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CHEMICAL STATUS EVALUATION OF PHREATIC UNDERGROUND WATERS IN THE CRIŞUL REPEDE HYDROGRAPHIC BASIN

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Abstract: The article describes the chemical status evaluation of groundwaters within the Crişul Repede hydrographic basin, between 1993-2003, respectively the ROCR01 groundwaters body, focusing on the observation of drilling analysis (points) from the industrial zone of Oradea Municipality which belongs to the Polluting Control Station. At the same time, was monitorized the extent of pollution concerning phreatic groundwaters stocks due to the anthropic activities and the impact different polluting sources might have on groundwaters resources.

Key words: groundwaters, pollution, monitorized indicators, threshold values

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INTRODUCTION

Regarding the necessity of implementing the WFD 2000/60/EC as well as the Directive *regarding the underground water protection against pollution and deterioration* of the national legislation by HG 53/2009 and OM 137/2009, ABAC monitories the underground water quality from the drillings of National Hydrologic Network.

Nine underground body waters were identified and delimited in the Crişuri hydrographic basin (for ex., ROCR01), named after the following structure: RO=Romania, CR=Crişuri hydrographic area; 01, 02, 03, 04, 05, 06, 07, 08, 09 the water body number within the Crişuri hydrographic area. The paper describes the chemical status of drillings, which have a free level (phreatic) within the Crişul Repede system, attached to the underground water body ROCR01.

The chemical status evaluation of the underground body waters within the Crişul Repede hydrographic basin was conducted by comparing the multi-annual average values obtained from 46 drillings of National Hydrology Network (NHR) (between 1993-2009) with the threshold values of MM NR. 137/2009. The determined indicators and which were not included in the Order were compared with CMA of the Law nr. 458/2002 regarding the drinking water quality modified and completed by the Law nr. 311/2004 and the natural background was taken into consideration, which were computed for each determined indicator. This analysis was carried out for all delimited underground water bodies and defined till the present time, afferent to Crişuri Hydrographic Basin.

FREE LEVEL DRILLING (PHREATIC) MONITORIZED IN THE CRIŞUL REPEDE SYSTEM

In the Crişul Repede Hydrographic Basin, the qualitative status evaluation was carried out by using the monitorized data of the NHR drillings from 1993-2009, which were compared with the thresholds values.

The observation of the dynamics and chemism evolution of Crişul Repede hydrographic basin was carried out on 46 control drillings which belong to the ROCR 01 water body, from which 28 drillings are of I degree, placed on the main watercourses of fluviatile valleys, on the alignments: Aleșd, Tileagd, Cacuciul Nou, Fughiu, Oradea, Cheresig; 9 drillings of II degree, placed in the interfluves (Crişul Repede-Crişul Negru) at: Nojorid, Girişu de Criş, Oradea – Aeroport; on the interfluves (Barcău-Crişul Repede) at Hodoș, Niuved, Borş, Tărian, şi Santăul Mic, which is positioned near the ash deposit of C.E.T. I Oradea and pertains to the pollution control station of underground waters.

To track down the underground water pollution sources, the determination of all polluting elements and their noxious actions in time within the Crişul Repede river'debris cone perimeter, an underground water pollution control station functions formed of 9 observation drillings.

To perform the chemical-physical analysis, taking into account the main pollution sources within the perimeter, the area was divided in 3 sectors, trying this way a more compact grouping: drillings-pollution sources.

Crişul Repede left bank sector, downstream Oradea

This sector comprises the observation drillings P2 and P4 (monitorization points located on the left bank sector of Crişul Repede, downstream the pig farm, from Ioşia – Sântandrei – Palota, for ex., S.C. Nutrientul S.A. Palota)

Crişul Repede right bank sector, downstream Oradea

Tabel 1 comprises the drillings of this sector:

Table 1. Monitorized points of the right bank sector of Crișul Repede

Nr. crt.	Drilling code	Drilling location
1	P1	Borş vama
2	P3	av. Sântion
3	P5	Sântion
4	P6	SC Sinteza SA
5	P7	Stația Peco (câmpuri nămol SC Zahărul SA)
6	P8	SC Cemtrade SA (fosta Alumina)
7	P9	Fabrica de Zahăr
8	P10	Stadion FC Bihor
9	P11= F4	Ferma Dosu și iazurile biologice ale Companiei de apă Oradea
10	P13 = F6	SC Orser SA (sere)
11	P14 = F7	Episcopia Bihor

The main pollution sources of this sector are: Water Treatment Station of Oradea, Sugar Factory, C.E.T. I, Peco Station, all being placed on the western industrial platform.

Santăul Mic sector

This sector comprises the F15=F1 – Santăul Mic drilling, having as a pollution source the ash waste dump area of S.C. Termoelectrica S.A. – sucursala Electrocentrale (CET I) Oradea.

CHEMICAL STATUS EVALUATION

Assessment approach of threshold values

The threshold values determination was made according to the elaborated methodology within the framework of the MATRA PPA06/RM/7/5 project „Rehabilitation measurements assessment of polluted underground waters due to dump wasting in order to achieve the environment objectives required by the WFD and Underground Water Directive", using the NBL values by comparing with a reference value. In Romania, taking into account the relevant usages of underground waters, reference values were used, the maximum concentrations admitted, according to the Law of drinking quality water nr. 458/2002 and the Law nr.311/2004 for modification and completion of 458/2002 Law.

To evaluate the underground waters chemical status, the determined concentrations in the established monitoring points according to the WFD 2000/60/EC must be compared with the European standards and the threshold values. The European standards are established for nitrates (50 mg/l) and pesticides (0,1 μg/l individual and 0,5 μg/l total) (Water Framework Directive 2000/60/EC).

In Romania, the threshold values for the ones included on the minimum list of the indicators that must be taken into consideration to evaluate the underground water bodies qualitative status as well as for NO_2 and PO_4 indicators, considered very important for the underground water quality determination.

The computed threshold values for all delimited underground water bodies in Romania are included in the Environment Ministry Order nr. 137/2009, and for the ROCR01 water body are presented in table 2:

Table 2. Threshold values of ROCR01 water body

Underground water body	NH_4 mg/l	Cl mg/l	SO_4 mg/l	As mg/l	Pb mg/l	NO_2 mg/l	PO_4 mg/l
ROCR01	1,7	250	250	0,03	0,010	0,50	0,50

Analysis and interpretation of monitorized data

For the underground water chemical status evaluation, the following stages were followed:

1. For each monitoring point (drilling), the average annual and multi-annual values for each chemical element analyzed, in 1993-2009.

2. The multi-annual average values were compared for each point with the threshold values of MM Order 137/2009 (those from table 2), and the NO_3 value was compared with the European standard limit.

3. The other indicators determined in this period, which were not included in the Order, were compared with CMA Law 311/2004 and the natural background values, established by ABAC.

4. If at least one element exceeds the threshold value, it is considered that the respective point is polluted.

5. If the polluted monitorized points number does not exceed 20% from the total monitorized points of an underground water body, is considered that this has **a good chemical status** and the polluted points are being considered local exceeding of the element's threshold values.

6. If at least 20% of an underground body water monitorized points are polluted, it is considered that this has **a poor chemical status**.

7. The elements for which the TV was not established, the **non-drinking status** were mentioned, taking into account the NBL values.

The monitorized drillings in this water body presents average values at the following indicators:

Ammonium indicator (NH_4) – presents multi-annual average values higher than 1, 7 mg/l in the observation drillings P2, P4 and in the P7 drilling. In the P2 drilling, the multi-annual average value is 2,13 mg/l, in the P4 observation drilling is 2.29 mg/l, and in P7 - 3.30 mg/l;

Figure 1 presents the annual average values in 3 observation points which exceed the multi-annual values.

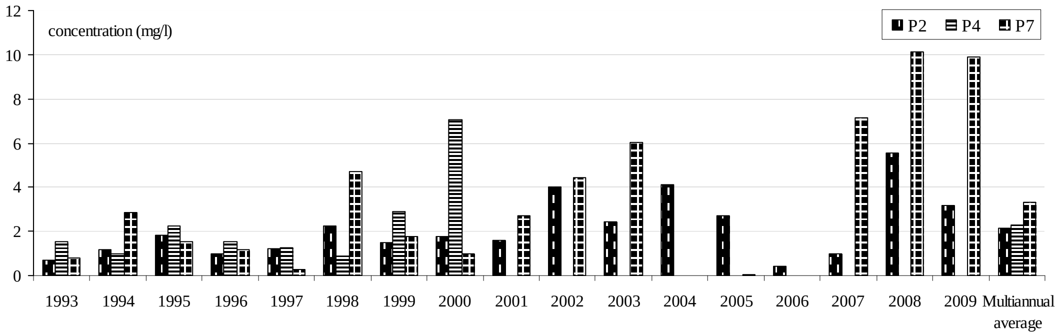

Figure 1. Periodic variation of the average values seen in the points with exceed for ammonium (NH_4)

From the chart it can be observed that the P2 observation point presents the maximum value of 5.54 mg/l recorded in 2008, in P4 were carried out determinations for NH_4 indicator in 1993-2000 and the maximum value recorded in 2000 was 7.04 mg/l, the exceeding ratio being 4.14; in P7 point, the annual maximum value recorded in 2008 was 10.13 mg/l.

The most intensive forms of underground water quality multiple depreciation were identified in the points placed near the pig farms of SC Nutrientul Palota as well as the area were sludge fields exist (SC Zahărul SA Oradea), where due to the lack of a proper equipment, the liquid waste infiltrates directly into the underground, as well as indirectly (from the manure deposits, zootechny farms, landfills, etc.)

Nitrates indicator (NO_3) presents exceeding of the threshold values (50 mg/l) in 11 drillings from 46 analyzed, 23.9 %. The drillings with significant exceeding are those placed in the western industrial area, as well as in the agricultural area Oradea – Bors. In the points which belong to the pollution control station, the following exceeding were determined: P4 – 137.6 mg/l, P5 – 131.54 mg/l, P1 – 75.45 mg/l, P3 – 66.8 mg/l, P13 – 63,9 mg/l, P14 – 76.0 mg/l; in Girişul de Criş drilling F1 – 80.72 mg/l, Oradea F1 – 72.1 mg/l, Oradea F2 – 64.7 mg/l, Borş F1 – 62.65 mg/l and Oradea Airport drilling F1 – 62.56 mg/l.

The phreatic aquifer contamination causes with nitrates in this area are generated by the inappropriate application of chemical manure deposited directly on the soil, humus mineralization and others. Figure 2 describes the annual average concentrations in the drillings which present exceeding towards the laws in force.

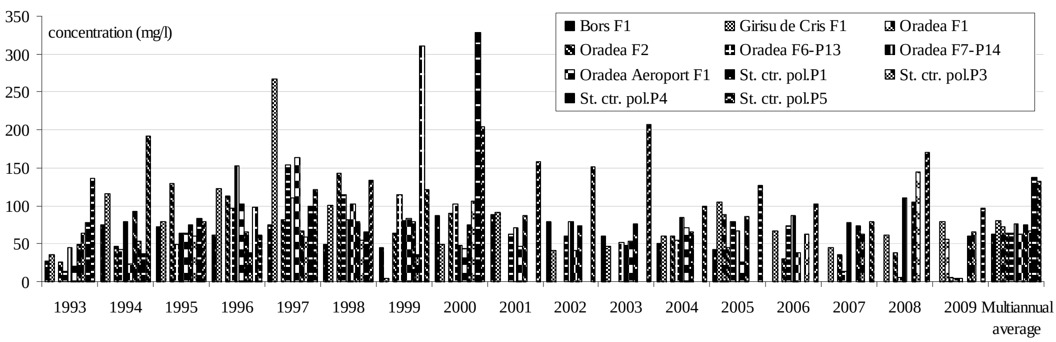

Figure 2. Periodic variation of the average values seen in the points with exceed for nitrates (NO_3)

In the F1 Bors drilling, the maximum value recorded in 2001 is 88.67 mg/l, an exceeding ratio of 1,8 times; in F2 Oradea drilling, the maximum concentration of 142.57 mg/l was recorded in 1998; in F6-P13 drilling Oradea, the annual maximum was 153.74 mg/l in 1997; in F F7-P14 Oradea drilling, the maximum value recorded in 1996 was 152.14 mg/l, the exceeding ratio being of 3.04 times; in F1

Oradea Airport area drilling, the annual maximum concentration recorded in 1997 was 163.25 mg/l, an exceeding ratio of 3.3. times; in the observation point P1, the maximum annual value recorded in 2008 was 104.38 mg/l; in P3, the maxim recorded in 2008 was 144.2 mg/l; in P4, the maximum annual values recorded in 2000 was 328.6 mg/l, the exceeding ratio being of 6.57 times and in 1999 was 310.72 mg/l; in the P5 observation point, the maximum value recorded in 200 was 204.1 mg/l.

Phosphates (PO_4) indicator presents threshold value exceeding (0.5 mg/l) in the Cheresig F1A drilling. In this drilling, the multi-annual average value is 4.51 mg/l and the maximum annual value recorded in 2003 was 16.7 mg/l. In the observation point of the Pollution Control Station P6, the maximum annual value recorded in 2009 was 1.29 mg/l.

The phosphate ion can derive from a series of sources, amongst them being the animal residues (the manure) and the humans' in anaerobe conditions.

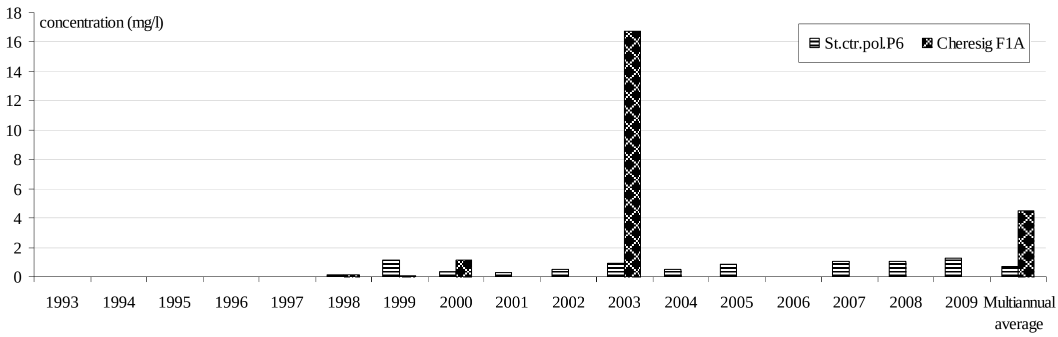

Figure 3. Periodic variation of the average values seen in the points with exceed values for PO_4

Sulphate (SO_4) indicator – has multi-annual average values higher than 250 mg/l in the following drillings: F1 Bors, the multi-annual value is 330 mg/l and the highest value was recorded in 1995 - 467.0 mg/l, in F6=P13 Oradea, the multi-annual average value is 299 mg/l, and the annual maximum was recorded in 1995- 506,7 mg/l; in the observation point Santăul Mic F1-P15, the average multi-annual value is 383 mg/l and the highest value was recorded in 2008 - 668.5 mg/l; in the P1 observation point, the average multi-annual value is 477.5 mg/l and the maxim was recorded in 2001 - 629.5 mg/l; in the observation point P6, the average multi-annual value is 284.9 mg/l and the maxima was recorded in 2009 - 436.4 mg/ (figure 4).

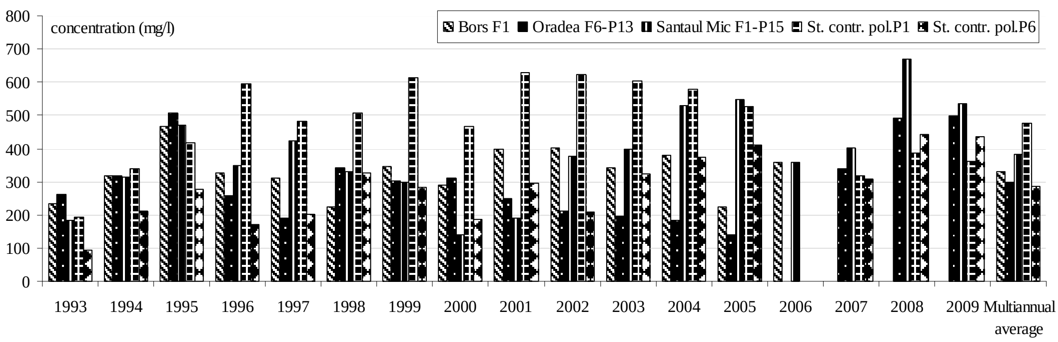

Figure 4. Periodic variation of the average values seen in the points with exceed values for $\mathbf{SO_4}$

Lead (Pb) indicator – presents average multi-annual values lower than the threshold value from 137/2009, but higher multi-annual average values were observed in the industrial zone: Oradea F5 = P12, the highest value was recorded in 2000 – 0.034 mg/l towards 0.01 mg/l, an exceeding of 3.4 times; in the Oradea F6 –P13 observation point, the highest value was recorded in 1997 - 0.036

mg/l; in P2 point – the highest average value of 0.026 mg/l was recorded in 2000; in P4, in 2000, the highest value recorded was 0.0336 mg/l; in the P6 (Sinteza area) and P7 observation points, higher multi-annual average values than 0,02 mg/l were recorded, starting with 1993 and including 1998; in P9 point, the annual maximum concentration was recorded in 2000 - 0,026 mg/l (figure 5).

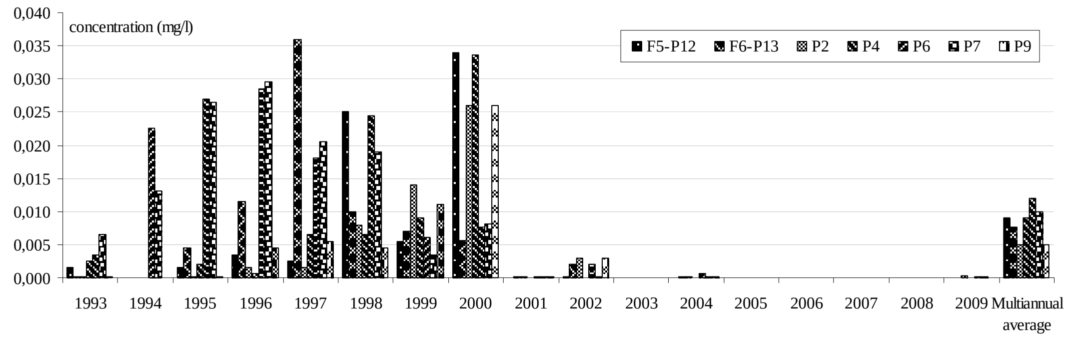

Figure 5. Variation of the average values seen in the points with exceed values for lead (Pb)

Lead is found in the drinking water only occasionally as a result of the natural deposits erosions. Its presence is mainly due to the sanitary facilities corrosion which contain lead, the lead alloys soldering/junctions and fittings or alloy armatures. Mainly, the lead pipes are susceptible of generating high levels in water if the water is acid or the water has an alkaline pH or contians high amounts of carbonate. Usual, the concentration has high variations depending on the contact period between the water and the pipes (Risk assessment methodology for health PHARE 2006/018-147.03.03/05.06).

In 1993-2009, indicators such as: **Iron$_{tot.}$**, **Mn**, **Ca**, **Mg**, **Na**, **K**, **Zn**, **Cr$_{tot}$**, **Cu**, **As**, **Ni**, **Se**, **Hg**, **Cd**, **HCO_3**, **total alkalinity**, **total hardness** were also monitorized. These elements not being included in the 137/2009 Order, the determined average values were compared with CMA from the Drinking Water law and NBL. Significant exceeding was observed at Mg and Ca.

Manganese (Mn) indicator presents multi-annual average value higher than those of NBL, 1,0 mg/l in all of the observation points of the pollution control station. In figure 6 it can be observed an annual average maximum of 19.38 mg/l in P7 point, in 2001, the exceeding ratio being of 19.38 times and the multi-annual average is 4.36 mg/l. Manganese from the raw water is found mainly in the natural sources, although higher concentrations in the underground waters were associated with the industrial pollution(Risk assessment methodology for health PHARE 2006/018-147.03.03/05.06).

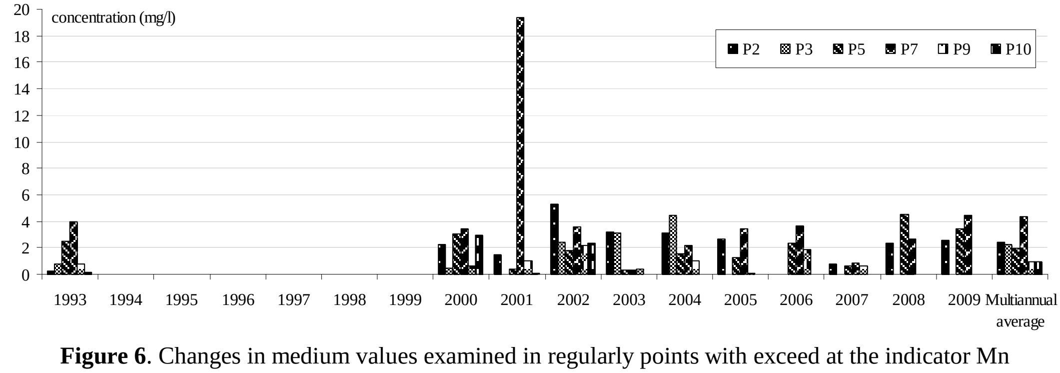

Figure 6. Changes in medium values examined in regularly points with exceed at the indicator Mn

Calcium (Ca) indicator was examined in all sections studied in 1993-2009, and shows the average annual value higher than the NBL (Natural Value Fund) on 11 points, a percentage of 30.6%. In Figure 7, we presented the monitoring points with multi-annual average values higher than 100 mg / l. This apparent significant overruns in the points located in the industrial area of Oradea. In this way, is possible to see important exceed for the points from Oradea city area. The more bigger multi-annual average was recorded in point P3 – 195.0 mg/l (figure 7).

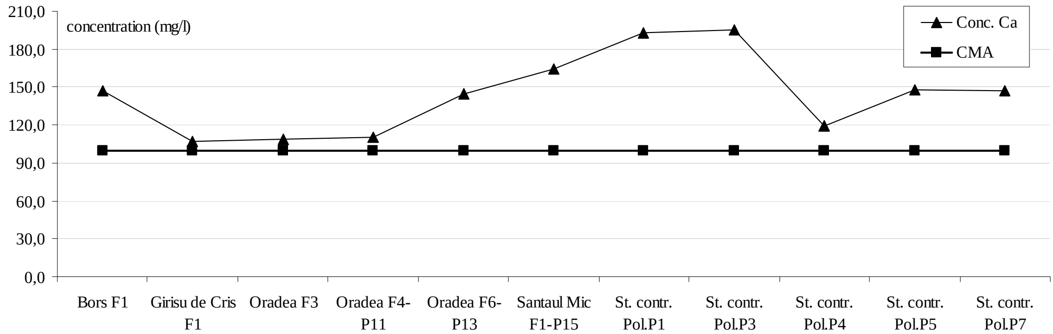

Figure 7. Medium variation for calcium ion (Ca)

CONCLUSIONS ABOUT GLOBAL CHEMICAL STATUS

For evaluation of the groundwater chemical status in the individual monitoring sites, in Crişul Repede watershed, the results were reported at the water body ROCR01.

Comparing the average values determined in period 1993-2009, with threshold values (TV) establish by Order 137/2009 and limit from Law 311/2004, were found, in all monitories points, the drilling have exceeded at one or more analyzed indicators.

For 46 points monitories in water body ROCR01 are leading to the following quality classes:

- 55.3 % of drilling have good chemical status;
- 34 % of drilling have low chemical status;
- 10.6 % of drilling have non-drinking character.

For 26 drilling, the indicators has no overcoming at the threshold values in accordance with Order 137/2009 and the result is a good chemical status.

In 16 drilling the annual average values are higher than TV (threshold values) from the Order 137/2009, especially in drilling belonging Pollution Control Station and have poor chemical status at the indicators: ammonium, nitrates, phosphates, sulphates. The pollution belong to zootehnical activity in the area of Oradea city and also from Palota and Cefa.

In 5 drilling, the result is a non-drinking character for water at the parameters manganese, iron and calcium, as a result of comparing average annual values with NBL (natural background values).

At local level, the indicator lead, has exceeded annual average and we can consider that area with a local pollution. Figure 8 and 9 show this three quality classes.

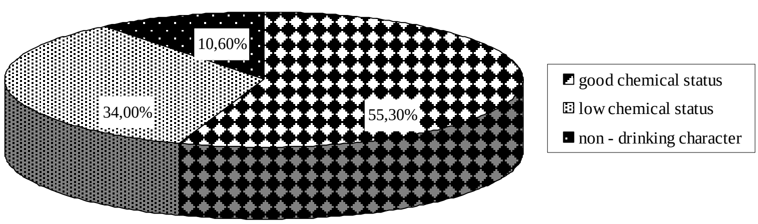

Figure 8. Ground water chemical status

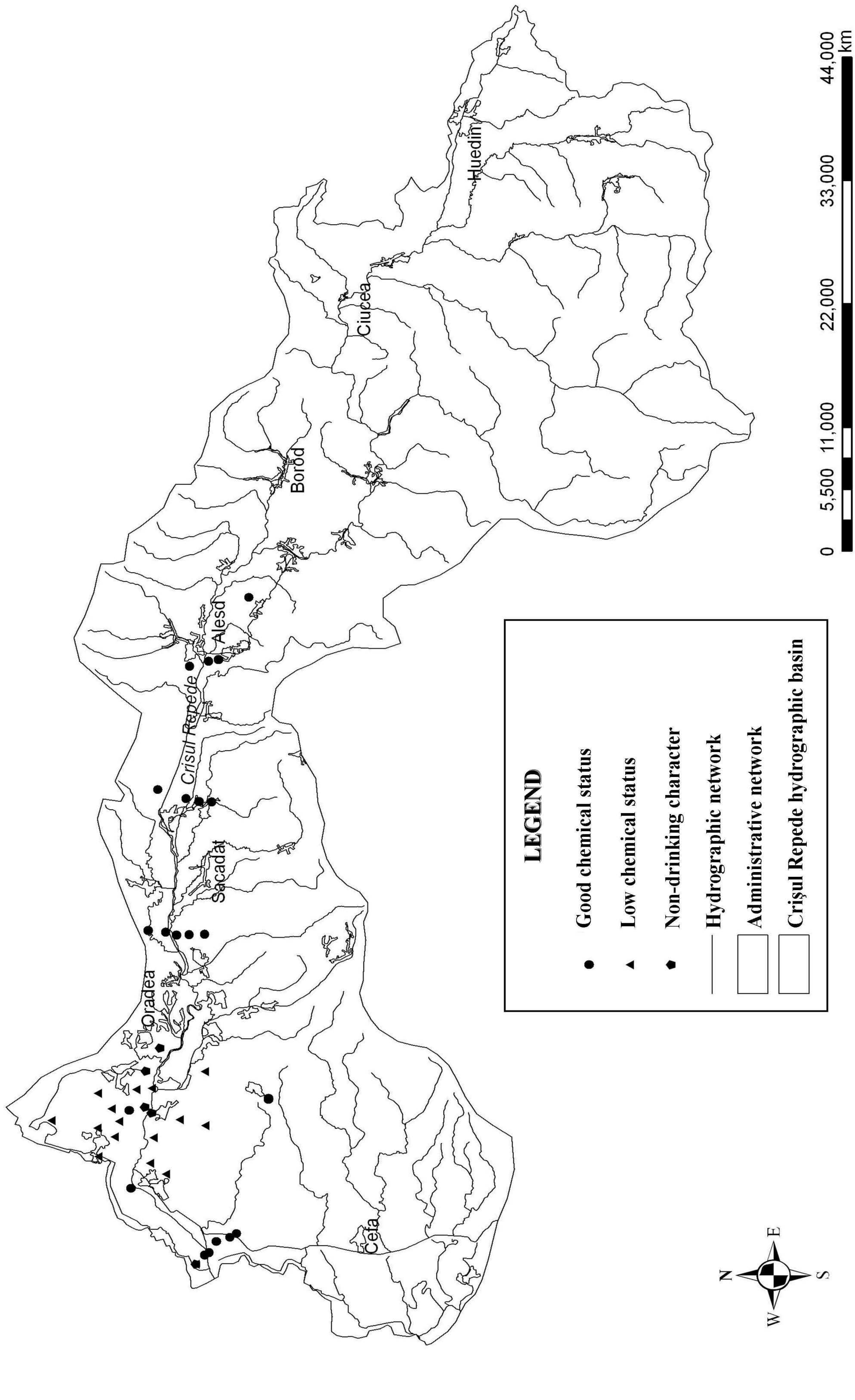

Figure 9. Ground water chemical status

These data show that groundwater aquifer resources, in particular, have a high risk of pollution, both long term and short term. For this reason, they can not provide water sources for population. Because groundwater is moving slowly through the basement, the impact of human activities can affect it for a long time. This means that pollution occurred with a few decades ago – in agriculture, industry or other human activities – can still threaten water quality today, and in some cases, it will continue to do so for several future generations.

Therefore, major emphasis should be placed primarily on pollution prevention. Finally, the ground waters are “hidden resources” which are quantitatively more important than surface waters and because of that pollution prevention, monitoring and restoration are more difficult than for surface waters due to their inaccessibility.

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