 0.0004 | 0.3335 | 0.0038 | 0.157 | 0.188 | 0.338 |
| H8 | 0.0035 | 0.0855 | 0.0029 | 0.0042 | 0.1026 | 0.0035 | 0.0075 | 0.1839 | 0.0063 | 0.092 | 0.110 | 0.198 |
| H9 | 0.0004 | 0.1470 | 0.0015 | 0.0005 | 0.1765 | 0.0018 | 0.0009 | 0.3164 | 0.0031 | 0.149 | 0.179 | 0.320 |
| H10 | 0.0040 | 0.1326 | 0.0008 | 0.0048 | 0.1591 | 0.0009 | 0.0086 | 0.2852 | 0.0017 | 0.137 | 0.165 | 0.296 |
| H11 | 0.0233 | 0.0445 | 0.0001 | 0.0279 | 0.0534 | 0.0001 | 0.0501 | 0.0957 | 0.0001 | 0.068 | 0.081 | 0.146 |
| H12 | 0.0411 | 0.0595 | 0.0001 | 0.0493 | 0.0714 | 0.0001 | 0.0884 | 0.1280 | 0.0001 | 0.101 | 0.121 | 0.216 |
| H13 | 0.0498 | 0.0913 | 0.0008 | 0.0598 | 0.1095 | 0.0009 | 0.1072 | 0.1964 | 0.0017 | 0.142 | 0.170 | 0.305 |
| F2 | 0.0033 | 0.0855 | 0.0002 | 0.0039 | 0.1026 | 0.0002 | 0.0070 | 0.1839 | 0.0004 | 0.089 | 0.107 | 0.191 |
| F3 | 0.0043 | 0.2514 | 0.0024 | 0.0051 | 0.3016 | 0.0029 | 0.0092 | 0.5408 | 0.0052 | 0.258 | 0.310 | 0.555 |
| F4 | 0.3731 | 0.5679 | 0.0015 | 0.4477 | 0.6815 | 0.0018 | 0.8028 | 1.2220 | 0.0031 | 0.942 | 1.131 | 2.028 |
| P4 | 0.9215 | 0.5005 | 0.0100 | 1.1058 | 0.6006 | 0.0120 | 1.9828 | 1.0770 | 0.0216 | 1.432 | 1.718 | 3.081 |
| P5 | 0.5834 | 0.7117 | 0.0031 | 0.7001 | 0.8540 | 0.0037 | 1.2554 | 1.5313 | 0.0067 | 1.298 | 1.558 | 2.793 |
| P6 | 2.1334 | 0.5375 | 0.0109 | 2.5601 | 0.6450 | 0.0131 | 4.5905 | 1.1565 | 0.0235 | 2.682 | 3.218 | 5.770 |
| P7 | 1.7778 | 0.4542 | 0.0047 | 2.1334 | 0.5450 | 0.0056 | 3.8254 | 0.9773 | 0.0101 | 2.237 | 2.684 | 4.813 |
| Minimum | 0.0002 | 0.0371 | 0.0000 | 0.0002 | 0.0445 | 0.0001 | 0.0004 | 0.0798 | 0.0001 | 0.037 | 0.045 | 0.080 |
| Maximum | 2.1334 | 0.7117 | 0.0109 | 2.5601 | 0.8540 | 0.0131 | 4.5905 | 1.5313 | 0.0235 | 2.856 | 3.427 | 6.145 |

## CONCLUSIONS

In this study, the monitoring of groundwater pollution and the assessment of the health risk in the southern sub-urban area of Romania revealed that pollution with nitrogen compounds is a serious problem for five groundwater wells. Statistical analysis of groundwater quality parameters in the suburban region of Ramnicu Valcea, Romania was used to assess groundwater quality for drinking water intended for human consumption. The analysed physical-chemical parameters were compared with maximum admissible values according to Romanian Law 458/2002 and WHO guidelines for drinking water quality.

The pH values were situated in the range 6.5 to 8.2 with an average of 7.18 pH unit. Only 15% of the analyzed groundwater samples exceed the EC limit as is imposed by Romanian Law (2500 µS/cm), but according to WHO guidelines all samples were above 400 µS/cm. Regarding the total dissolved solids, 50% of the analyzed samples were situated above WHO limit (1000 mg/L), being not suitable for human consumption, but could be used for irrigation.

Approximately 70% of the groundwater samples fall into hard water quality with values higher than 500 mg/L. For nitrates, 25% of the analysed samples exceeded the maximum admissible limit (50 mg/L) and 40% of the samples indicated ammonium higher than 0.5 mg/L. 10% of groundwater samples had higher nitrite values than the limit imposed by Romanian legislation (0.5 mg/L).

Typical bivariate graphs and principal component analysis were used to identify potential sources of nitrate, nitrite, and ammonium groundwater pollution in the study area. According to the correlation factor analysis contamination with nitrogen compounds was significantly associated with anthropogenic activities of agricultural nature, human and industrial activity especially in the south-east of the studied region. The geogenic processes due to the interaction between groundwater matrix and the soils /rocks specific to the studied area could be also a source of pollution.

The HQ indices for nitrates, nitrites and ammonium, and the $HI_{total}$ indices for the categories of men, women and children were calculated in order to assess the non-carcinogenic risk of nitrogen compounds to human health. The 25% from the obtained results for each group indicate that using groundwater samples from the studied region as a source of drinking water could present the highest health risk.

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## REFERENCES

[1] VELIS, M., CONTI, I.C., BIERMANN, F., Sustain. Sci. **12**, 2017, p. 1007, https://doi.org/10.1007/s11625-017-0490-9.

[2] PAREEK, A., DHANKHER, O.P., FOYER, C.H., J. Exp. Bot., **71**, no. 2, 2020, p. 451, https://doi.org/10.1093/jxb/erz518.

[3] OLIVARES, E.A., TORRES, S.S., JIMENEZ, B.I.S., ENRIQUEZ, C.O.J., ZIGNOL, F., REYGADAS, Y., TIEFENBACHER, J.P., Remote Sens., **11**, no. 11, 2019, p. 1290, https://doi.org/10.3390/rs11111290.

[4] SMERDON, B.D., J. Hydrol., no. 555, 2017, p. 125, https://doi.org/10.1016/j.jhydrol.2017.09.047.

[5] MILLER, J.D., HUTCHINS, M., J. Hydrol.-Reg. Stud., 12, 2017, p. 345, http://dx.doi.org/10.1016/j.ejrh.2017.06.006.

[6] PATEL, M.P., GAMI, B., PATEL, A., PATEL, P., PATEL, B., Groundw. Sustain. Dev., **10**, 2020, https://doi.org/10.1016/j.gsd.2019.100306.

[7] DEGAN, J., BOHLKE, J.K., PELHAM, K., LANGLAIS, M.D., WALSH, G.J., Environ. Sci. Technol., **50**, no. 2, 2016, p. 593, https://doi.org/10.1021/acs.est.5b03671.

[8] SINGH, B., CRASWELL, E., SN Appl. Sci., **3**, no. 4, 2021, p. 518, https://doi.org/10.1007/s42452-021-04521-8.

[9] DEVIC, G., DJORDJEVIC, D., SAKAN, S., Sci. Total Environ., **468–469**, 2014, p. 933, http://dx.doi.org/10.1016/j.scitotenv.2013.09.011.

[10] PIRVU, F., PAUN, I., CHIRIAC, F.L., NICULESCU, M., VASILACHE, N., PASCU, L.F., GALAON, T., Rom. J. Ecol. Environ. Chem., **2**, no. 2, 2020, p. 56, https://doi.org/10.21698/rjeec.2020.208.

[11] GORSKI, J., DRAGON, K., KACZMAREK, P.M.J., Environ. Sci. Pollut. Res., **26**, 2019, p. 2038, https://doi.org/10.1007/s11356-017-9798-3.

[12] HANSEN, B., THORLING, L., SCHULLEHNER, J., TERMANSEN, M., Sci. Rep., **7**, 2017, https://doi.org/10.1038/s41598-017-07147-2.

[13] JALILI, D., RADFARAD, M., SOLEIMANI, H., AKBARI, H., KAVOSI, A., ABASNIA, A., ADIBZADEH, A., Data Brief, **20**, 2018, p. 394, https://doi.org/10.1016/j.dib.2018.08.023.

[14] ZEIDAN, B., Groundwater Degradation and Remediation in the Nile Delta Aquifer, In: Negm, A. (eds) The Nile Delta. The Handbook of Environmental Chemistry, vol. 55, Springer, Cham., p. 159-232, https://doi.org/10.1007/698_2016_128.

[15] MEKKI, I., GHAZOUUANI, W., CLOSAS, A., MOLLE, F., Groundwater Sustain. Dev., 5, 2017, p. 101, https://doi.org/10.1016/j.gsd.2017.05.001.

[16] DU, Y., MA, T., DENG, Y., SHEN, S., LU, Z., Environ. Sci.: Processes Impacts, **19**, 2017, p. 161, https://doi.org/10.1039/c6em00531d.

[17] PATEL, P.R., HOGG, N., KIM-SHAPIRO, D.B., Cardiovasc. Res., **89**, 2011, p. 507, https://doi.org/10.1093/cvr/cvq323.

[18] BULLER, I.D., PATEL, D.M., WEYER, P.J., PRIZMENT, A., JONES, R.R., WARD, M.H., Int. J. Environ. Res. Public Health, **18**, no. 13, 2021, https://doi.org/10.3390/ijerph18136822.

[19] WHO (2017) Guidelines for Drinking-water Quality, 4th Edition, [01.09.2022].

[20] WHO (2011) Nitrate and nitrite in drinking water. Background document for development of WHO Guidelines for drinking water, [01.09.2022].

[21] LAW no. 458 regarding drinking water quality, July 8, 2002, republished in 2017, in Romanian, http://legislatie.just.ro/Public/DetaliiDocument/37723, [01.09.2022].

[22] ELUBID, B.A., HUANG, T., AHMED, E.H., ZHAO, J., ELHAG, K.M., ABBASS, W., BABIKER, M.M., Int. J. Environ. Res. Public Health, **16**, no. 5, 2019, https://doi.org/10.3390/ijerph16050731.

[23] RAHMAN, A., MONDAL, N.C., TIWARI, K.K., Sci. Rep., 11, no. 1, 2021, https://doi.org/10.1038/s41598-021-88600-1.

[24] UKAH, B.U., UBIDO, O.E., IGWE, O., Model. Earth Syst. Environ., **6**, 2020, p. 953, https://doi.org/10.1007/s40808-020-00731-y.

[25] AHMED, T.A., HASAN, Y.M., MONIR, M.U., SAMAD, M.S., RAHMAN, M.M., RIFAT, M.S.I., ISLAM, M.N., KHAN, A.A.S., BISWAS, P.K., JAMIL, A.H.M.N., Groundwater Sustain. Dev. **11**, 2020, https://doi.org/10.1016/j.gsd.2020.100441.

[26] NURFAIKA, PURNAMA, S., HARTONO, IOP Conf. Series: Earth and Environmental Science, **485**, 2020, https://doi.org/10.1088/1755-1315/485/1/012039.

[27] ADIMALA, N., Hum. Ecol. Risk. Assess., **26**, no. 2, 2019, p. 310, https://doi.org/10.1080/10807039.2018.1508329.

[28] SHENG, J, PING, Y, ZHANG, H, WANG, Z, J. Soils Sediments., **21**, 2021, p 419, https://doi.org/10.1007/s11368-020-02758-1.

[29] HELARD, D., INDAH, S., OKTAVIA, M., Water Supply **20**, no. 4, 2020, p. 1484, https://doi.org/10.2166/ws.2020.065.

[30] ZHANG, M., HUANG, G., LIU, C., ZHANG, Y., CHEN, Z., WANG, J., J. Hydrol., **582**, 2020, https://doi.org/10.1016/j.jhydrol.2019.124528.

[31] MURSHED, H.B., RAHMAN, A., UDDIN, M.J., RAHMAN, M., Int J Environ Clim Chang., **10**, no. 9, 2020, p. 24, https://doi.org/10.9734/IJECC/2020/v10i930227.

[32] NCIBI, K., HADJI, R., HAJJI, S., BESSER, H., HAJLAOUI, H., HAMAD, A., MOKADEM, N., SAAD, A.B., HAMDI, M., HAMED, Y., Irrig. Drain., p. 1, 2021, https://doi.org/10.1002/ird.2599.

[33] KUMARI, P., GUPTA, N.C., KAUR, A., SINGH, K., J. Geol. Soc. India., **94**, 2019, p. 595, https://doi.org/10.1007/s12594-019-1366-7.
[34] LI, Q., ZHANG, H., GUO, S., FU, K., LIOA, L., XU, Y., CHENG, S., Environ. Sci. Pollut. Res., **27**, 2020, p. 9000, https://doi.org/10.1007/s11356-019-06126-6.
[35] USEPA, Risk Assessment Guidance for Superfund, vol. I, Human Health Evaluation Manual (Part A), 1989.
[36] WEGAHITA, N.K., MA, L., LIU, J., HUANG, T., LUO, Q., QIAN, J., Water, **12**, no. 12, 2020, https://doi.org/10.3390/w12123341.
[37] YU, G., WANG, J., LIU, L., LI, Y., ZHANG, Y., WANG, S., BMC Public Health, **20**, 2020, https://doi.org/10.1186/s12889-020-08583-y.
[38] KARAMI, M.A., FAKHRI, Y., REZENIA, S., ALINEJAD, A.A., MOHAMMADI, A.A., MAHMOOD, Y., SAGHI, M.H., AHMADPOUR, M., Int. J. Environ. Res. Public Health, **16**, no. 21, 2019, https://doi.org/10.1080/03067319.2020.1743280.
[39] ABOTALEB, B., ALI, S., GHEZELSOFLA, M., KERAMATI, H., MORADI, B., FAKHRI, Y., Data Brief, **20**, 2018, p. 1822, https://doi.org/10.1016/j.dib.2018.09.035.
[40] OFTADEH, B.Z.G., SANY, S.B.T., ALIDADI, H., SAGHI, M., TAFAGHODI, M., SHAMSZADEH, S.H., FAKHARI, M., Nutrition Fasting Health, **7**, no. 1, 2019, p. 58, https://doi.org/10.22038/jnfh.2019.38879.1181.
[41] VALCEA COUNTY INSTITUTE OF STATISTICS, https://valcea.insse.ro/, [01.09.2022].
[42] TOXICOLOGICAL PROFILE FOR NITRATE AND NITRITE, 2017, https://www.atsdr.cdc.gov › toxprofiles, [01.09.2022].
[43] EUROPEAN FOOD SAFETY AUTHORITY, EFSA Journal, 2012, **10**, no. 10, https://doi.org/10.2903/j.efsa.2012.2918.
[44] ROMANIAN NATIONAL INSTITUTE OF STATISTICS, https://insse.ro/cms/, [01.09.2022].
[45] BOZDAG, A., GOCMEZ, G., Environ. Earth Sci., **69**, no. 3, 2012, p. 921, https://doi.org/10.1007/s12665-012-1977-4.
[46] SARIKHANI, R., KAMALI, Z., Environ. Earth Sci., **72**, no.7, 2014, p. 2369, https://doi.org/10.1007/s12665-014-3146-4.
[47] SHUGG, A., Thermal and Mineral Waters, 2014, p. 97, https://doi.org/10.1007/978-3-642-28824-1_9.
[48] VASILACHE, V., FILOTE, C., CRETU, M.A., SANDU, I., COISIN, V., VASILACHE, T., MAXIM, C., Environ. Eng. Manag. J., **11**, no. 2, 2012, p. 417.
[49] MARIN, N., DUMITRU, M., SARBU, C.E., PREDA, C.E., J. Environ. Prot. Ecol., **20**, no. 4, 2019, p. 1639.
[50] KODA, E., SIECZKA, A., OSINSKI, P., Sustainability, **8**, 2016, https://doi.org/10.3390/su8121253.
[51] LORENZO, T.D., CIFONI, M., LOMBARDO, P., FIASCA, B., GALASSI, D.M.P., Hydrobiologia, 743, 2015, p. 139, https://doi.org/10.1007/s10750-014-2018-y.
[52] QIN, H., QUAN, Z., YUAN, H., LIU, X., ZHU, Y., CHEN, C., GUO, J., WU, J., WEI, W., Water Air Soil Pollut., 225, 2014, https://doi.org/10.1007/s11270-014-1908-y.
[53] AKHTAR, N., ISHAK, M.I.S., BHAWANI, S.A., UMAR, K., Water, **13**, no. 19, 2021, https://doi.org/10.3390/w13192660.

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