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NITRATE POLLUTION IN PHREATIC GROUNDWATER BASIN CRIŞUL REPEDE

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Abstract: The article presents the assessment of pollution with nitrates from agricultural sources, Crişul Repede River Basin in the period 1993-2009, with emphasis on analysis of drilling (points) observation of the industrial area of Oradea belonging Pollution Control Station. Also present was intended degree of pollution of underground reserves of water, and historical pollution due to human activities and potential impact of various sources of pollution (factory farming) on groundwater.

Key words: agricultural source, nitrates, groundwaters, pollution, quality

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INTRODUCTION

Crişul Repede hydrographic basin is situated in the western part of Romania (figure 1), occupying an area of 3354 sqkm.

Assessment of nitrate pollution of groundwater Crişul Repede basin by comparing average annual values obtained from 45 wells National Hydrogeological Network (from 1993-2009), with maximum values allowed (CMA), in Directive 118/2006 on the protection groundwater against pollution and deterioration. Maximum allowable concentration for nitrate (NO3), by European Standards is 50 mg/l.

Romanian legal document that includes all the requirements of Directive 91/676/EEC is - Romania Guvern Decision 964/2000 approving the Action Plan for water protection against pollution by nitrates from agricultural sources.

As pollution is the main factor of nitrate pollution of groundwater Crişul Repede River, recorded in the local area Oradea, it is necessary to eliminate or reduce the amount of nitrates entering the groundwater. Prevent deterioration of groundwater quality and prevent any significant upward trend and the concentration of pollutants in groundwater must be done primarily through the implementation of Directive 91/676/EEC, on the nitrates and also Directive 91/271/EEC, Urban Waste Water Treatment.

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Criş river basin, the report made by the European Commission on how to implement Directive 91/676/EEC on the protection of waters against pollution caused by nitrates from agricultural sources have been identified areas vulnerable to pollution by nitrates.

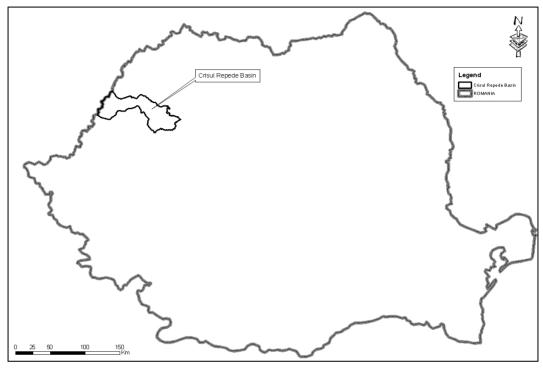


Figure 1. Crişul Repede river basin in the map of Romania (Source: Data from ABA Crişuri archives)

CAUSES PHREATIC WATER CONTAMINATION NITRATES

Nitrate pollution comes mainly from agriculture. Nitrogen is essential for life in water and suffers many chemical and biochemical processes. Appears mainly as nitrate (NO_3^-), nitrite (NO_2^-), ammonium (NH_4^+), nitrogen gas (NO) and fixed in organic compounds, among which there are continuous transformations groups / transit, forming "the nitrogen cycle". Excess lead to eutrophication (algae bloom), groundwater contamination, possible harm to human health: methaemoglobinaemia in children, gastric cancer (Manoescu et. al., 1994).

The two major sources, with significant share in groundwater pollution by nitrates are constantly washing soil impregnated with nitrogen oxides by rainfall and irrigation water, and surface water (rivers, lakes) where they evacuated the water waste loaded with nitrogen. In this case the pollution is produced by rising bank to an area located longitudinally River (generally its floodplain and low terrace), the width of the zone of influence varies depending on the size of the river floodplain and low permeability layers of it. Hotspots are generally confined to floodplain river hydro. These two sources that are of cvasipermanent are added to the random character generated by the use of chemical fertilizers on some categories of farmland. Besides agricultural activities, an important contribution to pollution by nitrates and other nutrients, in general, and agglomeration were not consistent in terms of collection systems (sewage) and treatment plants (failing that, lack of speed sewage, malfunctioning etc.).

The groundwater NO_3 is changed, transformed by microorganisms, reacts with iron, sulfates or bicarbonates etc. This soil is a good "filter" but if capacity is exceeded, the concentration of nitrogen will increase sharply. Nitrates are currently discharged into the soil will reach some aquifers in just years or decades (Bretotean, 1981).

DRILLING MONITORED IN CRIŞUL REPEDE BASIN

In Crişul Repede Basin nitrate pollution assessment was made based on monitoring data obtained in the National hydrogeological network during 1993 - 2009, which were compared with the maximum permissible values of the standards in force, is 50 mg/l.

Tracking the dynamics and evolution of nitrate pollution, water catchment groundwater Repede was conducted on a total of 45 monitoring wells, the water body belonging ROCR 01, of which 28 wells are in the order I placed in the main river valleys water courses, the alignments: Aleşd, Tileagd, Cacuciul Nou, Fughiu, Oradea, Cheresig; second order nine wells located in the interfluve areas (Crişul Repede - Crişul Negru) to: Nojorid, Girişu de Criş, Oradea - Airport, on the interfluve (Barcău – Crişul Repede) from, Borş, Tărian and Santăul Mic, which is located near the slag and ash depot of CET I Oradea (figure 2) and part of ground water pollution control station.

To detect sources of pollution of groundwater in the area of the cone of dejection Crişul Repede River station operates a groundwater pollution control, consisting of nine drillings.

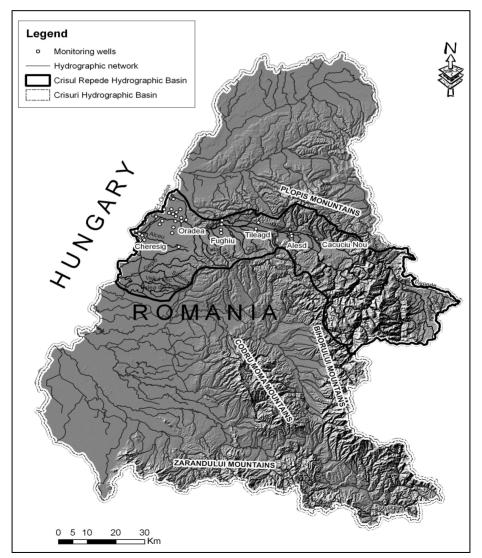


Figure 2. Location of monitoring wells in the Crişul Repede River Basin (Source: Data from ABA Crişuri archives)

ASSESSMENT OF POLLUTION WITH NITRATES (NO3)

Normally the concentration of nitrates in water sources is low (usually not exceeding 10 mg/l), but can be high if there are specific nitrate pollution (considerably more than 50 mg/l) due to the water were streaming agricultural land or contamination with human or animal droppings as a result of ammonia oxidation.

In conditions of anaerobiosis, nitrate can be reduced to nitrite by microbial activity (this condition leads to the persistence of nitrite) (www.recolta.ro).

 $NO_3 \rightarrow NO_2 \rightarrow NI_2 \leftrightarrow NH_3$

Nitrates shows the average annual value exceeding the threshold (50 mg/l) in 11 of the 45 wells analyzed, 24.4 %. Drilling with significant overruns on the platform are located in the western industrial, and agricultural area Oradea - Borş. In table 1 are average annual value and annual average values for points where there were overtaking.

Table 1. Annual average concentrations exceeding report, the points shows the indicator values exceeded average NO3
(Source: Data from ABA Crișuri archives)

	Annual average concentrations / ratio exceeded the NO3										
Year / Average annual	P1	P3	P4	PS	F6-P13	F7-P14	Oradea F1	Oradea F2	Borș F1	Oradea Aeroport F1	Girişu de Criş F1
Year / A	75.5 mg/l	66.8 mg/l	137.6 mg/l	131.5 mg/l	63.9 mg/l	76.0 mg/l	72.1 mg/l	64.7 mg/l	62.7 mg/l	62.6 mg/l	80.7 mg/l
1993	49.4	63.6	78.5	135.6	13.5	44.7	-	25.3	26.6	20.2	35,4
1994	92.7	52.7	36.5	192.2	42.5	79.0	-	46.0	75.2	22.7	116,1
1995	74.3	60.1	83.6	78.5	49.1	64.5	-	129.7	72.7	63.9	78,3
1996	65.9	37.5	98.3	61.1	96.1	152.1	-	113.2	61.2	102.6	123,2
1997	66.4	58.5	99.9	120.7	153.7	110.7	-	81.3	75.4	163.3	267,2
1998	78.7	53.9	65.0	133.7	114.8	81.4	-	142.6	49.7	101.9	101,3
1999	79.5	34.9	310.7	120.6	114.1	80.2	-	64.2	45.0	83.0	4,2
2000	75.3	105.8	328.9	204.1	101.7	47.2	-	90.3	87.4	43.7	49,6
2001	86.5	-	-	158.1	62.5	70.9	-	-	88.7	46.0	91,3
2002	73.9	-	-	151.8	59.5	78.6	-	-	79.4	41.0	41,2
2003	76.1	-	-	207.4	51.5	47.0	-	-	60.6	53.0	46,9
2004	65.0	-	-	99.0	54.8	85.0	-	60.4	50.4	70.5	60,5
2005	85.5	-	-	126.5	78.7	66.7	88.7	45.2	42.2	25.5	104,7
2006	-	62.6	-	102.5	72.9	87.6	-	29.4	-	38.7	66,9
2007	73.9	63.2	-	78.6	13.0	77.1	-	35.4	-	-	45,5
2008	104. 4	144.2	-	169.6	4.77	110.1	-	37.5	-	-	61,3
2009	59.6	65.0	-	96.3	3.84	4.1	55.6	4.8	-	-	78,6
Valori medii depășite	93.7 %	83.3 %	87.5%	100 %	64.7 %	76.5 %	100 %	50 %	69.2 %	50 %	64,70 %
Valori medii admise	6.25 %	16.7 %	12.5%	0.0	35.3 %	23.5 %	0.0	50%	30.8 %	50%	35,30 %

From the table we can see that there are points where the average of the annual monitoring is exceeded at 100 % throughout the period under review ie P5, F1 Oradea rate of 93.75 % and the point P1.

In figure 3 and table 1 are average annual values of the points in the industrial cities of Oradea and Bors and Santion. In these respects the nitrate ion concentration is relatively constant at points investigated, but far exceed limit of 50 mg/l, so the annual average and annual average.

Because of these values exceeding the maximum permitted is first time the existence of livestock farms and the irrational use of fertilizers on agricultural land.

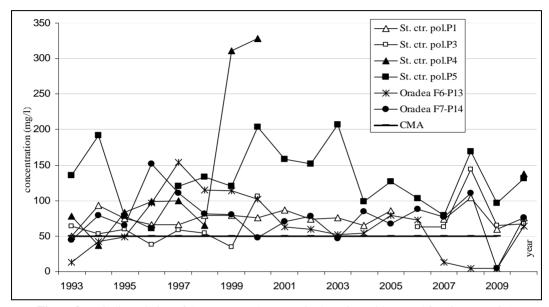


Figure 3. Periodic variation of the average values seen in the points with exceed for nitrates (NO₃⁻) (Source: Data from ABA Crișuri archives)

In a drilling Bors F1, the maximum value was recorded in 2001 by 88.67 mg/l, a ratio exceeding 1.8 times;

In drilling an F2 Oradea, maximum concentration of 142.57 mg/l, was recorded in 1998; F6 in Oradea, a drill - P13 (located in the SC Orser SA), was recorded annual maximum 153.74 mg/l in 1997;

In drilling an F7 - P14 Oradea (Episcopia Bihor area), the maximum value was recorded in 1996, 152.14 mg/l, report surpassed 3.04 times;

In drilling an F1 Oradea airport area, the annual maximum concentration of 163.25 mg/l was recorded in 1997, exceeding a ratio of 3.3 times;

In an observation point P1 (located in the customs area - Bors) maximum annual value of 104.38 mg/l, was recorded in 2008;

At the point P3 (located downstream Santion), maximum 144.2 mg/l was recorded in 2008;

At the point P4 (monitoring point located on the left side of Crişul Repede River downstream of the pig farms Ioşia - Sântandrei - Palota (for ex. SC Nutrientul Palota), a maximum annual amount in 2000 was 328.6 mg/l, exceeding ratio is 6.57 times, and in 1999 was 310.72 mg/l;

In an observation point P5 (located in the village Sântion) increasing the maximum value was recorded in 2000, 204.1 mg/l.

Figure 4 shows the annual variation of nitrate concentrations at sites monitored, located upstream of Oradea. From the graph it is observed that except for 1994, where the values exceed the limit of 50 mg/l and Fughiu F2 and Tileagd F2 points, other points shows the annual average below 50 mg/l.

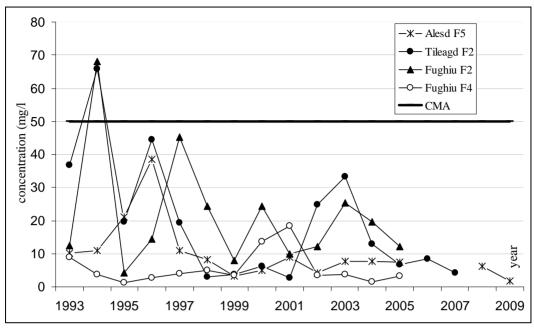


Figure 4. Evolution of annual average NO₃⁻ concentrations at sites upstream Oradea (Source: Data from ABA Crișuri archives)

VARIATION OF NITRATE CONCENTRATION WITH DEPTH DRILLING

Changes concentration of nitrate (NO3), with deep drilling explain nitrate pollution that occurs from the surface (figure 5). In wells with depths of up to 30 - 40 m are found the highest values of nitrate. The groundwater aquifer layers, especially in aerobic-anaerobic interface, there are nitrification and denitrification processes, which are influenced by the level of dissolved oxygen, organic carbon levels, the abundance of invertebrate fauna etc (Tudorache, 2010).

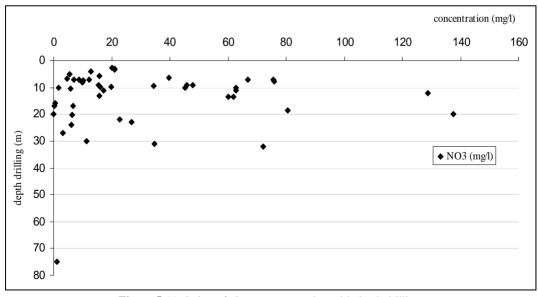


Figure 5. Variation of nitrate concentration with depth drilling (Source: Data from ABA Crișuri archives)

CONCENTRATION OF NITRATES IN THE DRILLING'S YEAR

The drillings that were executed during 1966 - 1976 (reference period) were analyzed in order to determine the nitrate content in the groundwater within the Crişul Repede catchment.

In figure 6 are shown the concentration of nitrate has been determined during the execution of drilling and multi-annual average concentration of nitrates in the period 1993 - 2009.

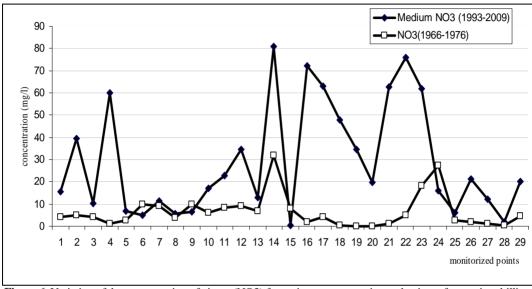


Figure 6. Variation of the concentration of nitrate (NO3) from nitrate concentration at the time of execution drilling (Source: Data from ABA Crișuri archives)

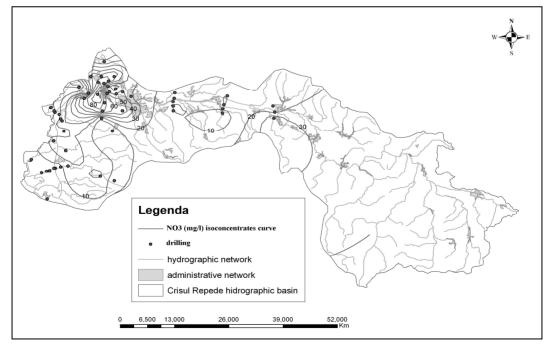


Figure 7. Spatial distribution of mean values of concentrations of nitrite ion (Source: Data from ABA Crișuri archives)

It can be seen ascending evolution in time, this parameter in areas with sources of pressure and impact of agricultural and livestock farms.

In figure 7 is represented by the spatial distribution of nitrate concentrations. On the whole analyzed area, the nitrate values extends from 1.68 and 665.0 mg/l. Lowest values are recorded for existing sources upstream Oradea (Aleşd) and downstream Oradea (Cheresig), while maximum values are recorded for groundwater sources in the area of Oradea (P5, P3 and P2).

MEASURES TO REDUCE POLLUTON BY NITRATES

Currently, the "Code of good agricultural practice" aimed at reducing pollution by nitrates and aply in vulnerable areas. Under this Code, shall take into account the conditions prevailing in different regions of the country, such as, for example, periods during which compliance is inadequate fertilizer application, the land application of fertilizer to steeply sloping, the land application of fertilizer to saturated, flooded, frozen or covered with snow, the land application of fertilizer near water courses, maintaining a minimum quantity of vegetation cover during periods (rainy) soil nitrogen in the absence of such a vegetation cover would cause water pollution by nitrates.

Other measures are:

- control of the sewage system leaks or inadequately maintained septic tanks and domestic wastewater discharged directly from the soil;

- control of the location of manure to prevent contamination of an aquifer located in a layer of karst or unprotected wells;

- control of surface water infiltration;

- establish and maintain sanitary and hydro areas, see HG 930/2005.

National Administration "Romanian Waters" draws attention to all those responsible that requires a rigorous management of waste and construction, expansion or upgrading of sewage treatment plants, mainly because groundwater pollution is a phenomenon almost irreversible and has serious consequences for the use of reserve underground drinking water supply. Remediation of water from groundwater sources is extremely difficult if not impossible.

CONCLUSIONS

Even while there was a decrease in the influence of pollution sources on groundwater aquifers, significant reduction in recent years due to the volume of industrial production and agro-livestock production, but also by putting into practice the measures for wastewater treatment, however groundwater quality has remained poor since the self-cleaning due to their slow pace.

The analysis performed on groundwater pollution by nitrates, Crişul Repede River Basin, stands above the allowable average values, both in the western industrial zone, the downstream area livestock farms Ioşia Sântandrei, Palota, and analyzed at the points Oradea border areas, where crops have been applied intense. Items monitored wells upstream Oradea (Aleşd, Tileagd, Fughiu) and downstream Oradea (Cheresig, Tărian) shows the annual average below 50 mg/l, corresponding in terms of nitrate content. The overall assessment of groundwater pollution in three rivers basin, most severe forms are maintained at multiple impairment of groundwater quality in certain areas, especially in rural areas where, because of lack of minimum facilities allow, liquid waste to reach the ground, both directly (through non-waterproof latrines, ditches and gutters, etc.) and indirectly through slow infiltration (from storage of manure, domestic waste pits improvised etc.).

Because groundwater flows slowly through the basement, the impact of human activities can affect a long time. This means that pollution that occurred decades ago - whether in agriculture, industry or other human activities - can still threaten water quality today and in some cases will continue to do so for several future generations. Therefore, an important emphasis should be placed primarily on *pollution prevention*.

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*** HG 964/2000, privind aprobarea Planului de Acțiune pentru protecția apei împotriva poluării cu nitrați din surse agricole;

*** HG 930/2005, privind aprobarea Normelor speciale privind caracterul și mărimea zonelor de protecție sanitară și hidrogeologică;

*** Ordinul M M nr. 137/2009, privind aprobarea valorilor prag pentru corpurile de ape subterane din România.

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