

**CONSIDERATIONS REGARDING EVALUATING NATURAL
BACKGROUND LEVEL (NBL) AND THRESHOLD VALUES (TV's)
FOR SOME QUALITY INDICATORS SPECIFIC OF
GROUNDWATER BODIES FROM SIRET HYDROGRAPHICAL
BASIN**

Dan Dăscălița¹, Ioan Vlad¹, Costică Plăcintă¹

Key words: water bodies, natural background level (NBL), threshold value (TV's).

Abstract. In this paper we are presenting the results of an assessment research regarding the determination of natural background level (NBL) and of threshold values (TVs) for some specific underground water quality indicators from GWSI05 body in Siret basin, in accordance with the Framework Directive 2000/60/EC and Groundwater Directive 2006/118/EC. We have described the stages of calculation and analyzed the results from which have been proposed rational and realistic threshold values for each studied quality indicator. Significant research results were synthetically presented at the end of paper. In addition to the groundwater body GWSI05, we presented and a brief characterization of other 5 groundwater bodies from Siret basin.

**Establishing levels and proposals for natural threshold values
for groundwater bodies in siret basin**

Definitions. According to art. 2.12 from Water Framework Directive (2000/60/EC), a **groundwater body** represents a distinct volume of groundwater from an aquifer or multiple aquifers. A **water body at risk is a waterbody** that signals the presence of one or more indicators of pollution, anthropogenic or endogenous products.

Natural background level (NBL) is the natural concentration of an indicator substance or value in a groundwater products, which corresponds to very small anthropomorphic changes or unaffected conditions.

Threshold value (TV) - the value of a parameter that has been overrun, characterizes it as being at risk and requires action from the competent authorities under the legislation in force.

¹ Siret Water Directorate, 1, dan_dsclt@yahoo.com.

Chemical status of a water body is determined by the whole situation of the properties values and characteristics. These parameters are set for any polluting chemical ion, substance or indicator present in water, which defines the status of a water body and are called „determinants”.

The concentration one or more parameters at a given moment is the level at which lies the water body analyzed. The principles for classification of water quality under the laws in force are defined by different criteria. Water Framework Directive (2000/60/EC) and Groundwater Directive (GWD-2006/118/EC) are integrated legislation stipulating, among others, the objective of "good status" for all waters in Europe. These directives provide a sustainable and integrated management for river basins, including mandatory targets, clear deadlines and an integrated program of measures based on scientific, technical and economic analyses, as well as information and consultation of public. To answer new requirements in a cooperative mode, the EU Member States, Norway and the European Commission have agreed on a Common Implementation Strategy (CIS) for the Water Framework Directive (WFD).

To assess the chemical status of groundwater, the concentrations measured in monitoring points established under the WFD, should be compared with European standards and threshold values (TV's). European standards are set for nitrates (50 mg/l) and pesticides (0.1 mg/l individually and 0.5 mg/l total). For other pollutants, Member States must deduct TV. They should be set at the most suitable (national, district on the river basin, or groundwater body) level. So, in addition to nitrates and pesticides, should be taken into account the following minimal list of the parameters:

- substances, ions or indicators which may appear natural and/or as a result of human activities: As^{3+} , Cd^{2+} , Pb^{2+} , Hg^{2+} , NH_4^+ , Cl^- , SO_4^{2-} ;

- synthetic substances: trichlorethylene, tetrachlorethylene;

- parameters of saline or other intrusion: conductivity or Cl^- and SO_4^{2-} .

GWD, in Annex II.A, give the following advice for fixing TV's.:

- be based on the analysis of the degree of interaction between groundwater and associated aquatic ecosystems and/or terrestrial ecosystems dependent;

- be based on actual and potential uses of groundwater entitled (drinking water supply, irrigation, etc.) or their functions;

- to include all pollutants which characterizes groundwater bodies as being at risk and may not achieve the objectives of Article 4 of WFD;

- be based on the hydrogeological characteristics of the groundwater bodies, including information on the natural background levels and the water balance;

- take into account the origin of pollutants, their possible natural origin, toxicology and trends dispersion, persistence and their bioaccumulation potential;

- take into account the high levels of natural background due to natural causes hydrogeological;
- be supported by a mechanism of control of data collected, based on evaluation of data quality and analytical considerations.

Given the multitude of issues to be considered when calculating threshold values, it is obvious the need of using conceptual models of groundwater flow and hydrochemical properties in the groundwater body, elucidate the general schedule „water supply - course – discharges water”. The conceptual model is not a numerical one, but a work scheme for understanding the hydrological system studied.



Fig. 1. Groundwater bodies in the range of activity of the Directorate of Water Siret

Characterization of groundwater monitored by Siret water directorate

In Siret Basin District have been analyzed a number of 6 groundwater bodies (fig. 1), from which 5 from freatic and a deep, transboundary one named after the following structure: RO = Romania; SI = Siret basin; 01-06 = number of water

bodies space in the Siret basin. We underline that none of these groundwater bodies is at risk.

Body ROSI01 (Cârlibaba) is located in the mountains and Obcina Suhardul Mestecanis. It is a body accumulated in fissures in crystalline limestone and dolomite, and crystalline series of Tulghes. Groundwaters are collected and moved on cracks and surfaces at the contact between crystalline and different types of Quaternary deposits. The natural water supply of this waterbody is made predominantly from rainfall.

Body ROSI02 (Dorna Depression). The aquifer is alluvial, represented by granular formations (sands, gravell and blocks), age Holocene. The potential aquifer of this water body is weak, with flows that rarely exceed 0.3 l/s. Groundwaters are drinkable, but have been reported some areas where are exceeded the admitted limits on iron and organic substances. The aquifers layers are supplied from rainfall, and because are not protected, are vulnerable to pollution.

Body ROSI03 (Siret Valley Siret River and tributaries). The water body develops in the valley and terraces of Siret and its tributaries. It's Quaternary as age, its rocks consist of sand and gravel with blocks, that have average thicknesses of approximately 5m.

The type of water is bicarbonate or calcium bicarbonate-calcium-magnezium. The two borders of the Siret have completely different behaviors in terms of hydrogeology. Hydrostatics level is free in general. Springs occur at the contact between the terraces of Siret, Suceava and Moldova with their floodplains. In Suceava's floodplain and river terraces, the groundwater aquifer is quartered in gravel deposits, which downstream become smaller.

In the floodplain and river terraces of Moldova, groundwater aquifer consists of gravell and blocks and less sand. Water discharge and improved quality of groundwater have allowed the construction of large catchments (Timisesti, Berchișești, Lunca, etc.). Bistrița's floodplain and terraces have aquifers consisting of sands, stones and blocks, with average thickness of 5-10 m and more.

The hydrogeological regime of Bistrița Valley is influenced by hydroelectric facilities which have been executed on the river course. Water supply to aquifer is made from rainfall, and less from surface waters. In Troțuș's floodplain, aquifer deposits consist of sand, stones and blocks. The direction of groundwater flow is generally from high areas into low areas.

Body ROSI04 (Hăghimaș Mountains). The body is located in Hăghimaș mountains, type fissure-karst, being accumulated in Triassic, Jurassic and Cretacic deposits represented by dolomite, dolomite limestone, conglomerates and sandstone.

Code/Name	Area (Km ²)	Characterization/ Geol/Hydrogeol.			Water use	Polluters	Degree of global protection	Risk		Border (country)
		Type	Under pressure	Strate cover				Quality	Quantity	
1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.
1. GWS001 Caribaba	90	F	Mixed	0/var.	PO		PM,PU	Nu	Nu	Nu
2. GWS002 Depression Dorna	129	P	No	3-5	PO,I,Z	I,M	PM,PU	Nu	Nu	Nu
3. GWS003 Siret River valley and its tributaries	4286	P+k	No	2-10	PO,I,Z,IR	I,M,A	PM,PG	Nu	Nu	Nu
4. GWS004 Mountains Haghimas	141	F+K	Mixed	0/var.	PO		PM	Nu	Nu	Nu
5. GWS005 Lower Siret Plain	2145	P	No	2-12	PO,I,Z,IR	M,A	PM,PG	Nu	Nu	Nu
6. GWS006 Suceava (Samatran)	3857	P	Yes	40	PO,I,Z		PVG	Nu	Nu	Yes/Ucraina

Area: surfaces only Romania.

Predominantly Type: P - porous, K - Karst, F - fissure.

Under pressure: Yes / No / Mixed.

Strate cover: thickness in meters of the package cover.

Water PO - water supply population, IR - irrigation, I - industry, P - fish, Z - animal husbandry.

Polluters: I - Industrial; A - Agricultural; M - domestic; Z - nototechnical.

The degree of global protection: PVG - very good, PG - good, PM - average PU - unsatisfactory, PVU - highly unsatisfactory.

Qualitative and quantitative risk: Yes / No

Border: Yes / No

- RoS001 - is accumulated in limestone and dolomite crystalline and crystalline series of Tulgheș: upper precambrian age - paleozoic
- RoS002 - is albarial aquifer; represented by granular formations (sands, stones and blocks) age holocen
- RoS003 - develops stones and riverside terraces of the Siret River and its tributaries and quaternary age
- RoS004 - is accumulated in storage: Triassic, Cretaceous and Jurassic, represented by dolomite, dolomite limestone, conglomerates and sandstones
- RoS005 - develops stones, and blocks and sands of quaternary age
- RoS006 - develops deposits consist of: clays, manna, intercalations of sand and limestone and limestone -sandstone -dolomite age Samatran

Tab. 1 - Characteristics of groundwater bodies

Aquifer is generally represented by springs, with water flow between 0,5-500 l/s. Groundwaters are bicarbonate-calcium-magnesium.

Body ROSI05 (Siret Lower Plain). The body is permeable, accumulated in Quaternary deposits developing in plains. Aquifers are quartered in the sand deposits generally located at depths of 1-5 m. Alluvial deposits consist of: gravel, blocks and sand, and stores most important aquifer in the lower basin of Siret River. These deposits have thicknesses that can reach over 100 m, including the deep layers of Căndești. The predominant type of water is bicarbonate or calcium bicarbonate-calcium-magnezium. Groundwater supply is done from underground, from the piemountain plain or from springs at the contact with this area.

Body ROSI06 (Suceava). This groundwater body is porous-permeable, being developed in Sarmatian formations consisting of an alternation of clays, marls, sand and thin layers of limestone and sandstone. Accumulation of water is possible between 50-250 m, below this depth waters have low potential or are strongly mineralized.

The main features of groundwater bodies are presented in Table 1.

Steps for determination of natural background levels (nbl) and threshold values (tvs) for groundwater bodies

3.1. Introduction

To determine background and threshold values of groundwater bodies, is necessary to use a conceptual model and an integrated process, to follow three fundamental aspects:

- Characterization of potential pollutants and parameters of any indicators of pollution, including descriptions of properties that influence their route and transport, eg.: transport in and outside the aquifer, including transport in unsaturated zone, the media hydrogeochemistry, ecotoxicological and toxicological and possible impacts on ecosystems;
- Characterization of water bodies, including a description of hidrogeochemical characteristics of aquifers, the quality of the environment (natural and anthropogenic influence) and any dependent of the quality of quantitative aspects (such as variability of water levels due to hydrological cycle during the year, the interactions between groundwater and surface water, or water balance in the long term).
- Characterization of receptors, including aquatic ecosystems, terrestrial ecosystems dependent and groundwater.

To establish the nature and threshold values for groundwater bodies, the following steps should be taken:

The first step is to select criteria or so called receptors, which are relevant to the water body considered. In general they can be surface water bodies,

terrestrial ecosystems (protected), that depend on groundwater, water users (drinking water, irrigation, industrial and other water users).

The second step is to determine the criteria for each of the relevant receptors. Criteria in use are the relevant standards for uses such, as the standard for drinking water, standard for irrigation water, etc. In this case, the relevant standards in Romania are set for the quality of drinking water and surface water quality. The lower critical value can be considered as a criterion or intermediate value. If there is a very good understanding of the conceptual model, factors for taking into account mitigating and/or dilution may be applied. Thus, results that the criteria values are higher. Within the European project that studied TV's in several countries, such factors were never implemented.

In this stage should be identified and selected chemical parameters that determine threshold values. Nitrates and pesticides should be always taken into account in assessing chemical status. In addition to pesticides and nitrates, the following minimum list of parameters should be considered for each groundwater body:

- Substances or ions or indicators which can occur both naturally and as a result of human activities: As^{3+} , Cd^{2+} , Pb^{2+} , Hg^{2+} , NH_4^+ , Cl^- , SO_4^{2-}
- Synthetic Substances: trichlorethylene, tetrachlorethylene;
- The indicators of saline or other intrusions: conductivity, Cl^- and SO_4^{2-} depending on the Member State.

In the third step, criteria are compared with the natural background level (NBL). The highest of them will be chosen as TV. Natural parameters for this step is essential because the main objective of establishing TV is these values that serve to identify the relevant issues in terms of groundwater quality. Without taking into account natural stock levels, TV can be chosen over or around the natural stock levels, which of course will result in a lot a lot of analysis of observation drilling where TV are exceeded, while anthropogenic impact will not be clear. So, if natural parameters, the natural background level (NBL) form the basis for the establishment of TV to identify problems caused by anthropogenic pressures and impacts. For artificial substances, NBL is zero.

Practical steps taken are:

Step 1

- Creation of the database using all existing chemical analysis;
- Grouping them on water bodies;
- Arrangement of drilling data (for a more comfortable use in alphabetical order);
- Numbering the drillings (for an easy use).

Step 2

- Organizing groups of anions and cations;

- Convert from mg/l in mEq/l;
- Calculating the ionic balance;
- Error checking ionic balance.

Step 3

- Statistics: total number of indicators analyzed, calculating the minimum, maximum, average and median;
- Eliminate errors in ionic balance (errors > 10%);
- Statistics will eliminate values that do not correspond.

Step 4

- Average concentration is calculated in each drilling for each indicator (using pivot table);
- Average concentration is calculated for drillings remaining after removing ionic balance errors and inadequate values described above;
- Ordering data representing the means, made in Excel;
- Calculating percentile of 90.

1.2. Determination of Threshold Values (TV's)**3.2.1. Selection criteria**

Establish the criteria for determining the TV's was conducted for all groundwater bodies from Siret basin. Based on the use of body water, were fixed relevant quality indicators. In determining the threshold value have been made comparisons with the values of water quality indicators established under the Drinking Water Act No. 458/2002 and Law 311/2004, which supplements and amends Act 458/2004. We also appealed to the values set in STAS1342/1991 – drinking water (if not set maximum values for drinking water in the two laws 458/2002 and 311/2004).

To get TV's most critical values for drinking water, have been made comparisons with the NBL, and the majority of the critical values of waterbody taken into the study.

As a result, appeared several variants, indicating 2 significant cases:

- Critical value is bigger than the NBL, in this case the critical value becomes TV.
- Critical value is smaller than the NBL, in this case, NBL, becomes TV.

It should be noted that we encountered some difficulties in determining the threshold values for situations in which were few available values, or for situations with very high values of indicators due to natural background. These were eliminated from the database. Given the high values of natural background for some indicators (chlorides, nitrates, metals, etc.) found only in the database out of the study (mostly), after a concrete analysis, for threshold values and natural values were established higher values.

1.2.2. Determining the criteria

Limit values of criteria are fixed by laws that regulate the quality features of water bodies. These values for relevant quality parameters are presented in table 2.

Table 2. Value of criteria for determining threshold values (TV's)
La valeur des critères pour établir les valeurs - seuil

Nr. crt.	Parameter	UM	Ground-water directive 2006/118	NTPA 01 Waste water outlet directly into surface water	NTPA 02 Waste water directly into sewage	Ord. 161/2006 Surfaces water	Drinking Water Law 311/2004	EU Drinking Water directive
1	Nitrate NO ₃ ⁻	mg/l	50	25 (37)	-	13	50	50
2	Pesticides	µg/l	0,1	-	-	-	0,1	0,1
3	Pesticides (total)	µg/l	0,5	-	-	-	0,5	0,5
4	Arsenic As ³⁺	mg/l	-	0,100	-	0,020	0,010	0,010
5	Cadmium Cd ²⁺	mg/l	-	0,200	0,300	0,001	0,005	0,005
6	Lead Pb ²⁺	mg/l	-	0,200	0,500	0,010	0,010	0,010
7	Mercury Hg ²⁺	mg/l	-	0,050	-	0,0003	0,001	0,001
8	Nickel Ni ²⁺	mg/l	-	0,500	1,000	0,025	0,020	0,020
9	Zinc Zn ²⁺	mg/l	-	0,500	1,000	0,200	5,000	-
10	Ammonium NH ₄ ⁺	mg/l	-	2 (3)	30	1	0,5	0,5
11	Potassium K ⁺	mg/l	-	-	-	-	-	-
12	Chloride Cl ⁻	mg/l	-	500	-	50	250	250
13	Sulphate SO ₄ ⁻	mg/l	-	600	600	120	250	250
14	Trichloroethylene	µg/l	-	-	-	10	10	10 (sum)
15	Tetrachloroethylene (perclorotilena)	µg/l	-	-	-	10	10	10 (sum)
16	Conductivity	µS/cm la 20C	-	-	-	-	2500	2500
17	Nitriti NO ₂ ⁻	mg/l	-	1 (2)	-	0,1	0,5	0,5
18	Iron	mg/l	-	5,000	-	0,500	0,200	0,200
19	Manganese	mg/l	-	1,000	2,000	0,100	0,050	0,050
20	Selenium Se ²⁺	mg/l	-	0,100	-	0,002	0,010	0,010
21	Sodium Na ⁺	mg/l	-	-	-	50	200	200
22	Fluorides	mg/l	-	5,0	-	1,5	1,2	1,5
23	Total Cyanides	mg/l	-	0,1	1,0	0,05	0,05	0,05

Bodies of underground water are characterized in terms of chemistry, mainly by Cl⁻, SO₄⁻, NO₃⁻, NO₂⁻, NH₄⁺, Na⁺, K⁺, Ca²⁺, Mg²⁺, Fe²⁺³.

3.2.3. Comparison with natural background level

We have made comparisons between the concentrations of the background natural and the most restrictive criteria. Highest of these were established as Threshold Value (TV's).

1.3. Database to determine background concentration

We used data from 1965-2007 period. For springs we used data from 2006 and 2007. Description of the database is presented in table 3. For characterizing water bodies in terms of hydrogeology, we built up a technical database of the drillings (quantitative and qualitative elements). The database is written in Excel and includes data from the period 1965-2007 for all studies drillins from Siret Basin (without Bârlad and Buzău basins).

This database was used to determine natural background values and threshold values, and for their takeover to achievement maps in GIS format.

Map with locations of drillings originally taken in the study for groundwater bodies, from the Siret basin Hydrographical is presenting in fig. 2.

3.4. Checking the ionic balance

In general are included values with errors under $\pm 10\%$ where were determinated all major ions. In ionic balance have been analyzed the following anions and cations (and other indicators in some cases):

- Cl^- , SO_4^- , NO_2^- , NO_3^- , HCO_3^- , CO_3^- , PO_4^-
- NH_4^+ , Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Fe^{2+3} , Mn^{2+}

Since in the period 2000-2007 was analyzed Fe total, all previous records with Fe^{2+} were corrected with these data.

3.5. Calculation and verification statistics

After calculating the minimum and maximum values, these were checked with primary records, where ionic balance was placed in the margin of error $\pm 10\%$.

3.6. Checking fixed residuum

We verified that the fixed residuum determined be higher than the sum of cations and anions.

3.7. Replacing censored values

Values of 0000 and lower than the LOD/2 were replaced with LOD/2.

Observations:

- We met two cases relating to the method:
 - During a study period the calculation mode of LOD (detection limit) was different;
 - During a study period, the method of analysis changed, but for the period beginning is not known the old method of LOD.
- There have been found several cases regarding reporting mode:
 - The laboratory has reported a value 0000;
 - Laboratory has reported <LOD and Monitoring has recorded as 0000;
 - Laboratory has reported <LOQ (cuantification limit) and Monitoring has recorded as LOD, LOD/2, LOQ/2, <LOQ ;

Tab. 3 - Database available for the characterization of groundwater bodies, from Siret Water Directorate, for the period 1965-2007

Water body	Number drilling (wells)	Number remaining drilling	Total samples	Number of samples remaining after checking ionic balance	Number of samples removed after conducting ion balance	Number of samples remaining after application of the criteria:			Observations
						Criterion Cl ⁻ <200 mg/l	Criterion NO ₃ ⁻ <10 mg/l	Criterion OXC<2 mmol/l (oxidabilitate)	
1	2	3	4	5	6	7	8	9	10
ROSI01	1 drilling + 1 spring	1+1	6	4	2	4	4	2	<ul style="list-style-type: none"> • F1 – Botoș-Ciocănești; • Spring Cârlibaba 2
ROSI02	9	9	312	186	126	186	178	0	<ul style="list-style-type: none"> • 8 samples removed after criterion NO₃⁻
ROCSI03	408	265	8228	6205	2023	5660	4476	610	<ul style="list-style-type: none"> • 545 samples removed after criterion Chlorides; • 1729 samples removed after criterion NO₃⁻ • 5595 samples removed after criterion. OXC.
ROCSI04	2 springs	2	4	4	0	4	4	0	<ul style="list-style-type: none"> • Izvor Damuc • Springs 3 wells
ROCSI05	137	28	3461	1850	1611	622	1012	240	<ul style="list-style-type: none"> • 1228 samples removed after criterion Cloruri; • 838 samples removed after criterion. NO₃⁻ • 1610 samples removed after criterion. OXC.
ROCSI06	4	4	5	5	0	4	3	1	
Total	562	310	12016	8254	3762	6480	5677	853	

o Laboratory has reported <LOQ (informative quantification values) and Monitoring has reported the value in parenthesis, as informative value.



Fig. 2. Map with locations of drillings originally taken in the study for groundwater bodies, from the Siret Basin

3.8. Checking the depth of hydrogeological drillings

The database did not include all recorded depths of drillings. Verification was done after the technical fiches of drillings.

Database for water bodies ROSI01-ROSI06

From the database verified according to the principles above, have been selected only those drillings that refer to water bodies examined.

Training database

- Elimination of suspect records that have been marked;
- Disposal of records that do not belong closing ionic balance in the spread of $\pm 10\%$;
- Removing records of statistical calculations;
- Ordering drillings after: name, code INHGA, year;
- Assigning an index for each drilling.

Determination of average values

- Pivot table was used to average values of main indicators, grouped on general indicators and metals;
- Comparison was made according to criteria of anthropogenic impact.

Determination of level of natural background concentrations (NBL) and threshold values (TV's)

- Were excluded hydrogeological drillings whose values do not meet the criteria of anthropogenic impact;
- Have been calculated values percentiles 90% for indicators according to the criterion;
- From the relevant criteria, the most strict values were chosen;
- Values were compared for selected criteria with the NBL value, for criterion 1+2 ($\text{Cl}^- < 200 \text{ mg/l}$; $\text{NO}_3^- < 10 \text{ mg/l}$), and the smallest value was chosen;
- Were obtained threshold values (TV's) that were recorded (expressed in mg/l).

Checking data distribution and conclusions

- Verifications have been made of the data distribution on each drilling, with different records of the period under review after the event (1965-2007).
- All data sets that represent indicators NO_2^- , PO_4^{3-} , NO_3^- , and the vast majority of the remaining indicators had a lognormala distribution;
- Using the median instead of arithmetic mean is more appropriate.

Determination values of Natural Background Level (NBL) and the Threshold Values (TV's) for GWSI05 is presented in table 4, also "Summary of analysis and determining the Natural Background Level (NBL) and the Threshold Values (TV's) of water bodies from Siret Basin", respectively our proposals for each body of the NBL and TV's are presented in table 5. In figure 4, we present

Nr. Crt.	Indicators of quality	NBL - 1 90% GWSI03 after: - Oxc-stmno/l - NO ₃ < 10mg/l - Cl < 20mg/l		NBL - 2 90% GWSI03 after: - NO ₃ < 10mg/l - Cl < 20mg/l		Percentile 90%		Limits of Law 438/2002 (Law 311/2004) mg/l	TV using NBL - 1		TV using NBL - 2	
		I	II	I	II	I	II		I	II	I	II
1	Number of drilling											
2	Cl ⁻ (mg/l)	1	1	28	28	1	28		1	1	28	28
3	NO ₃ ⁻ (mg/l)			146,32	126,33		183,15	230			183,15	126,33
4	NO ₂ ⁻ (mg/l)			5,12	5,01		8,93	30			8,93	5,01
5	SO ₄ ⁻ (mg/l)			0,04	0,15		0,10	0,5			0,1	0,15
6	HCO ₃ ⁻ (mg/l)			105,16	138,06		255,75	230			255,75	138,06
7	PO ₄ ⁻ (mg/l)			391,35	425,09		625,68				625,68	425,09
8	NH ₄ ⁺ (mg/l)			0,03	0,13		0,43	0,04			0,43	0,13
9	Na ⁺ (mg/l)			0,25	0,37		0,87	0,5			0,87	0,37
10	Ca ²⁺ (mg/l)			11,98	126,79		213,62	200			213,62	126,79
11	Mg ²⁺ (mg/l)			87,89	82,80		115,4	100			115,4	82,80
12	K ⁺ (mg/l)			37,38	44,32		73,82	50			73,82	44,32
13	Fe ²⁺ (mg/l)			0,46	1,31		2,25				2,25	1,31
14	Mn ²⁺ (mg/l)			0,39	0,36		0,98	0,2			0,98	0,36
15	Ox.C (mg)			8,09	10,47		0,01	0,05			0,01	0,0
16	Cu ²⁺ (μg/l)			0,0	0,23		0,5	100			19,17	10,47
17	Ni ²⁺ (μg/l)			0,0	0,98		4,11	20			0,50	0,23
18	Zn ²⁺ (μg/l)			0,0	0,86		2,5	3000			4,11	0,98
19	Hg ²⁺ (μg/l)							1			2,50	0,86
20	Pb ²⁺ (μg/l)							10				
21	Cr ³⁺ (μg/l)							30				
22	Cl ⁻ (μg/l)			0,0	0,07		0,17	5			0,17	0,07
23	As ³⁺ (μg/l)							10				
24	Al ³⁺ (μg/l)							200				

Table 4. – Determination of Values of Natural Background Level (NBL) and the Threshold Values (TV's) for GWSI05

TV	Ca	Mg	Na ⁺	K	Fe	NH ₄ ⁺	Mn	Hg	Pb	Cr	Cu	Zn	Cd	As	Al	Ni	NO ₂	NO ₃	SO ₄ ²⁻	Cl	HCO ₃	PO ₄ ³⁻
UM	mg/l				µg/l												mg/l					
GW501	38,5	24	13,5	3,2	0,6	0,56	0,25	-	-	0,5	8,6	5,3	-	-	-	-	1	0,05	18	24	200	0,04
GW502	60	13	14	0,6	5,0	0,6	0,20	-	-	-	-	-	-	-	-	-	3,5	0,05	37	15	220	-
GW503	136	40	100	2	1,2	1,5	0,14	-	-	-	4	7	0,3	-	-	10	16	0,5	140	120	490	0,6
GW504	72	10	55	34	0,1	0,5	0,005	-	-	96	5	15	2,0	-	-	9	1	0,003	31	5	390	0,007
GW505	180	105	290	20	1,0	1,6	0,03	-	-	-	2	5	0,7	-	-	5	25	0,5	280	790	630	0,6
GW506	72	31	530	60	0,8	1	-	-	-	-	-	-	-	-	-	-	8	0,6	310	16	640	-
Law 458/2002 Law 311/2004	50	200			0,2	0,5	0,05	1	10	50	100	5000	5	10	200	20	50	0,5	250	290		
STAS 1342/1991	100	50			0,1	0	0,05	1	50	50	50100	7000		50	30	100	45	0	200	290		0,1
	180	80			0,3	0,5	0,3								200		0,3	400	400			0,5
NBL	Ca	Mg	Na ⁺	K	Fe	NH ₄ ⁺	Mn	Hg	Pb	Cr	Cu <td>Zn</td> <td>Cd</td> <td>As</td> <td>Al</td> <td>Ni</td> <td>NO₂</td> <td>NO₃</td> <td>SO₄²⁻</td> <td>Cl</td> <td>HCO₃</td> <td>PO₄³⁻</td>	Zn	Cd	As	Al	Ni	NO ₂	NO ₃	SO ₄ ²⁻	Cl	HCO ₃	PO ₄ ³⁻
UM	mg/l				µg/l												mg/l					
GW501	38,4	22,6	12,2	3,2	0,5	0,45	0,25	-	-	0,5	8,6	5,30	-	-	-	-	1	0,04	17	19	195	0,01
GW502	61	12,5	13,2	1	4,7	0,5	0,16	-	-	-	-	-	-	-	-	-	3,3	0,05	36	14	210	-
GW503	138	40	78,5	1,8	2,32	1,5	0,14	-	-	-	2,5	4,64	-	-	-	-	10	0,23	106	113	520	0,1
GW504	72	9	46	30	-	-	-	-	-	91	5	14	2,0	-	-	8	1	0	30	4	322	-
GW505	116	74	214	2,25	1	0,9	0,01	-	-	-	0,5	2,5	0,2	-	-	4,2	9	0,1	236	184	630	0,4
GW506	70	30	430	45	0,62	0,95	-	-	-	-	-	-	-	-	-	-	7,4	1,5	534	15,4	634	-
Law 458/2002 Law 311/2004	50	200			0,2	0,5	0,05	1	10	50	100	5000	5	10	200	20	50	0,5	250	290		
STAS 1342/1991	100	50			0,1	0	0,05	1	50	50	50100	7000		50	30	100	45	0	200	290		0,1
	180	80			0,3	0,5	0,3								200		0,3	400	400			0,5

Table 5. Summary of analysis and determining the Natural Background Level (NBL) and the Threshold Values (TV's) of water bodies from Siret Basin



Fig. 3. Map of drillings remaining after achievement steps and criteria presented, on the basis of which have established the Natural Background Levels (NBL) and Threshold Values (TV's) for each groundwater body from Hydrographical Siret Basin

"Map of drillings remaining after achievement steps and criteria presented, on the basis of which have been established the Natural Background Levels (NBL) and Threshold Values (TV's) for each groundwater body from Hydrographical Siret Basin".

4. Conclusions

4.1. General conclusions from the Siret basin Area

- Were taken in study 559 hydrogeology drillings and 3 springs. Through elimination, after application of ionic balance criterion, were remained in study, 307 drillings and 3 springs;

- Initial total number of samples taken in the study were 12 016; after application of ion balance criterion, remained 8254 samples, being removed 3762 samples;
- Samples remaining in the study after application of the 3 criteria are: 6480 to the criterion chlorides, 5677 after nitrates criterion and 853 after OXC criterion;
- Through introduction of modernization and development of integrated monitoring water system, decreased the annual number of samples of water (at 6 years) to study the hydrogeological drillings, which do not fall within the vulnerable zones;
- For drillings hydrogeological study remaining after removal criteria determining the NBL and TV, we had not values to some indicators: Hg^{2+} , Pb^{2+} , As^{3+} , Al^{3+} , etc., reason which have not been established NBL and TV to these indicators;
- In some cases due to non-compliance minimum criteria NBL 2 ($Cl^- < 200$ mg/l NO_3^- and < 10 mg/l), the databases have been defined "poor", which is why were performed on synthetic analysis on the database majority remaining outside the study;
- Criterion OXC < 2 mmol/l became in many cases non-practicable, due to massive reductions of records from databases afferent of water bodies;
- All the 6 water bodies are not subject to risk.

4.2. Conclusions regarding the body ROSI05 (Siret Plain lower)

The chemical water from this water body (including Rimnicu Sărat BH), is generally bicarbonated in mountain area and partly in the area subcarpathian (given the influence of flint palaeogene) and heavily chlorinated in Lower Siret Plain and hilly areas.

Mineralization is generally low (below 250 mg/l in the mountain area, from 250 – 500 mg/l in Subcarpatian) and increased to over 10 g/l in the eastern plain and in areas with deposits salifer (profile hydrogeological Latinu Independenta to drilling F5 with average values of 9560 mg/l). Mineralization is chlorosodium, sulfurous, complex. In the Plain Lower Siret, chlorine content is highest and reaches values that exceed the regular 12 g/l.

Due to mineral paragenesis, a large part of the phreatic water of the body exceeds natural drinking water, to indicators: chlorine (214 mg/l), phosphate (0.43 mg/l), magnesium (74 mg/l), calcium (116 mg/l) and iron (over 1 mg/l).

Bibliography

- Bretotean M., R. Macaleț Tenu A., Tomescu G, Radu E. T. Munteanu, Radu C., D. Dragusin - *The groundwater bodies at risk in Romania*, Hydrogeological Magazine, Nr. 1, Bucharest, 2006;
- Serban P., Gălie A, - *Water management. Principles and rules of european*, Publishing Tipored, București, 2006;
- Guidelines on record resources exploitation water use and protection of groundwater, INHGA-LHIM-PT-F-03-INH-B-2006;
- Grontmij Nederland bv, Witteveent Bos, Ecorys, BDO - European Guide - Chemical status of groundwater and the threshold values, version 2.0., 25-10 – 2007, EVD, Agency for Affairs International and Public Cooperation International Unit, PO Box 20105, 2500 EC, The Hague, The Netherlands, 2006;
- Law on the quality of drinking water, no. 458/2002 and Law 311/2004; European Directive 118/2006/CE for groundwater;
- Directive of the European Parliament and European Council 60/2000/EC establishing a framework for Community action in water policy;
- Synthesis of water, Water Directorate Siret.