GEOCHEMICAL MODEL OF THE GROUNDWATER AT COUNTY-WIDE SCALE IN ROMANIA. CASE STUDY

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ABSTRACT

This paper presents a functional model for the investigation of the groundwater quality expanded to the size of a county of Romania, considered as a case study. Were followed several steps: defining the surface area of the study, establishing the methodology of the investigation (the sampling method and the quality indicators), design of the experimental field, applied methodology and getting a set of functional groundwater geochemical model of the entire county. Were determined for each groundwater sample a total of 20 physical and chemical quality indicators and overall analytical determinations were subjected to a total of 119 samples of water from underground with free level. Each sample was located with a GPS receiver, so all the results are a georeferenced database for the entire county. We have mapped the distribution of the pollutant concentrations to a number of relevant nutrient pollution category and a map of the "nitrates" indicator, the pollutant with the highest amplitudes of the concentrations recorded.

Key words: groundwater pollution, nutrients, geochemical model

INTRODUCTION

The theme of world water resources is focused in recent years on the closer relantionship between water and food safety. The access to water means the access to food and the access to a better quality of the water means a better quality of the food. Instead, the water crisis means that translate life crisis: the crisis of the access to the water, water quality problem and man's relationship with water. Approximately one and a half billion people from worldwide have no access to water, resource essential for life, in other words, they have no right to life because their life expectancy is very low due to poor living standards.
Moreover, another two billion people live in cities that do not have sewer, toilets and minimum hygiene civilized . In Romania , the degree of connection to sewerage equivalent population is 56.96 %, and the degree of connection to wastewater treatment plants is 45.57%. In recent years (2007-2011), 2,997,173 billion euros have been invested for nationwide expansion and rehabilitation works of water infrastructure[1].
The other component of the global water crisis is the issue of water availability in required quantity and quality for life living. Pure water gives us the chance to a healthier life, but water quality is reflected in the behavior of a nation to the

water and all of us in the direction of the protecting and preserving its quality. The high quality water quality standards and the life of a nation, for a high quality water speaks of how this nation has acted to water throughout its history and at the same time, a more responsible now and in the future to take an appropriate policy by preserving and protecting water quality through sustainable water management policies.
In Romania, nationwide, 79.55 % of all surface water bodies assessed in 2011 meet the environmental objective (have good ecological status / good ecological potential) and 20.45 % do not meet environmental objectives. Regarding the assessment of groundwater bodies, in 2011, 81.6 % of groundwater bodies achieve quality objectives and only 18.4% do not meet quality objectives.
International organizations and world leaders have warned the World Water Although Romania is not on a the map of the water crisis, the water resources of our country are relatively low and unevenly distributed in time and space. Therefore stakeholders in water resource management must join efforts channeled into action to protect and conserve the water resources in terms of the quality and the quantity. All these efforts ultimately be to protect and secure the population and other water users by providing necessary subsistence water resources, and to protect people when the waters can become a hazard to life and their family.
Although the biological needs of man are about 2.5 liters / person / day , in reality consumption are much higher. Public water supply is done in centralized or individualized [2] mostly centralized supply is specific urban area, but in recent years has expanded this system in rural areas. However, it is still used widely in food groundwater individual system. There are numerous studies and research that highlight the fact that the groundwater pollution has grown in recent decades. Pollutant impact extented on the soil by numerous industrial emissions, use in agricultural practice, the varieous chemicals for raising of the soil fertility and to combat pests and diseases lead to degradation of it, with negative effects of the quality of the groundwater. Taking into account all these considerations, in these paper presents the results of the evaluation of the groundwater quality within Dambovita county.
Dambovita County is located in Southern Carpathians, in the contact area of the Romanian Plain with subcarpathians. Targoviste is the most important town in this region (about 90 000 inhabitants). All of the county population is about
537 000 inhabitants[3].
With an area of 4054 **k**m ², is one of the small counties, covering about 1.7% of Romania surface. Administrative boundaries of the county totaling 360 km. It is bordered to the west by Arges county, a distance of 139 km, east on 120 km Prahova county, south - east of Ilfov 20 km to the south of Giurgiu and Teleorman on 36 km and 30 km and Brasov conty on North a distance of 15 km.

EXPERIMENTAL PART

Methodologies used to investigate underground waters in Dambovita county, as study case analyzed, were conducteed as:
-the method of investigation proposed to characterize the physico - chemical groundwater is a network of the existing wells in the villages in the county. [4]

For the design of the experimental field was used as cartographic physical map of the county Dambovita scale 1: 400 000 . (Figure 4)
To achieve geographical spread of the samples was performed at the county level squared network , network nodes form a square with equidistance of 10 km . This resulted in a network of cellular sampling points extended to the entire county. The network to be fully functional, a total of four cells were removed from the sampling program, coresponding of the area with mountains were the groundwater is poor, practically it is found only in the colluvial deposits at the base of slopes.
Thus the proposed experimental field has a network of 51 cells, each cell having an area of 100 km^2. Certainly in marginal areas of the county , such a cell will only partially cover Dambovita surfaces. Map field experimental design is shown in Figure 1.
From the methodological point of view the following approaches are proposed:

- Methodology of investigation: sampling of groundwater (aquifers) of existing wells and analysis of 20 quality indicators in laboratory quality indicators proposed analysis for the investigation are: pH, electrical conductivity , filterable residue,COD, ammonium, nitrates, nitrites, total nitrogen, phosphate, total phosphorus, sulphur, chlorides, potassium, copper, sodium, iron, calcium, magnesium, molybdenum, boron (Table 1);
- For each cell was harvested at least one groundwater sample, resulting in the minimum number of samples to be characterized: 51.

For some selected cells (corresponding to areas where the activities related to groundwater) will be sampled groundwater samples 2-3 . All sampling points will be located via GPS.

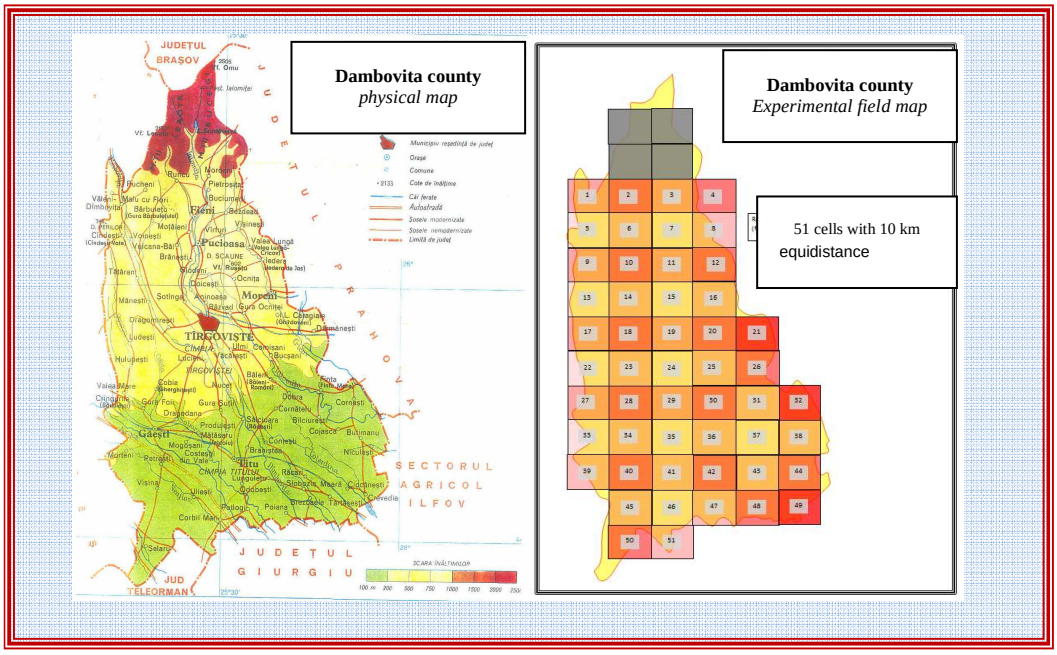

Figure 1 *- Design of the experimental field*

Table 1- The quality indicators and test methods

No. crt.	Quality indicators	Test methods
1	pH	SR EN ISO 10523:2012
2	Electrical conductivity	SR EN 27888-97
3	Filterable residue	STAS 9187-84
4	Ammonium	SR ISO 7150/1-01
5	Nitrates	SR ISO 7890/3:2000
6	Nitrites	SR EN 26777:2002/C91:2006
7	Total nitrogen	SR EN 12260:2004
8	Phosphates	SR EN ISO 6878:05
9	Total phosphorus	SR EN ISO 6878:2005
10	Sulphates	STAS 8601-70
11	Chlorides	SR ISO 9297-01
12	Potassium	SR EN ISO 7980-2002
13	Copper	SR EN ISO 17294-2005
14	Sodium	SR EN ISO 7980-2002
15	Iron	SR EN ISO 17294-2005
16	Calcium	SR EN ISO 7980-2002
17	Magnesium, ,	SR EN ISO 7980-2002
18	Molybdenum	SR EN ISO 17294-2005
19	Boron	SR EN ISO 17294-2005
20	COD	SR EN ISO 8467-01

Location of the groundwater sampling points is shown in figure 2.

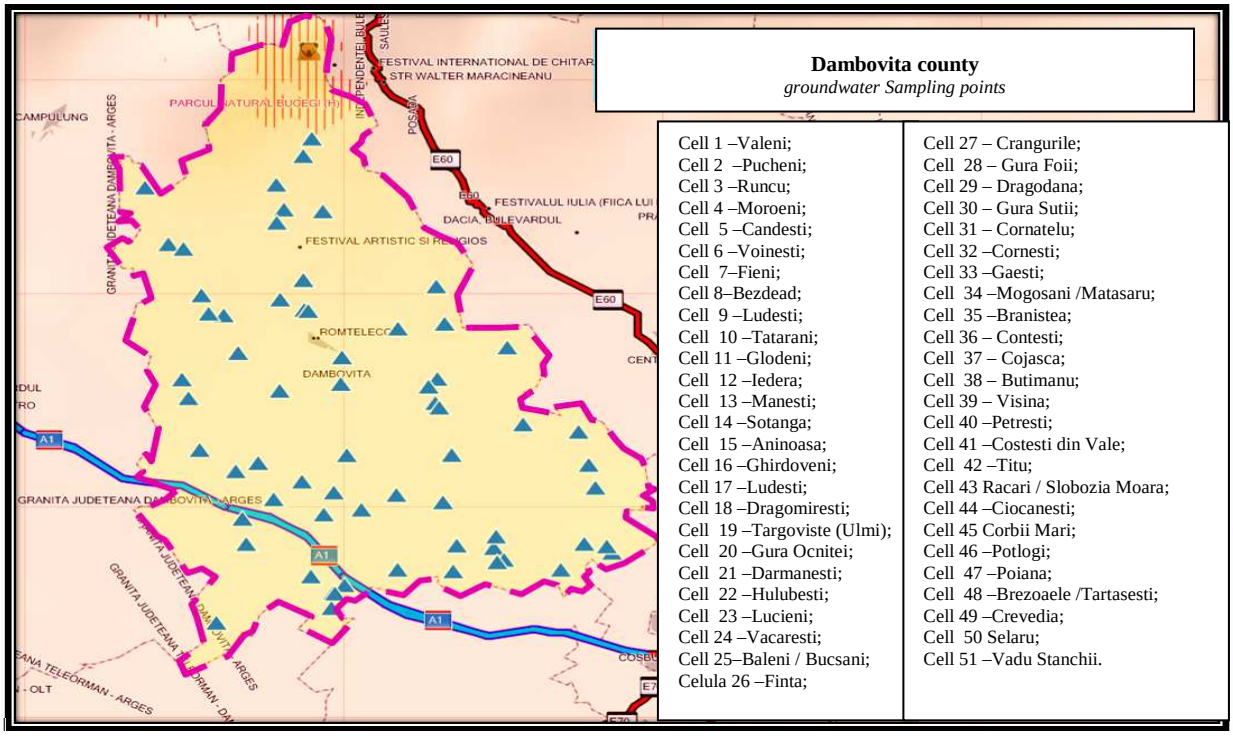

Figure 2 *– Locations of the groundwater sampling points, Dambovita county*

RESULTS AND DISCUTIONS

Analytical results revealed the characteristics of the nutrient pollution county-wide:

- the content of the "nitrogen" in groundwater samples from the two campaigns in Dambovita investigation is shown in figure 3;

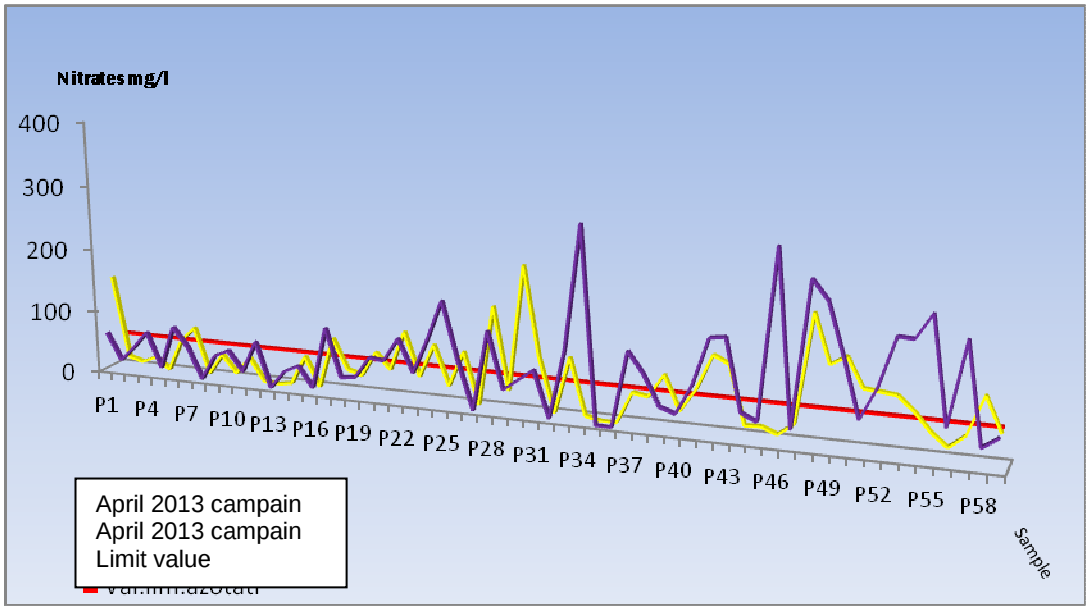

Figure 3 - *content of the "nitrogen" in groundwater samples*

The first Campaign held in April 2013: 11.8% were of the order of mg / l, 55.9% were in the tens of mg / l (27.1% exceeded the limit), 32.2% were hundreds of mg / l and exceeded the limit, exceeding the limit allowed were 1.03 times (P23) ÷ 6.01 times (P34)

In the second Campaign held in May 2013: 18.6% were of the order of mg / l, 64.4% were in the tens of mg / l (23.7% exceeded the limit), 16.9% were hundreds of mg / l and exceeded the limit, exceeding the limit allowed were 1.1 times (P6) ÷ 4.5 times (P30).

Distribution maps of the „Nitrates" quality indicator is shown in figure 4

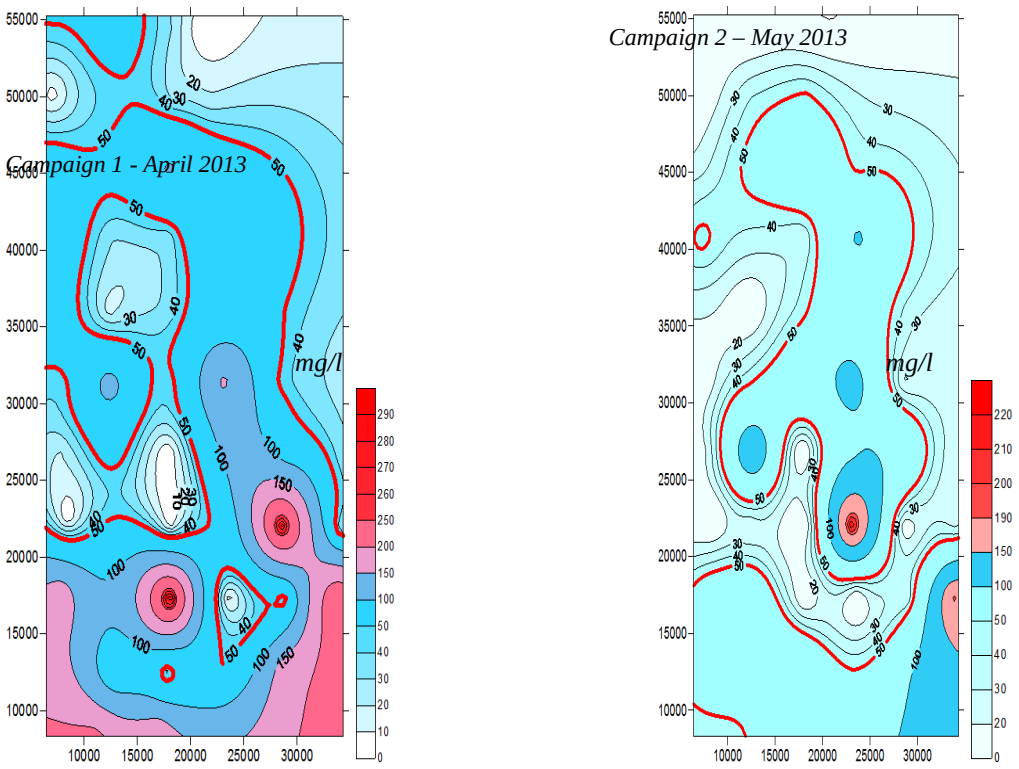

Figure 4 *– Distribution maps of „nitrates"*

- the content of the "nitrites" in groundwater samples from the two campaigns in Dambovita investigation is shown in figure 5

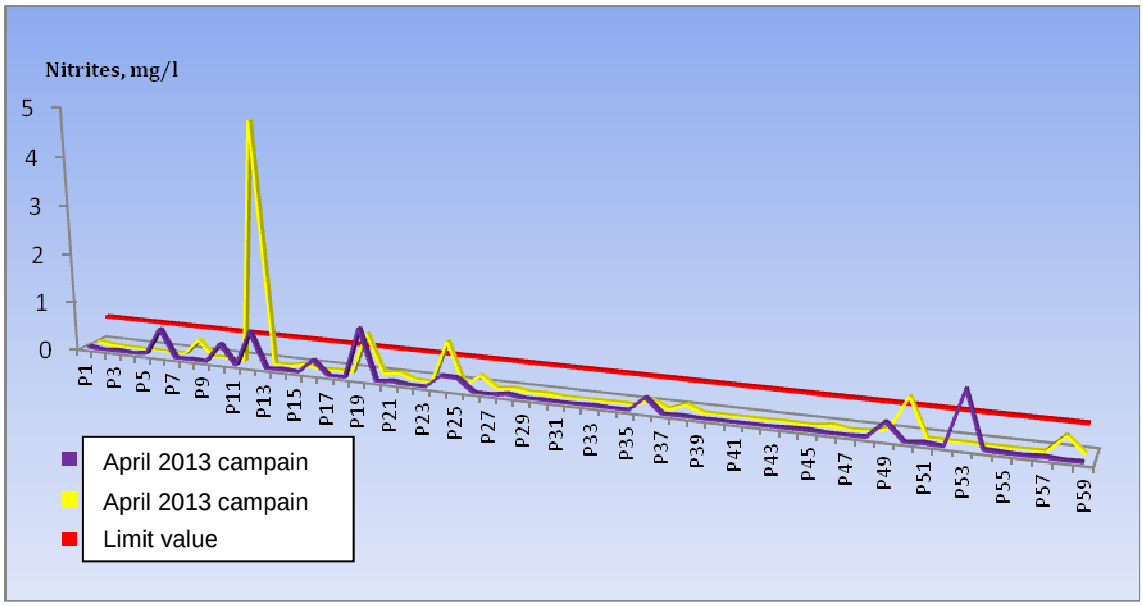

Figure 5 *- content of the "nitrites" in groundwater samples*

The first Campaign held in April 2013: exceeding the limit allowed were 1.1 times ÷ 2.2 times.
The second Campaign held in May 2013: exceeding the limit allowed were 1.5 times ÷ 9.8 times.
Distribution maps of the „Nitrites" quality indicator is shown in figure 6.

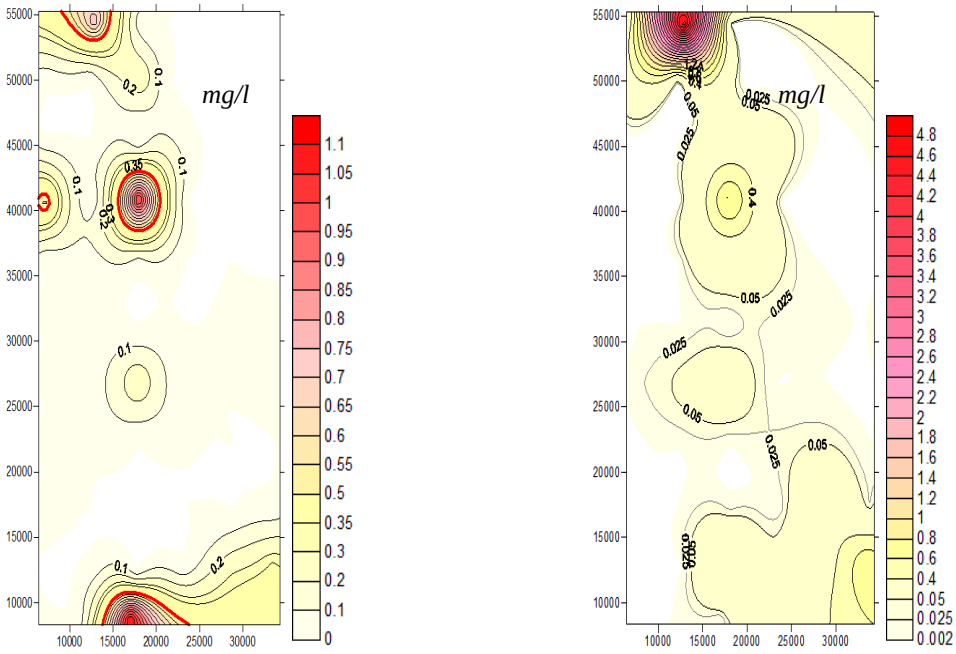

Figure 6 *– Distribution maps of „nitrites"*

- the content of the "ammonium" in groundwater samples from the two campaigns in Dambovita investigation is shown in figure no.7

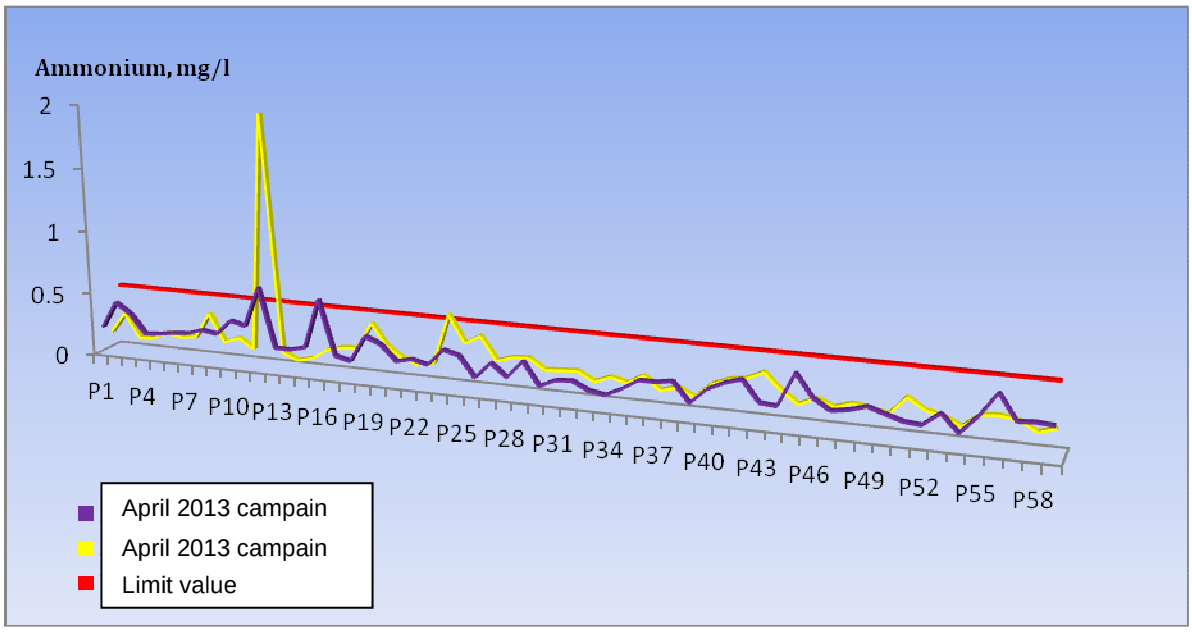

Figure 7 *- content of the "ammonium" in groundwater samples*

It is found that only four of the total samples were recorded exceeding the permissible limit value (by 1.2-1.3 times in Campaign 1, respectively 1:1-4 in Campaign 2).

Distribution maps of the „Ammonium" quality indicator is shown in figure 8

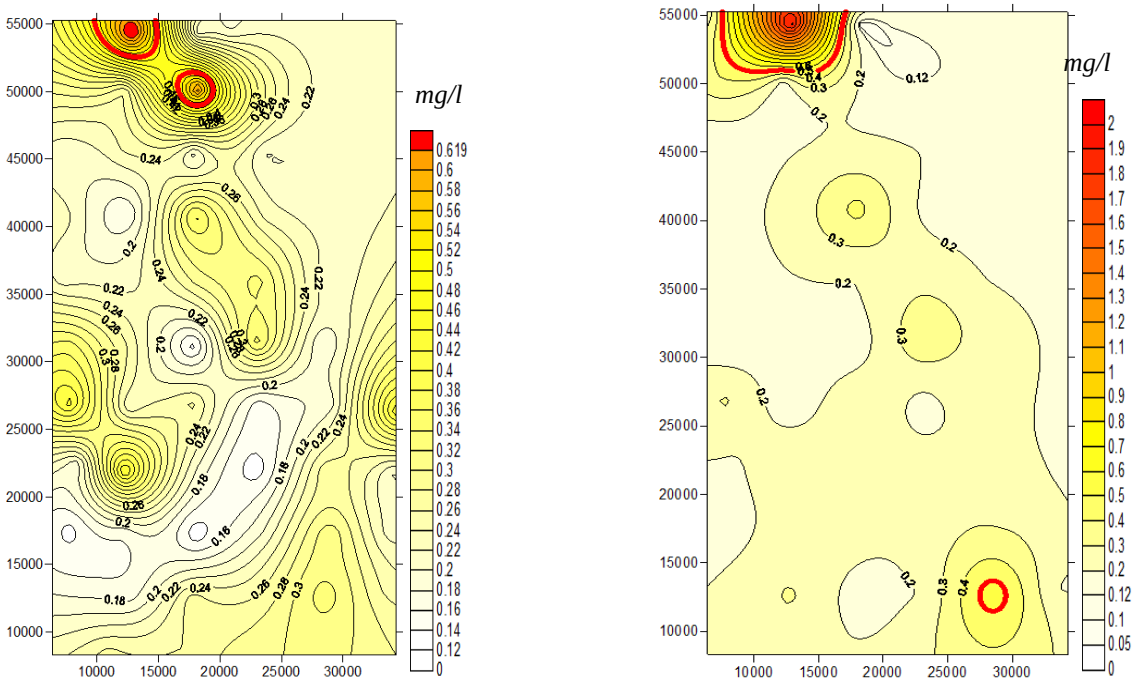

Figure 8 *– Distribution maps of „ammonium"*

For other indicators of quality analysis of the results revealed:

- the pH values recorded in both sampling campaigns, which were within the range allowed by water environmental relgementations;
- the organic load (COD) showed values below the allowed limit, with an exception in the first campaign (P46), an exception in the second campaign (P21);
- charging indicator mineral residue expressed by global filters: in both sampling campaigns were most determined values hundreds of mg / l (60%); values were recorded and order thousands of mg / l, standing out those determined in samples P17, P27, P50 (experimental field located in cells C11, C43, C49) were P50 highs in Campaign 1 with 3604 mg / l and P27 in campaign 2 with 2814 mg /l

Distribution of the concentration of samples with high levels of residue was recorded on the eastern side of the county.

- sulphates were recorded exceeding the value limit of 1.03 ÷ 2.1 times (in both sampling campaigns) in samples P16, P17, P27, P29, experimental field in cells C7, C11, C43, located on the side eastern part of the county;
- among the „heavy metals" analyzed and standardized in water law reglementation, noted sodium that exceeded the limit of 1.09 times (P44 in Campaign 1) ÷ 2.6 times (P50 in Campaign 1).
- quality indicator „chloride" were recorded in samples exceeding the limit value in the cells located on the eastern side experimental field, as follows:
  - In Campaign 1: 1.06 ÷ 4.2 times - P17 (cell 11), P27 (cell 43), P50 (cell 49), P58 (cell 46);

- o In Campaign 2: 1.3 ÷ 2.09 times - P17 (cell 11), P34 (cell 41), P45 (cell 32), P49 (cell 49).
- for „phosphates" indicator highest values were recorded in samples located in cells C9, C22, C50, on the western side of the county.

CONCLUSION

The analysis of the results for quality indicators studied highlight a pollution extended on county wide scale, induced by quality indicator "nitrates". In Figure 9 is shown the magnitude of the effects is "nitrates" pollution in Dambovita county wide scale.

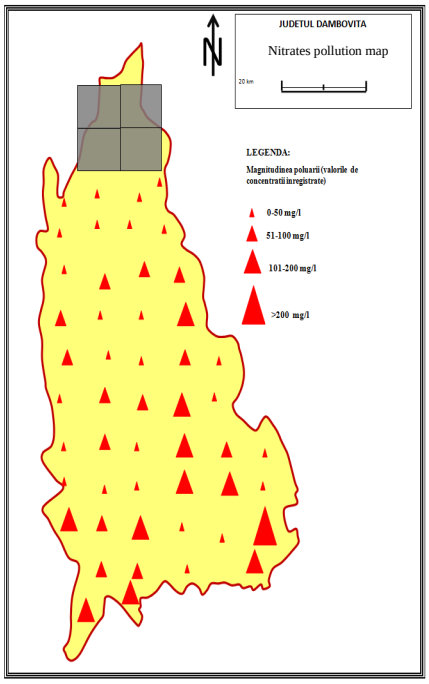

***Figure 9** – "Nitrates" pollution map*

The highest values of the "nitrates" were recorded in groundwater samples from localities: Ciocanesti, Crevedia, Costesti Vale, Tartasesti, Brezoaele, Selaru, Vadu Stanchii, Contesti, Cojasca, Baleni, Bucsani, Gura Sutii, Ghirdoveni.

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[2] http://apmdb.anpm.ro/upload/88644_11STAREA%20factorilor%20de%20mediu%20DB-noiembrie-2012.pdf

[3] Proiectul „Controlul Integrat al Poluării cu Nutrienţi", http://www.inpcp.ro/ro/page/13/welcome.html

[4] Romanian Law 458/2002 for quality of the drinking water, Official Journal, Part I, no. 552 din 29.07.2002.