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ANALYSIS OF GROUNDWATER QUALITATIVE PARAMETERS IN THE HILL AND PLAIN SECTOR OF DAMBOVITA COUNTY – ROMANIA

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Abstract

Water intended for human consumption (whether natural or after applying appropriate treatment techniques) must comply with the values of quality parameters according to the laws and regulations in force. The geographical area analysed in this study covers part of Dambovita County and lies at the contact between the Outer Subcarpathian Hills at the Curvature and Candesti Piedmont, the High Plain of Targoviste and Titu Subsidence Plain. Considering that the population in this area is also supplied with water from individual wells, which capture surface aquifers, changes in some potability parameters may appear punctually, inducing a number of health impairments if consumed over a long period of time. 12 sample points have been chosen in localities considered to be vulnerable and a number of parameters (pH, Ca^{2+}, Cl^-) have been analysed in the laboratory. Analyses have revealed excessive MAC (Maximum Allowable Concentration) in some locations such as Glodeni and Gheboaia.

Rezumat – Apa destinata consumului uman (in stare naturala sau dupa aplicarea tratamentelor) trebuie sa corespunda valorilor parametrilor de calitate, conform legislatiei si regulamentelor in vigoare. Arealul studiat in aceasta lucrare acopera o parte din judetul Dambovita si se intinde de la Subcarpatii de Curbura pana la Piemontul Candesti, Campia Mare a Targovistei si Campia Titu. Luand in considerare ca populatia din acest areal este aprovizionata cu apa din surse proprii, care capteaza apele de suprafata, schimbarile anumitor indicatori de calitate pot aparea punctual, inducand o serie de probleme de sanatate, daca este consumata pe termen lung. Au fost stabilite 12 puncte de prelevare in localitati considerate a fi vulnerabile si a fost analizat in laborator un numar de indicatori (pH, Ca, Cl). Analizele au evidentiat depasiri ale CMA (Concentratia Maxima Admisibila) in anumite localitati, precum Glodeni si Gheboaia.

Keywords: hydro-structures, mineralisation, plain, potability markers

1.INTRODUCTION

Durable development and water demands, alongside climatic changes with an impact on the quantitative-qualitative variability of water bodies entail the necessity to conduct studies that should highlight the equation of demand-satisfaction of people’s needs in terms of not altering their health. There are, in this respect, numerous studies underlying this attempt [1-5]. All point out the types of structures and chemical composition of ground waters, with correlations between lithology and water bodies.

Supply of free aquifers, as is the case here, is mainly from liquid or solid precipitation and from the relation between the hydrographical network and hydro-structures, when it becomes active. This occurs on the entire active surface of the aquifer and is influenced by the climatic particularities of the area (precipitation, temperature) which may lead to vertical variations in the piezometric level and modifications in the chemical composition of water [6].

Changes in the chemical composition of water were also induced by anthropic activities (agriculture, exploitation of hydrocarbons, etc.). As regards the elements of chemism of waters, pollution sources, environment protection and health, there are also numerous specialized studies [7-14].

The **study area** represents the central part of Dambovita County, at the contact between the hill and plain units (fig.1: Geographical position*)*. Water samples that were chemically analysed in laboratory were taken in areas covering localities where people use individual wells that intersect with surface aquifers and are vulnerable to infestations with various chemical components resulting either from economic activities or from a variation in the piezometric level due to the seasonal fluctuation of supply sources induced by climatic conditions.

The points where researched samples were collected are located in the plain and hill area distributed, hydrogeologically speaking, between the two large hydrographical basinal units as follows: Finta, Targoviste, Comisani, Glodeni (ABA Ialomita – Buzau), Lucieni, Gaesti, Cobia, Gheboaia, Picior de Munte, Viisoara, Dumbrava (ABA Arges–Vedea – Dambovita).

These are aquiferous structures, mainly phreatic, interdependent on external factors. Within the Picior de Munte – Gura Sutii perimeter, ground waters accumulate at great depths and their direction of flow towards the plain entails the gradual saturation of characteristic psephitic deposits and leads to their discharge as springs or as supplying younger alluvia thus resulting in rich phreatic aquiferous layers (http://www.rowater.ro/daarges) [19]. Vulnerability degree is variable, being influenced by the thickness and type of the covering layer, generally argillaceous and with thickness ranging, for instance, between 3.0 - 6.0 m in the Arges River Meadow and terraces and 20.0-200.0 in the east of the Wallachian Depression – http://www.rowater.ro/daarges.

Water quantity and quality condition in this region is monitored by the National Hydrological Network through hydrogeological drillings, which, in 2006, in the entire Romanian Plain (that includes the area investigated), numbered 931 (295 located in the meadows of the main water courses; 119 in the terrace area; 517 in interfluve areas) [3].

Phreatic groundwater bodies on the territory of Dambovita County are divided between the Arges-Vedea-Dambovita Hydrographical Basin (ROAAG02 Campia Titu, ROAAG05 the Arges River Meadow and terraces, ROAAG12 Eastern sector of Wallachian Depression) in the south-west and the Buzau-Ialomita Hydrographical Basin (ROIL 13 the Ialomita Meadow) in the north-east (fig. 2:Phreatic groundwater bodies delimited in the analysed geographical area). These hydro-structures are the cumulative result of several geological, geomorphological, hydrological and climatic factors.

Observations on quality and chemical structure of ground waters in these hydro-structures date back to the 1960's (Pricajan et al., 1963 si Scafa, 1970, Feru et al., 1966, 1969; Scafa, 1970; Maieru et al., 1990; Capraru, 1991) (fig. 3:Titu Plain. ROAG02 Piper and Schoeller Diagrams, fig. 4:The ROAG05 body the Arges River Meadow and terraces Piper and Schoeller Diagrams) and were later included in the study *Background support to compensate for additional costs and income foregone resulting from disadvantages resulting from the implementation of the 2000/60/EC Directive and the 38 art. of the 1698/2005 Regulation (EC) and assessment of potential groundwater resources and surface of agrosystems in areas vulnerable to climate change in southern Romania (J.M. Adler).* http://www.madr.ro/attachments/article/153/ADER-411-faza-4 2014 ADER 4.1.1./2011 (INHGA) [20].

According to the management plan of the Arges – Vedea – Dambovita hydrographical area, natural background levels (NBLs) for the main chemical compounds found in the analysed water bodies do not exceed the threshold values (TVs) imposed by the 2000/60/EC Directive, under article 38 of the 1698/2005 Regulation (EC) (www.madr.ro) (table 1).

Table 1. Natural background levels (NBL) and threshold values for groundwater bodies assigned to ABA Arges – Vedea – Dambovita (ROAAG02 Titu Plain, ROAAG05 Arges River Meadow and terraces, ROAAG12 Eastern sector of Wallachian Depression)

		NH4 (mg/l)	Cl (mg/l)	SO4 (mg/l)	Cd (mg/l)	Pb (mg/l)	NO2 (mg/l)	PO4 (mg/l	Cr (mg/l)	Ni (mg/l)	Cu (mg/l)	Zn (mg/l)	Hg (mg/l)	As (mg/l)
ROAAG02	NBL	0.490513	54.53287	89.06833	0.000218	0.00256	0.286769	0.120225	0.000938	0.001383	0.011814	0.22906	0.00009	0.000098
	TV	0.5	250	250	0.005	0.01	0.5	0.5	0.05	0.02	0.1	5.0	0.001	0.01
ROAAG05	NBL	0.998025	127	109.46	0.001534	0.012348	0.173207	0.584	0.007347	0.003864	0.011717	0.16486	0.0001	0.000225
	TV	1.2	250	250	0.005	0.02	0.5	0.7	0.05	0.02	0.1	5.0	0.001	0.01
ROAAG12	NBL	1.306971	82.78	126.7	0.000335	0.002633	0.28	0.597591	0.008018	0.001	0.004744	0.081333	0.000216	0.009748
	TV	1.6	250	250	0.005	0.01	0.5	0.7	0.05	0.02	0.1	5.0	0.001	0.01

(Source: http://www.madr.ro/attachments/article/153/ADER-411-faza-4 2014 ADER 4.1.1./2011, INHGA)

Lithostratigraphy and tectonic structure provide viable premises for storing large quantities of groundwater and influence the hydrodynamic model of flowing. Porous-permeable geological deposits from the Quaternary are to be noted, consisting of various granulation, gravels and boulders, often with clay interlayers. These are generally assigned to the Candesti Formation (Middle Romanian-Lower Pleistocene) and the Fratesti Formation (Upper Romanian-Lower Pleistocene). They are both deep and shallow structures, phreatic and discontinuous in surface. The aquifer system is under pressure, with the exception of areas of supply and natural discharge where ground waters have a free level and function under a quasi-stationary regime (piezometric levels are constant or with very small variations in time) [20]. Waters stored in the deposits of these formations – of Candesti and Fratesti – have low mineralisation, below 0.6-0.7 g/l, while the hydrochemical facies with major occurrence is calcium-magnesium bicarbonate [5]. Natural hydric load is from surface waters – main rivers (for the study area Dambovita, Ialomita, Arges) accompanied by those from the secondary hydrographical network but only during the periods when they become active (fig. 5:Basic diagram of the connection between the aquifer from the Piedmont Plain of Targoviste and surface waters, fig. 6:Basic diagram of the groundwater supply from the Piedmont Plain of Targoviste, Lazuri - Vacaresti catchment, fig. 7:Basic diagram of hydrodynamics from Candesti Piedmont (Hulubesti –Butoiu catchment). At the same time, supply is also from rainfalls and as a result of solid precipitation melting [1, 2].

According to the: lithological type of reservoir rocks, degree of porosity, depth of hole, land morphology, relation with surface waters and anthropogenic impact, quantitative and qualitative characteristics of water vary within a wide range. According to ABA Arges–Vedea and Ialomita–Buzau, water bodies are classified as not being at risk in terms of quantity, while the water supplied by the exploitation boreholes is, generally, potable, of the best quality, except one small area located between the Cricovul Dulce and the Ialomita (south of the diapiric folds and hydrocarbon exploitations of Moreni-Gura Ocnitei). Exceeding the normal limits of certain parameters (ammonium, chlorides, phosphates, sulphates) is due either to the local natural geochemical background or to accidental pollution. Exploitations of building material in the Dambovita and the Ialomita riverbeds have caused the dip of the piezometrical level by 1-3 m in the Quaternary hydro-structures within the terrace systems [2]. Furthermore, the decrease of (natural) water quantity of the two main rivers of the Ialomita–Buzau hydrographical basin according to the scenario imposed by global changes and mentioned by Adler (2014) for the period 2021-2050 (the Buzau hydrographical basin, from an annual average reserve of 826.22 million m^3/year – 1971-2000), to 756.0 million m^3/year; the Ialomita hydrographical basin, from 1237.0 million m^3/year to 1118.0 million m^3/year) may lead to the increase of the degree of mineralisation of phreatic waters with consequences on their quality.

2.MATERIAL AND METHODS

This study takes into account the analysis of certain quality indicators of the water within the perimeter of the localities where samples were taken, in accordance with the natural background levels (NBLs) of water bodies – table 1. Samples were taken during the first three weeks of August 2014, in the time interval 6.30-7.00, considering that overnight water had had time to homogenise. For each point five successive samples were taken (measuring water temperature), with volumes ranging from 1 to 5 l, with lab results being resumed in case of inconclusive results. Sterile polyurethane containers were used for sampling. August was chosen because, in the last decade, it has been observed that there is roughly a one-month gap of the thermal peak (summer days, occurrence and permanence of tropical days with 25-35^0 and above), with soil temperatures which may exceed 50-55^0 C, decrease of rainfall quantity, which leads to the phenomenon of meteorological dryness followed by the meteorological drought and pedological drought. Rainfall quantities were below the climatological norm only on small areas and low quantitatively.

Determination of calcium quantity in waters

The procedure aims to determine calcium in water by the complexonometric method using STAS 3662-90.

Reagents and consumables

The reagents used must be of quality for analysis or equivalent quality (Sodium hydroxide, Ethyl alcohol, Hydrochloric acid, Composite indicator, Calcium chloride, EDTA).

The molar concentration of the ethylenediaminetetraacetic solution is calculated based on the formula:

$$c_{EDTA} = \frac{c_{et.Ca2+} \cdot V_{et.Ca2+}}{V_{EDTA}} [mol]$$

in which:

c_{EDTA} = molar concentration of EDTA solution [moles];

$c_{et.Ca2+}$ = molar concentration of standard Ca2+ solution (CaCl2) [moles];

$V_{et.Ca2+}$ = volume of standard Ca2+ solution (CaCl2) used [ml];

V_{EDTA} = volume of EDTA solution needed to titrate the standard Ca2+ solution [ml].

Determination of the chloride content in waters

Chlorides are ionic forms of the element chlorine and are present in nature in a wide variety of concentrations. Water reservoirs generally contain small amounts of chlorides, which evolve in rivers and ground waters. Due to partial water evaporation, the highest concentration is found in the sea. This analysis aims to determine the content of chlorides in wastewaters, by the titrimetric method using SR ISO 9297:2001(Mohr Method) [17].

The solution is gauged using the formula:

$$c_{M(AgNO3)} = \frac{c_{et.Cl-} \cdot V_{et.Cl-}}{V_{AgNO3)}} [mol/l]$$

where:

$c_{M(AgNO3)}$ = molar concentration of AgNO3 solution [moles/l];

$c_{et.Cl-}$ = molar concentration of Cl- (NaCl) standard solution [moles/l];

$V_{et.Cl-}$ = volume of standard Cl- (NaCl) solution used [ml];

$V_{AgNO3)}$ = volume of AgNO3 solution needed to titrate the standard Cl- solution [ml].

Determination of water pH

This procedure aims to determine water pH by the electrochemical method using the method shown by SR ISO 10523:2009.

3.RESULTS AND DISCUSSIONS

Calculating the calcium content

The amount of Ca^{2+} is calculated as follows:

$$\left[Ca^{2+}\left(\frac{mg}{l}\right)\right] = \frac{1000 \cdot 0,4008 \cdot V_{EDTA}}{V_{proba}} [mg/l]$$

where:

0.4008=amount of calcium in mg, corresponding to 1cm^3 of EDTA solution 0.01M;

V_{EDTA} = volume of EDTA solution used for titration [ml];

V_{proba} = volume of water sample used [ml].

The average of results is shown in table 2. To determine the calcium content in water, the MAC (Maximum Allowable Concentration) is 300 mg/l, in this case we can see that 2 samples exceed the limit: Glodeni, 396.79 mg/l, and Gheboaia, 308.62 mg/l; long-term consumption may have adverse effects on the health of the population consuming it. The lowest value was recorded at Finta, 23.25 mg/l. Figure 8 (Results of calcium concentration) shows the difference between results and their relation to the MAC.

Table 2. The average measured values

No.	Sample points	Ca Average mg/L	Chloride Average mg/L	pH Average mg/L
1.	Cobia	187.25	72.32	7.12
2.	Comisani	123.93	72.90	7.12
3.	Dumbrava	100.68	52.51	6.59
4.	Finta	23.25	30.95	7.90
5.	Gaesti	47.29	12.15	7.67
6.	Gheboaia	308.62	519.87	7.13
7.	Glodeni	396.79	251.83	6.85
8.	Lucieni	184.69	66.10	7.25
9.	Marcesti	230.06	138.28	7.02
10.	Picior de Munte	82.24	254.73	6.67
11.	Targoviste	88.42	25.02	7.32
12.	Viisoara	46.97	33.27	6.30

In terms of calcium content, the healthiest waters are at Finta, Gaesti, Viisoara. These waters represent no danger to the human or animal consumption.

Calculating the chloride content

The amount of chlorides [mg Cl- /l] is calculated as follows:

$$\left[\mathbf{Cl^-}\left(\frac{\boldsymbol{mg}}{\boldsymbol{L}}\right)\right] = \frac{(\boldsymbol{V_s} - \boldsymbol{V_b}) \cdot \boldsymbol{c_{M(AgNO3)}} \cdot \mathbf{35453}}{\boldsymbol{V_{proba}}} [\mathbf{mg\,Cl^-\ /l}]$$

where:

V_s = volume of AgNO3 solution used to titrate the analysed sample, in ml;

V_b = volume of AgNO3 solution used to titrate the witness sample, in ml;

V_{proba} = initial volume of water sample taken for determination, in ml;

$c_{M(AgNO3)}$ = real concentration of AgNO3 solution, in moles/L;

35453 = conversion factor, [mg/mol].

The average of determinations is shown in table 2.

For chlorides, the MAC required by law is 500 mg/l. The results show that concentration at the sample point of Gheboaia, 519 mg/l, exceeds the limit and so long-term consumption may affect people’s health. The chloride limit is imposed because exceeding it results in a change of taste. From this point of view, the best waters in terms of chlorides are at Gaesti, Finta, Targoviste and Viisoara. Water represents no danger if drunk by animals or used for irrigations. All values are to be found in fig.9: Results of chloride determinations.

Calculating water pH

Water pH (mg/l) of groundwater had the following recorded values (table 2).

Due to the large number of factors that may influence the results of this analysis (such as water temperature, accuracy of device, the time between sampling and analysis), results may have a lower or higher degree of uncertainty.

For pH, the MAC is between 6.5 and 8.5; hence we can deduce that the only sampling point not corresponding to this MAC (table 2) is Viisoara with a pH of 6.3. It should be noted that the pH is influenced by a number of factors and water pH varies naturally. pH variations of water samples can be observed in fig. 10: Results of pH determinations.

4. CONCLUSIONS

- By lab analyses, we have tried to highlight which areas have an aquifer whose chemical composition is altered as compared to the global analyses established by INHGA. These areas are within the localities in which the population is supplied with water from individual wells.
- With **chlorine**, observations can be made based on the difference of concentrations resulting

from analyses, for example Gheboaia and Picior de Munte. Moderate chlorine concentrations are not very harmful to the people if a chloride limit is imposed because at concentrations higher than 250 mg/l water acquires a particular taste. The other samples have insignificant results due to compliance with the requirements of the law and the way they influence the population and related ecosystem.

- Determinations of **calcium** in water show that at Gheboaia and Marcesti sample points relatively high values were recorded as compared to the results from the other sample points, but they do not exceed the MAC; therefore, they do not create a hazard for the population or animals that consume that water or for the water used for irrigations.
- For the **pH**, the results are within the limits imposed by the law, hence no modifications or interventions are needed.
- Long-term water consumption from aquifers with altered chemical properties, as is, in this case, Chlorine and Calcium value, may lead to the occurrence or aggravation of a number of gastrointestinal and urological-biliary affections.

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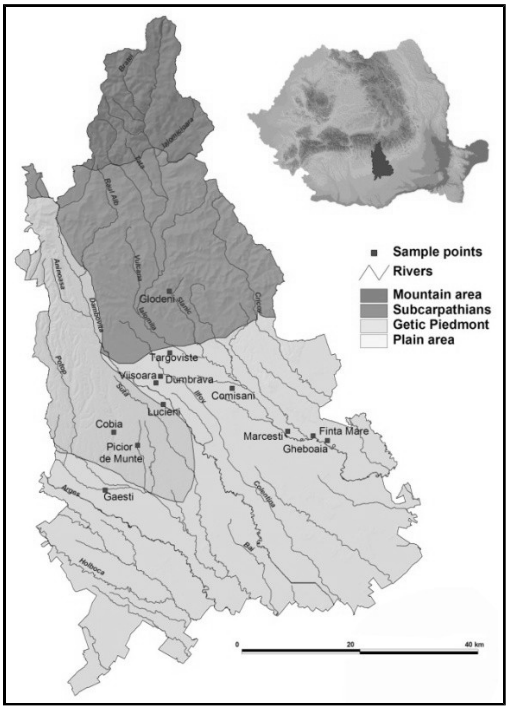

Figure 1 Geographical position

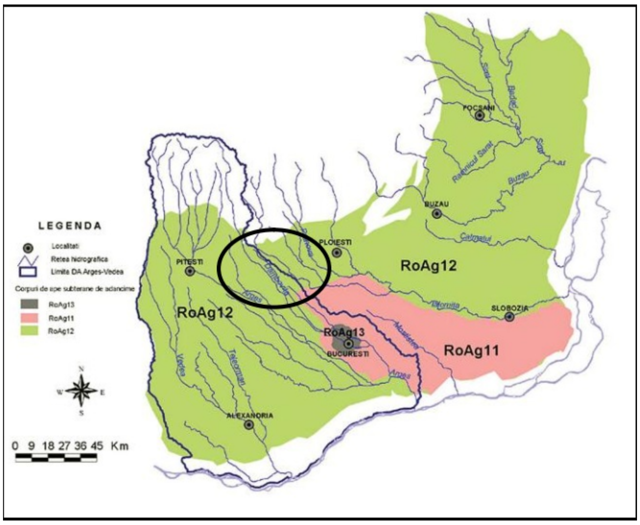

Figure 2 Phreatic groundwater bodies delimited in the analysed geographical area (INHGA archive)

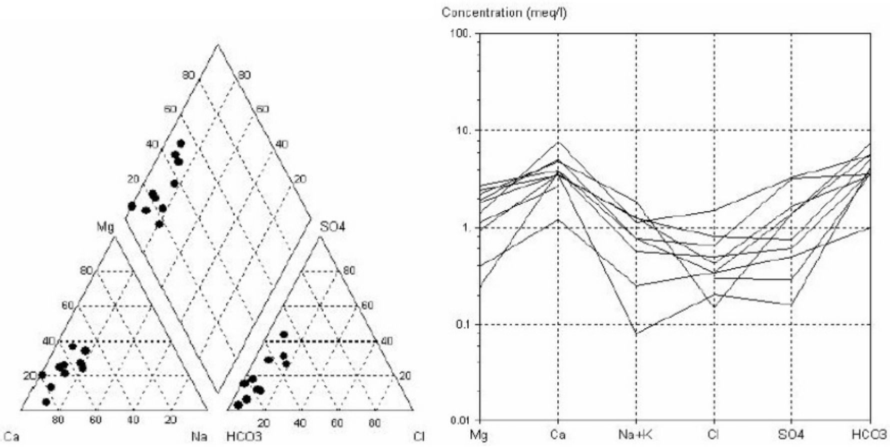

Figure 3 Titu Plain. ROAG02 Piper and Schoeller Diagrams (http://www.madr.ro/attachments/article/153/ADER-411-faza-4).

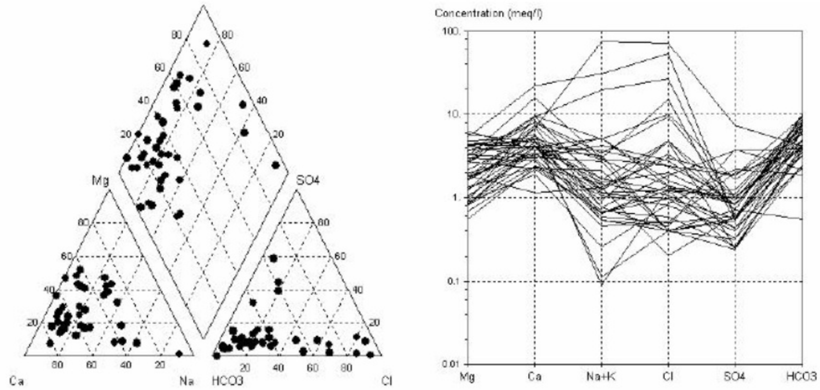

Figure 4. The ROAG05 body the Arges River Meadow and terraces Piper and Schoeller Diagrams (http://www.madr.ro/attachments/article/153/ADER-411-faza-4)

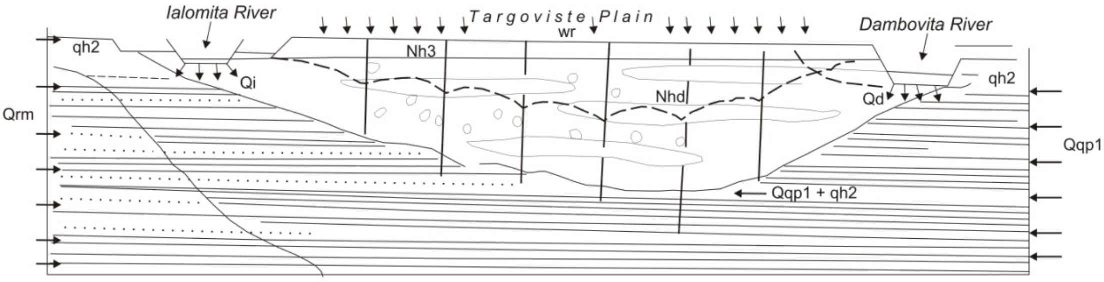

Figure 5. Basic diagram of the connection between the aquifer from the Piedmont Plain of Targoviste and surface waters (Istrate & Murarescu, 2000): wr – intake of water from rainfall, Qi – intake of waters from the Ialomita river, Qd – intake of waters from the Dambovita river, Qqp1 – intake from the Lower Pleistocene hydro-structure, Qrm – intake from the Romanian hydro-structure, qh2 – Upper Holocene, Nh3 – hydrostatic level, Nhd – hydrodynamic level

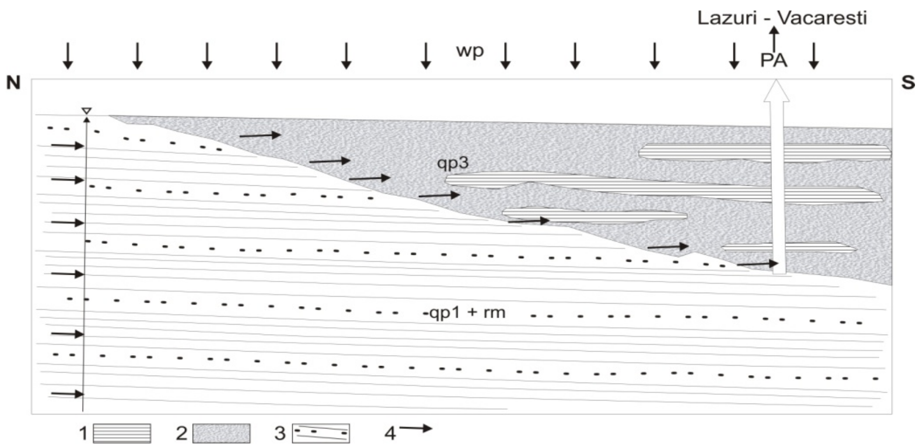

Figure 6. Basic diagram of the groundwater supply from the Piedmont Plain of Targoviste, Lazuri - Vacaresti catchment (Istrate & Murarescu, 2000): 1 - impermeable layers; 2, 3 - permeable layers; 4 - water flow direction; wp – water precipitation; qp1+rm - Lower Pleistocene + Romanian; qp3 – Upper Pleistocene; DW – deep well

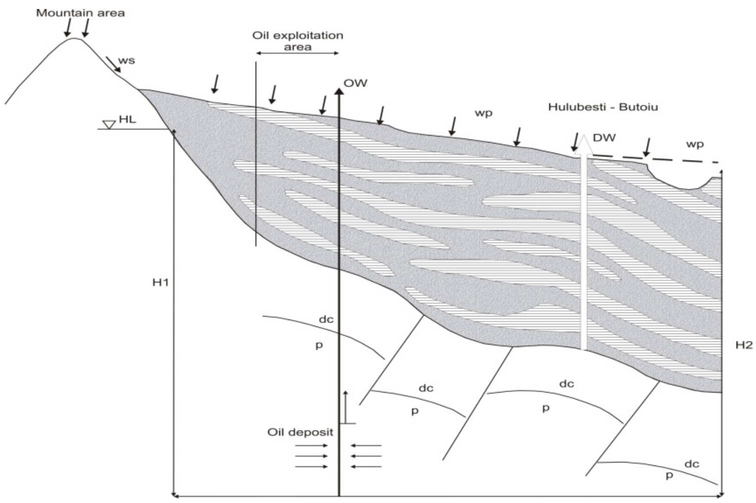

Fig. 7. Basic diagram of hydrodynamics from Candesti Piedmont (Hulubesti –Butoiu catchment) (Istrate & Muraresc u, 2000): HL – Hydrostatic level; H1 – Hydrostatic level 1 (high area); H2 – Hydrostatic level 2 (low area); DW – deep well; OW – oil well; dc – Dacian; p – Pontian; wp – water precipitation; ws – surface water drainage

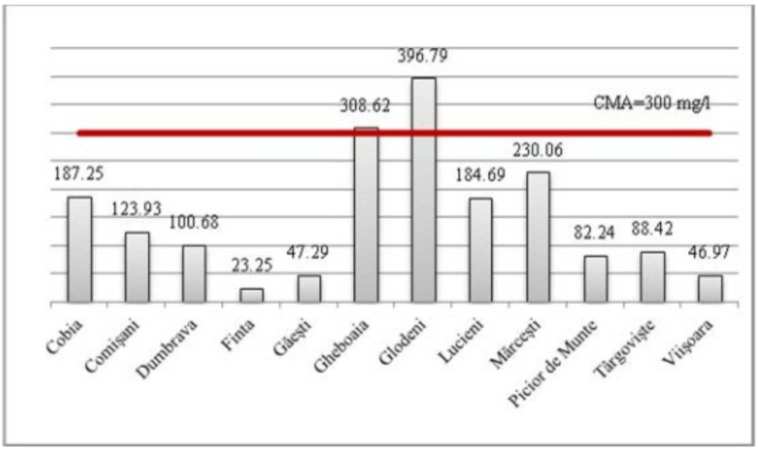

Figure 8. Results of calcium concentration

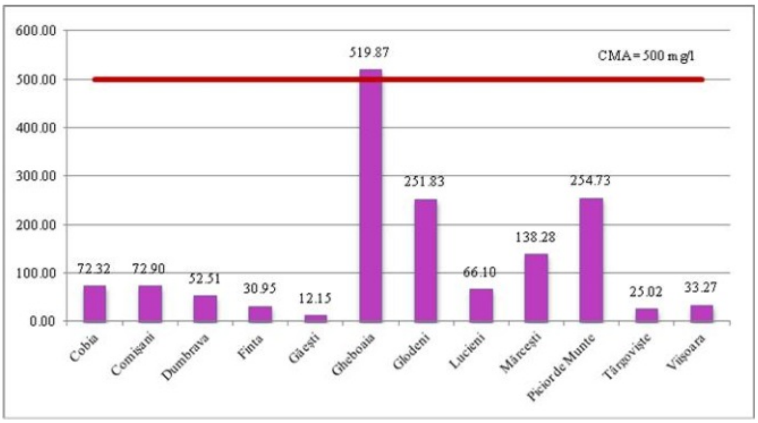

Figure 9. Results of chloride determinations.

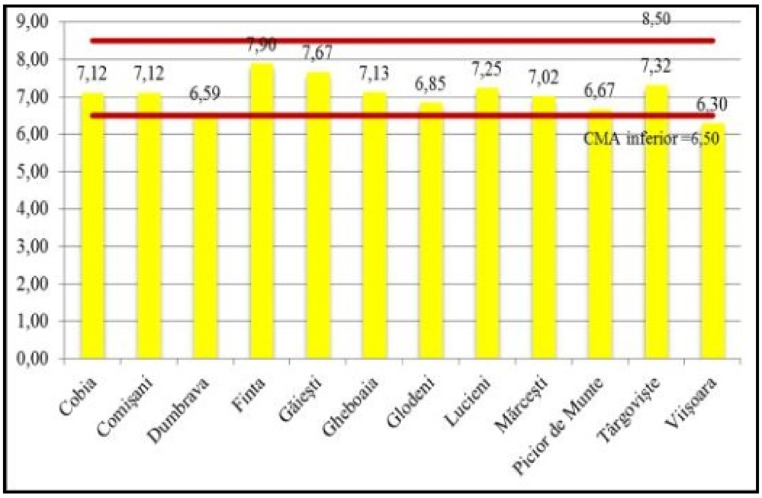

Figure 10. Results of pH determinations