MONITORING THE EFFECTS OF EXCESSIVE USE OF CHEMICAL FERTILIZERS ON UNDERGROUND WATERS BY USING THE GIS TECHNIQUE

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ABSTRACT. – Monitoring the Effects of Excessive Use of Chemical Fertilizers on Underground Waters by Using the GIS Technique. This paper highlights the increase of nitrates and nitrites content in the underground waters, in correlation with the levitation to the underground of the nitrogen quantity on the agricultural lands, by using a modelling method through the GIS technique.

The research is conducted for the underground waters of an area of Prut River catchment, and for the assessment of NO₂, NO₃ concentration, water samples are taken from a limited number of boreholes (44 boreholes). These boreholes are randomly distributed in the area and only some pieces of information are acquired from the laboratory tests. Based on this source data, by means of an interpolation method under software Surfer 8.1, the maps of NO₂, NO₃ concentration distribution were created. The spatialisation is made on 1880 cells and the results set out herein are at the level of a 2015 survey year.

The Romanian Law on fresh water sets out that although the nitrites and nitrates are within the admitted maximum limits 0.5 mg/l and 50 mg/l, respectively, another indicator should also be taken into consideration:

$$\frac{Nitrates}{50} + \frac{Nitrites}{3} \le 1$$

Thus, in the application, the mathematical modelling generated a map of the above mentioned indicator distribution. One can notice that, under certain circumstances, although the NO_2 and NO_3 indicators are within the admitted maximum limits, this indicator is still exceeded. This leads to the conclusion that in certain areas of the analyzed region there is significant chemical pollution, fact that leads to safety actions concerning the use of well water.

Keywords: modelling, underground waters, spatial distribution.

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1. INTRODUCTION

The incorrect irrigation and drainage, associated with other inappropriate practices (monoculture or short term cropping systems, excessive loosening of the soil, especially through numerous superficial works etc.) to which are sometimes added the inexistence of anti-erosion systems of culture on the agricultural versants, determine the appearance and intensification of physical and chemical degradation of lands.

Both the physical pollution through processes such as: water or wind erosion, the destructuring, compacting etc. and chemical pollution through the alluvial transport with significant pesticide quantities, contribute in this manner even more to sensitizing, favouring and emphasizing the degradation of the quality of underground waters, considered as being "the last hope of drinkable water".

The activity of knowing the quality of underground waters is carried out at the level of large hydrographic basins, on morphological units, and within them, on aquiferous structures (underground), through the hydrogeological stations, comprising one or more observation forages.

The probable causes for which in the majority of causes the groundwater do not correspond to the requirements to use them in potable purposes:

• The pollution of surface waters;

• The conditions and natural hydro geochemical processes that favour the passage to solution of different anions and cations;

• The intensive development of agriculture in the last decades with the excessive use of chemical fertilizers based on azoth and phosphor and of pesticides, led to their accumulation in the soil (or the accumulation of degradation products);

• The effects of the passivity of former zootechnical complexes of high capacities regarding the measures for the conservation of environment factors;

• The climatic, hydro geological particularities and the exploitation of irrigation systems that contributed to the mineralization of organic matter from the soil and the migration of substances resulted from these processes.

A special problem regarding the quality of underground waters is represented by their content in nitrates $-NO_3$ and nitrites $-NO_2$.

In order for the underground waters to be considered appropriate from the qualitative point of view, it is necessary that the quality indicators belong to the maximum admitters-MAC concentrations, imposed through the Law of Potable Water no. 410 /2002 modified and completed with Law 311/2004. In addition, the assessment of underground water quality supposes a complex action of interpreting all the quality indicators, of correlating the values obtained in the laboratory for different indicators, even in the situation that, by comparison with MAC, we ascertained that the concentrations were situated within these limits.

The main sources of accumulated nutrients are represented by the direct evacuations from agriculture, drains and erosion, and by the effluents of the localities' sewage stations.

We estimate that the largest part of the quantity nutrients is due to the sources from agriculture (diffusion sources). For the underground waters to be considered potable, the value of indicators NO_3 and NO_2 must be situated within MAC, imposed by the Law of potable Water (NO_3 -50 mg/l, NO_2 -0,5 mg/l). On the other hand, although the values of NO_3 concentrations, respectively NO_2 do not exceed MAC, a certain condition for which the following formula is applied, must be complied with:

$$\frac{nitrates}{50} + \frac{nitrites}{3} \le 1.$$

In which the nitrates and nitrites concentrations are expressed in mg/l.

2. STUDY AREA

The underground waters from the Prut River catchment area are quartered in porous-permeable deposits of Quaternary and Tertiary age disposed over older Cretaceous, Silurian and Presilurian formations, situated at different depths but which, because of climatic and layer conditions generally have reduced debits and high content of salts.

The underground waters within the Moldavian platform, in relation with the natural possibilities of drainage, respectively of their connection with the surface waters are: under pressure (depth) and phreatic (free).

In the category of free underground waters, we include the aquiferous waters without pressure, where we notice a supply area and an unloading area; therefore, they are naturally drained.

The phreatic waters are accumulated in the first horizon of permeable rocks and are supplied from precipitations, from the hydrogeological neighbour units and locally from the overflow of rivers.

The waters under pressure are accumulated in permeable deposits intercalated between the loamy-clay layers distributed on several levels are encountered in the areas sectioned by the valleys of rivers. The supply of this type of aquiferous is ensured from the hydrogeological superior units through the higher end of the layer and the drainage occurs through the lower end.

Most of the times, the deposit conditions are favourable to the water mineralization; to these, the salts from the soils washed from the infiltrated precipitations are frequently added, and as a result the phreatic waters have a higher mineralization degree.

In the Prut catchment area (Fig. 1) the groundwater are quartered in sandy deposits of quaternary age, with clay intercalations of small hydrogeological importance and gypsum horizons. In these conditions, the exploitable conditions are encountered in the rivers' meadows, in weakly permeable and sulphated deposits. Generally, we notice the sulphated waters with mineralization and high hardness with a reduced debit degree.



Fig. 1. Study area: Iași City

3. METHODS OF THE RESEARCH

3.1 Entry data

As entry data, we used the values NO_2 , NO_3 (mg/l) determined in the Laboratory Water Quality belonging to the Prut Water Direction at the level of 2015. The analyses were made on water samples assayed from 44 observation forages from the Prut hydrographic basin (located through the STEREO 70 coordinates) belonging to the National System of underground waters quality Surveillance, e.g. (Table 1).

Then we calculated the value of the indicators assessing the water potability:

$$\frac{nitrates}{50} + \frac{nitrites}{3} \le 1$$

| Forage no. | Plan coor in the STERO X (m) | | NO2 (mg/l) | NO3 (mg/l) | $\frac{\text{INDICATOR:}}{\frac{nitrates}{50} + \frac{nitrites}{3}}$ |
|---------------|------------------------------------|------------|---------------|---------------|--|
| 1 | 634150.562 | 751325.439 | 0.026 | 5.065 | 0.1100 |
| 2 | 633863.404 | 750817.791 | 0.42 | 44.67 | 1.0334 |
| 3 | 658289.763 | 722926.687 | 0.803 | 19.621 | 0.6601 |
| 4 | 667731.251 | 701856.350 | 0.0385 | 97.695 | 1.9667 |
| 5 | 667133.890 | 701741.096 | 0.016 | 0.8 | 0.0213 |
| 6 | 665339.264 | 701495.313 | 1.022 | 261.53 | |
| 7 | 696082.457 | 653053.352 | 0.570 | 5.80 | |
| 8 | 693880.402 | 653097.634 | 0.240 | 8.30 | 0.2460 |
| 9 | 690868.400 | 653521.559 | 0.05 | 3.70 | 0.0900 |
| 10 | 691156.982 | 650027.408 | 1.40 | 46.90 | 1.4030 |
| 11 | 691159.514 | 649927.431 | 0.37 | 5.75 | 0.2367 |
| 12 | 710883.965 | 637421.058 | 0.10 | 3.80 | 0.1095 |
| 13 | 706655.705 | 634513.032 | 0.38 | 5.55 | 0.2360 |
| 14 | 720455.610 | 622856.785 | 0.12 | 1.80 | 0.0743 |
| 15 | 717542.139 | 619381.882 | 0.15 | 1.00 | 0.0700 |
| 16 | 740100.524 | 589639.041 | 0.006 | 30.55 | 0.6130 |
| 17 | 747776.891 | 570825.278 | 0.0495 | 27.075 | 0.5580 |
| 18 | 743885.527 | 538616.078 | 0.008 | 27.385 | 0.5504 |
| 19 | 739858.249 | 611963.055 | 0 | 17.225 | 0.3445 |
| 20 | 615773.355 | 714936.515 | 0.0785 | 3.865 | 0.1035 |
| 21 | 646264.066 | 708012.499 | 0.023 | 3.35 | 0.0747 |
| 22 | 646069.205 | 707807.432 | 0.041 | 0.59 | 0.0255 |
| 23 | 645874.343 | 707602.365 | 0.052 | 16.275 | 0.3428 |
| 24 | 659898.363 | 683348.529 | 0.098 | 9.36 | 0.2199 |
| 25 | 658908.750 | 682923.178 | 0.169 | 9.715 | 0.2506 |
| 26 | 637665.861 | 688184.548 | 0.055 | 3.05 | 0.0793 |
| 27 | 646075.989 | 683997.085 | 0.0735 | 0.2975 | 0.0305 |
| 28 | 646222.338 | 658591.021 | 0.05 | 1.50 | 0.0475 |
| 29 | 711030.507 | 631622.380 | 0.09 | 8.80 | 0.2062 |
| 30 | 711249.593 | 634829.224 | 0.195 | 4.40 | 0.1530 |
| 31 | 649494.205 | 651871.758 | 0.03 | 2.25 | 0.0552 |

Table 1. Drilling parameters of the study area

| Forage | Plan coordinates in the STERO 70 projection | | NO2 (mg/l) | NO3 (mg/l) | INDICATOR: $\frac{nitrates}{1} + \frac{nitrites}{1}$ |
|--------|---|------------|---------------|---------------|---|
| | X (m) | Y (m) | (8/-) | | 50 3 |
| 32 | 655811.718 | 647330.530 | 0.07 | 1.25 | 0.0488 |
| 33 | 655421.985 | 646920.496 | 0.02 | 1.20 | 0.0292 |
| 34 | 657439.168 | 646271.449 | 2.02 | 1.54 | 0.7045 |
| 35 | 657113.880 | 647263.549 | 0.45 | 43.50 | 1.0200 |
| 36 | 637851.363 | 720103.554 | 0.066 | 2.65 | 0.0750 |
| 37 | 670722.327 | 674719.812 | 0.38 | 3.85 | 0.2020 |
| 38 | 748618.872 | 557241.570 | 0.467 | 48.65 | 1.1287 |
| 39 | 746724.431 | 556993.839 | 0.0085 | 11.615 | 0.2351 |
| 40 | 745319.914 | 580868.538 | 0.015 | 1.06 | 0.0262 |
| 41 | 745945.104 | 546232.553 | 0.043 | 2.675 | 0.0678 |
| 42 | 745845.131 | 557225.907 | 0.021 | 0.275 | 0.0125 |
| 43 | 749219.143 | 602851.455 | 0.06 | 0.775 | 0.0355 |
| 44 | 746924.780 | 592018.866 | 0.03 | 0.97 | 0.0294 |

3.2 The creation of thematic layers regarding the distribution of NO_2 , NO_3 concentrations

Because their evaluation is made by assaying water samples from a limited number of forages distributed randomly in the territory, according to the laboratory analyses, only punctual information is obtained (Biali et al., 2013).

Starting from a limited number of forages and respectively samples, it is only possible to approximately assess the quality of underground waters from the entire territory, being difficult to elaborate in due time the most adequate intervention measures.

Starting from this source data, the concentrations of different pollutants (in the case of our application) represented in MNT are generally derived with the help of an interpolation. For this application GIS we used the Surfer 8.1 software (method of interpolation – Kriging) (Fig. 2).

Among the 12 interpolation methods put at the disposal by Surfer we chose in order to space the punctual information the Kriging interpolation method and obtain of thematic layers regarding the distribution of NO_2 (Fig. 3) and NO_3 concentrations (Fig. 4).

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Fig. 2. Detail Surfer software; choosing the method of interpolation and setting the pixel size



Fig. 3. The thematic layer regarding the distribution of NO_2 (mg/l) in the territory studied in 2015; 3D representation



Fig. 4. The thematic layer regarding the NO $_3$ (mg/l) distribution in the territory studied in 2015 3D representation

4. RESULTS AND DISCUSSIONS

Starting from the values of concentrations determined in the laboratory on water samples assayed from the 44 forages, after the interpolation, we obtained concentrations in 1880 points.

Also we will achieve a spatiality of the indicator $\frac{nitrates}{50} + \frac{nitrites}{3}$.

The values obtained afterwards in all the raster points (located through the X and Y coordinates) after interpolation, in each point situated in the centre of a cell (Table 2).

With Surfer software one obtains the thematic layer regarding the distribution of the values of the indicator $\frac{nitrates}{50} + \frac{nitrites}{3}$ (Table 2) and (Fig. 5).

| Cell | X (m) | Y (m) | NO ₂ | NO ₃ | nitrates nitrites | | |
|------|------------|------------|-----------------|-----------------|---------------------------------|--|--|
| No. | Stereo '70 | Stereo '70 | (mg/l) | (mg/l) | $\frac{50}{50}$ + $\frac{3}{3}$ | | |
| 1 | 742762.1 | 542913.2 | 0.031926 | 23.3845 | 0.478331865 | | |
| 2 | 740609.7 | 545061.8 | 0.035238 | 24.0515 | 0.492776112 | | |
| 3 | 740609.7 | 547210.4 | 0.051815 | 22.16654 | 0.460602676 | | |
| 4 | 742762.1 | 547210.4 | 0.041741 | 18.80309 | 0.389975532 | | |
| 5 | 742762.1 | 542913.2 | 0.031926 | 23.3845 | 0.478331865 | | |
| | | | | | | | |
| 1465 | 652363.3 | 691165.2 | 0.245243 | 49.75168 | 1.076781388 | | |
| 1466 | 654515.7 | 691165.2 | 0.296957 | 63.04128 | 1.359811051 | | |
| 1467 | 656668 | 691165.2 | 0.352662 | 77.70399 | 1.671633735 | | |
| | | | | | | | |
| 1500 | 676039.2 | 693313.8 | 0.388856 | 44.77624 | 1.025143427 | | |
| 1501 | 678191.5 | 693313.8 | 0.505746 | 29.65145 | 0.761611042 | | |
| 1502 | 628687.5 | 695462.4 | 0.066127 | 3.256486 | 0.087171995 | | |
| | | | | | | | |
| 1568 | 671734.5 | 699759.5 | 0.396986 | 49.84778 | 1.129284183 | | |
| 1569 | 673886.8 | 699759.5 | 0.55154 | 29.90772 | 0.782001106 | | |
| 1570 | 624382.8 | 701908.1 | 0.070366 | 3.463758 | 0.09273046 | | |
| | | | | | | | |
| 1614 | 669582.1 | 704056.7 | 0.466425 | 45.10777 | 1.057630446 | | |
| 1615 | 622230.4 | 706205.3 | 0.07223 | 3.654572 | 0.097168085 | | |
| 1616 | 624382.8 | 706205.3 | 0.069843 | 3.942739 | 0.102135922 | | |
| | | | | | | | |
| 1879 | 637296.9 | 744879.7 | 0.257995 | 19.82124 | 0.482423055 | | |
| 1880 | 635144.5 | 747028.3 | 0.290876 | 28.09792 | 0.658916941 | | |

Table 2. The values obtained after interpolation with SURFER, in each of a cell



Fig. 5. The thematic layer regarding the distribution of the values of the indicator $\frac{nitrates}{50} + \frac{nitrites}{3}$ in the territory studied in 2015 (3D representation)

4.1. The interpretation of results obtained

For the results interpretation, we compared the values of NO_2 and NO_3 measured in the laboratory on water samples taken in 2015 from the 44 surveyed boreholes of Prut catchment area, with the maximum admissible values of Law no. 458/2002, as amended and supplemented through Law no. 311/2004.

The maximum admitted concentration for NO₂ is of 0.5 mg/l, and for NO₃ is of 50 mg/l. The value of indicator $\frac{nitrates}{50} + \frac{nitrites}{3}$ should be lower or equal to 1 (Table 3).

| Range of values | Indicator | | |
|-------------------|--|--|--|
| | | | |
| Range of values | NO ₂ (mg/l) | | |
| 0 mg/l - 0,5 mg/l | 93,5 % | | |
| >0,5 mg/l | 6,5 % | | |
| | | | |
| Range of values | NO ₃ (mg/l) | | |
| 0 mg/l - 50 mg/l | 93,2 % | | |
| >50mg/l | 6,8 % | | |
| | | | |
| Range of values | $\frac{nitrates}{50} + \frac{nitrites}{3}$ | | |
| 0-1 | 89,65 % | | |
| >1 | 10,35% | | |

Table 3. Summary of the results

5. CONCLUSIONS

1. Monitoring the underground water quality implies a complex action of assessing all quality indicators and of performing the existing correlations between indicators. It is not enough to compare the determined value of each quality indicator with the CMA required by the Law on fresh water, being required to interpret, from a chemical point of view, the existing correlations between various quality indicators.

2. The activity of knowing the quality of the underground water at the level of large catchment areas can only take place within a GIS, where the punctual pieces of information acquired following the laboratory tests in a limited number of profiles are subject to spatialization within a MNT, in order to conduct a complex analysis at each point of the analyzed area.

3. The NO_{2} concentration exceeds CMA in up to 6.5 % of the analyzed area and the NO_{3} concentration exceeds CMA by 6.8% (according to Table 3).

4. The indicator: $\frac{nitrates}{50} + \frac{nitrites}{3}$ exceeds the maximum admitted value

by 10.35 % (according to table 3).

5. The use of GIS enables the spatialization of these indicators in the area, and thus the knowledge of areas with exceeded concentrations is important. Through permanent monitoring, the potability sanitary bodies can classify the water sources based on the concentration of nitrates and nitrites in the water, compared to CMA, so that these would not be used, in order to prevent the occurrence of diseases.

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