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THE ORIGIN OF AMMONIUM IN CARBONATED MINERAL WATERS AND ITS UNDERGROUND TRANSPORT TO ONE PRODUCTION WELL IN MIDDLE CIUC DEPRESSION FROM EASTERN CARPATHIANS

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Abstract

In many cases in Romania, the mineral waters (in the Neogene Volcanic area of the Eastern Carpathians), especially the carbonate waters, have ammonium in concentration over 0.5 mg/l. The main issue regarding the presence of ammonium is identifying if the concentration is due to the anthropogenic pollution or it is of endogenic origin.

The geological, hydrogeological and hydrochemical data analysis resulted in a conceptual model of the aquifer's spatial position, groundwater movement and mineralization, and ammonium occurrence. The geological and tectonic aspects, aquifer's recharging, groundwater flow direction, absence of surface pollution sources and correlation of hydrochemical data, all indicate the underground origin of ammonium. The aquifer is generated in pliocene - quaternary granular deposits. In the basement of these granular deposits, in the fracture areas, the groundwater is mixed with carbon dioxide and ammonium emissions, produced in the volcanic chambers. The surface data correlation and the hydrochemical data analysis resulted in the confirmation of the deep ammonium origin.

After groundwater flow modeling and ammonium transport simulation, the ammonium plume size and preferential transport directions have been finally elucidated.

Keywords: *ammonium origin, ammonium plume, groundwater flow, mass transportation modeling, mineral waters*

Introduction

In a great part of cases, in Romania, the mineral carbonated waters have ammonium concentrations of over 0.5 mg/l. The presence of ammonium is accepted over this limit only in case of endogenic origin of this cation. The goal of this study is to demonstrate the ammonium origin, the geological and hydrogeological conditions of mineral water occurrence and to identify the underground ammonium migration.

The study takes into consideration the spatial extension of the aquifer's structure, the genesis of carbonated water resources, the groundwater flow, both in uninfluenced mode and under the conditions of a production well with a flow rate of 10 l/s, as well as the identification of the ammonium origin and the main access routes of this cation through the porous medium.

Materials and Methods

General presentation

The study area is located in Romania, in the intramountain depressions of Eastern Carpathians, in Harghita County, north of Miercurea Ciuc city, area known as the Middle Ciuc Depression. The zone presents itself as a submerged area due to the deep tectonic fractures. In the western part are present the volcanic mountains of Northern Harghita Chain, to the north and the south the tectonic uplift from Sandominic, respectively Jigodin, and in the eastern part are the mountain chains of Hasmas and Ciuc (Figure 1).

In the Middle Ciuc Depression, the basin area consists of sedimentary pliocene - quaternary deposits. The deposits cover the older fractured formations, their thickness varying between a few meters and 250 - 400 m. In these deposits are generated groundwater resources. Near the tectonic fractured areas, due to the mixture of the water stored in the granular rocks and the carbon dioxide manifestations coming from the depth, carbonated mineral water resources are occurring. In some of the cases, the presence of the ammonium cation with a concentration comprised between 0.9 and 3.5 mg/l were determined.

Taking into consideration that the limit for ammonium in mineral waters is 0.5 mg / l, unless ammonium has an endogenous origin, the study aims to elucidate the origin of the ammonium and the propagation of this cation in the groundwater in Ciceu area, where a well with a depth of 150 m was drilled for mineral water exploitation.

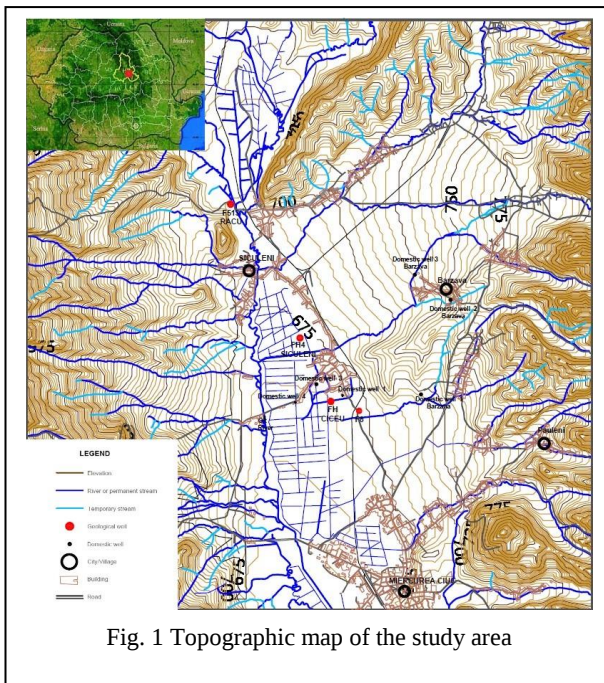


Fig. 1 Topographic map of the study area

The achievement of these objectives involves the construction of a conceptual model concerning the ammonium occurrence, the groundwater flow, the dominant groundwater chemical facies, the analysis of the presence of ammonium and finally modelling of the groundwater flow and the transport of the ammonium through the porous medium.

The conceptual model

The aquifers exposed to modelling are complex systems with a high variability of their characteristic parameters. By conceptualisation or by construction of the conceptual model (Dassargues 1995), can be found the fundamental assumptions that support the modelling. The fundamental assumptions may include aspects relating to the aquifer's geometry, litho - stratigraphic characteristics, homogeneity, anisotropy, recharge and discharge of the aquifer's formations, groundwater flow regime, boundary geometry, chemical compounds involved in transfer and the transfer mechanisms within porous media, the presence or absence of the pollution sources and their temporal and spatial distribution, the chemical processes inside the aquifers, etc. The geometry of the aquifer is dependent on the geology of the region. The Middle Ciuc basin area is a sedimentary type, having pliocene – quaternary sands and gravels, in alternance with impermeable clay deposits and coal beds. In the western and northern part, the sedimentary basin limit (Radulescu 1964, Ionescu et al. 1985, Seghedi et al 1995, Szakács & Seghedi 1995, László 1999) is represented by volcanic rocks (volcanogenic – sedimentary formations and andesitic rocks). In the north - eastern part, the crystalline formations outcrop. On the eastern boundary of the pliocene-quaternary basin there are (Bancila 1941, 1958, Pricajan & Bandrabur, 1955 Patruilus et al 1962, Murgeanu et al 1963, Mutihac & Ionesi 1974, Mutihac & Mutihac 2010) mostly cretaceous formations, such as sandstones, marlstones and calcareous marls and to a lesser extent Jurassic and Triassic deposits, represented by manly limestones, sandstone marls and respectively white limestones.

In the south – eastern and southern boundary of the sedimentary basin, andesitic rocks are present.

The sedimentary basin of Middle Ciuc was formed (Airinei et al. 1965) on a lowered area, along the tectonic fractures that have a north north west - south-south-east direction (figure 2). As a result of the geological and hydrogeological boreholes researches, the geometry of the pliocene - quaternary deposits, which fill the basinal area, as well as the information regarding the groundwater flow, were obtained. In an overview, the morphology of the sedimentation basin (figure 3) is also found in the spatial form of the deep aquifer's formation. Consequently, with the boundaries of the sedimentation basin, the aquifer formations are in vicinity to the ground level with low thicknesses (3-10 m), while in the axial areas of the basin they can reach 60 - 80 m thickness, being found at depths between 70 and 230 m. In the marginal areas of the basin, deep aquifer deposits are located under the porous quaternary deposits, either of the main river terraces or of the dejection fans, forming with them unitary hydraulic structures.

The lithology of the main aquifer consists of pliocene - quaternary rocks, like fine to coarse gravels, interbedded with sands, ranging from fine to medium sands and only rarely coarse sands. Both the lower and the upper aquifer base are bordered by impermeable or partially permeable clays. According to the lithological distribution of the permeable rocks, it is observed that the aquifer's structure presents an advanced degree of inhomogeneity and anisotropy. In a global appreciation, it can be concluded that the main aquifer from the Middle Ciuc Depression extends in surface and depth in concordance with the pliocene - quaternary sedimentation basin. The stream network is subordinated to Olt River and the drainage basin area, the surface waters being completely discharged into this river. The course of Olt is

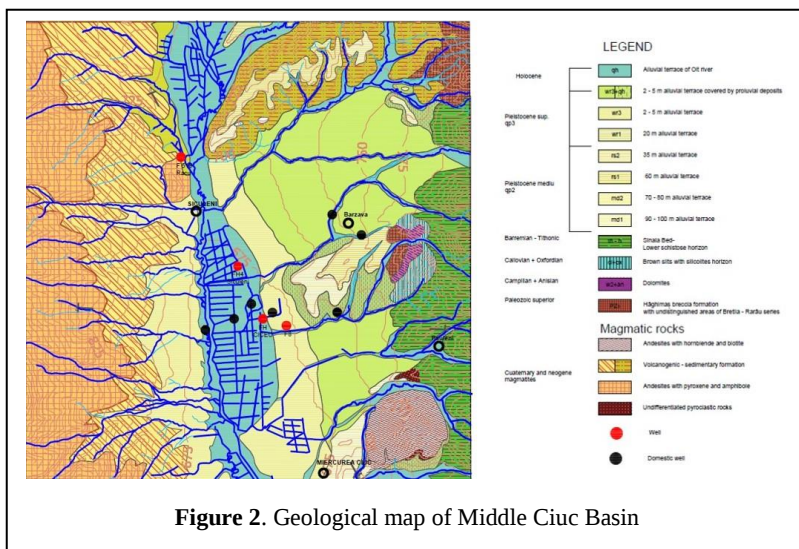


Figure 2. Geological map of Middle Ciuc Basin

oriented approximately north – south, with an average slope of 2.5 ‰. At the exit point from the Middle Ciuc basin, the river Olt has a multiannual average flow rate less than 5 m³ / s, and in Sanraieni, with the probability of 80%, the daily flow rate is of 0.55 m³ / s. In the western, eastern and north eastern part of the main hydrogeological structure, the surface waters subordinated to Olt River have a direct connection with the deep aquifer through the porous quaternary deposits in which the phreatic aquifer is generated. In these areas, the aquifer's structure is recharged both from surface waters and from atmospheric precipitations at levels ranging from 710 to 720 m on the western side, 730 to 780 m on the north east and 725 to 820 m on the eastern boundary.

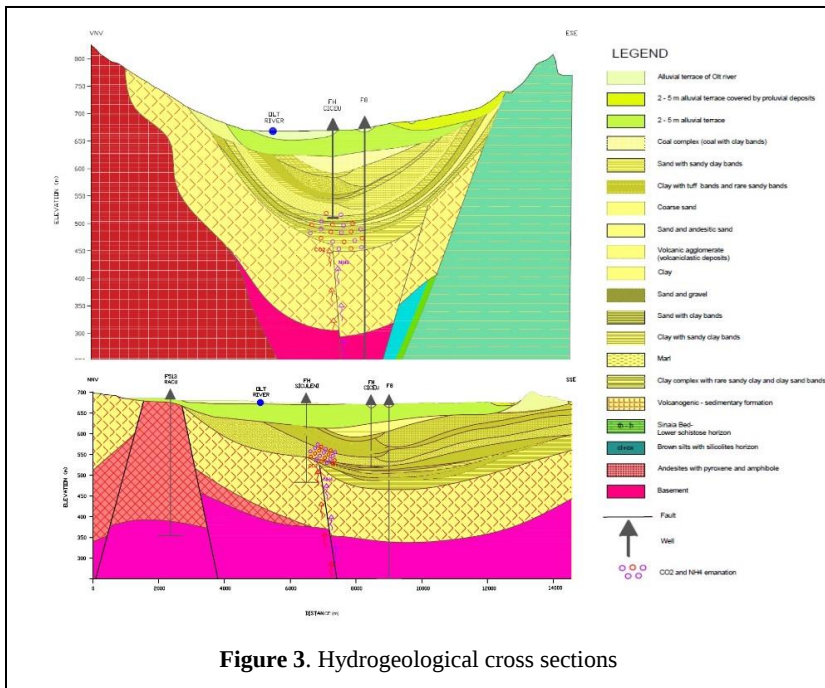


Figure 3. Hydrogeological cross sections

The atmospheric precipitation has values up to 1200 mm in the high geomorphological zones, while in the depression area it drops to 520 - 540 mm. If the recharge of the main aquifer is produced from surface waters and atmospheric precipitation infiltration, in some areas, the discharge of the groundwater is diffused into the stream network subordinated to Olt River and, in others cases, the discharge is carried out through the springs.

Taking into account the known data from the axial area of the aquifer's structure, based on the field observations of the deep wells and the vicinity of the natural boundaries, from the domestic wells, as well as from the observations made on the rivers, a potentiometric map has been edited. On the basis of this cartographic material, the groundwater flow conditions were underlined, without the influence of drainage. In consequence, in the eastern part of the main aquifer, the groundwater flow is produced from the east north east at the elevation of 820 m to the elevation of 680 m in the west south western part. In the western part, the direction of groundwater flow is from the west, at the maximum elevation of 725 m to the east to the elevation of 680 m, while in the vicinity of the Olt River the groundwater flow is convergent with the river from the elevation of 680 - 685 m in the northern part, to the elevations of 660 - 665 m in the southern part. If in the marginal areas the hydraulic gradients have high values (0.09), they are decreasing substantially to 0.009 - 0.004 in the convergence area of the groundwater flow. The hydrodynamic spectrum of the groundwater flow depends not only on the ehipotentials configuration, but also on the hydraulic properties of the aquifer's environment.

Therefore, after the hydrodynamic tests were carried out on the well FH Ciceu, the transmissivity with a value of $11 \text{ m}^2 / \text{day}$, the hydraulic conductivity of 0.5 m/day and the storage coefficient, specific to a confined aquifer, of 0.0005 were calculated. (figure 4)

Due to the fact that the basement of the Middle Ciceu sedimentary basin is strongly fractured, on the deep faults zones the circulation of the carbon dioxide (CO_2) and other volatiles occur. Within the deep aquifer structure, near these tectonic accidents, the mixture of groundwater from the granular rocks and the carbon dioxide coming from the depth is achieved. The result of this process is the carbonated water with a greater or lower carbon dioxide concentration, which is depending on the distance to the tectonic accident.

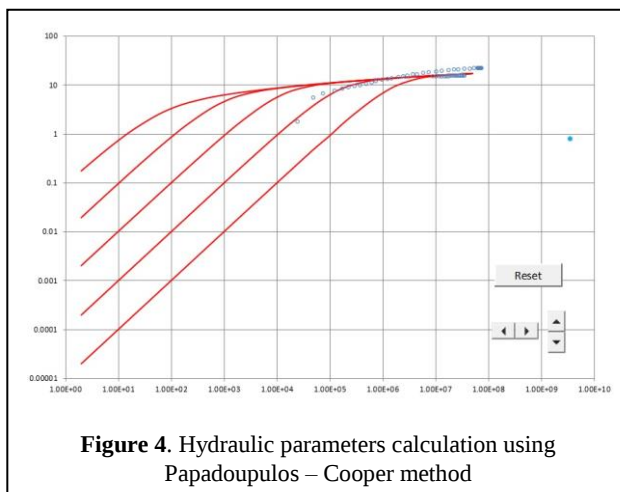


Figure 4. Hydraulic parameters calculation using
Papadopoulos – Cooper method

In groundwater, the carbon dioxide presence accelerates the mineral disintegration processes, resulting in soluble chemical compounds such as carbonates, hydrogen carbonates, calcium sulphates, sodium, magnesium, potassium, alkaline silicates, chlorides and other salts. The dissolution rate depends on the mineral type, solution pH, temperature and on the presence of some reaction accelerators. In addition to the chemical elements specific to shallow aquifers such as hydrogen carbonates, there are also chemical species that originate in the deep groundwater and that are mobilized by the carbon dioxide circulation. Among these, species of chlorides, boron and even ammonium ions can be found predominantly in areas with volcanic or post volcanic manifestations.

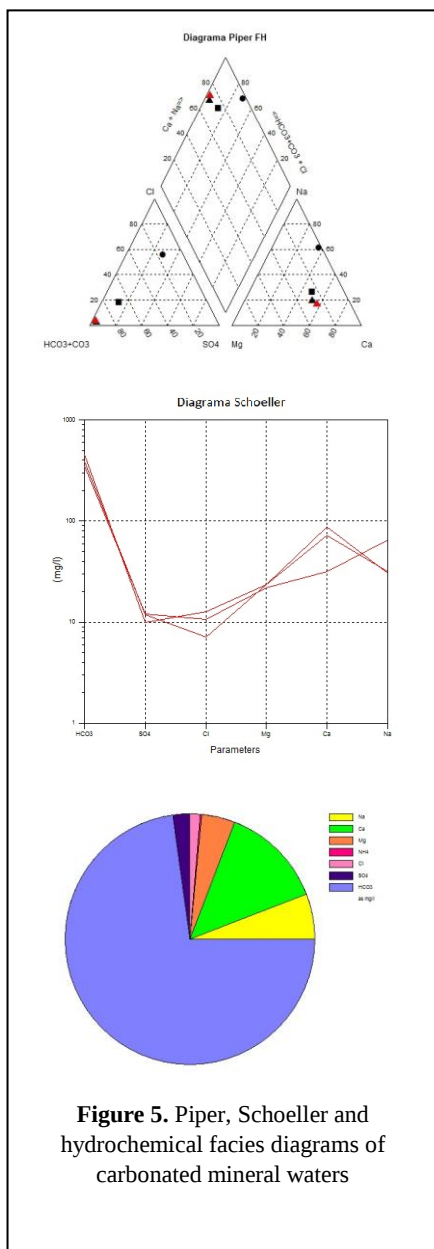


Figure 5. Piper, Schoeller and hydrochemical facies diagrams of carbonated mineral waters

Analysis of the mineral water samples indicate that the hydrochemical facies of groundwater corresponds to the predominantly hydrogen carbonated type with a massive presence of calcium, followed by sodium and magnesium cations and only to a much lesser extent of potassium. In the case of anions, the hydrogen carbonates are present in the greatest concentrations. The sulphates and chlorides are in a much lower proportion, but in approximately similar concentrations (figure 5). The hydrochemical facies of the groundwater is in line with the ability of the main minerals to be dissolved. Thus, in the underground aqueous solution, the dissolution of the main minerals is done by the solubilisation of dolomite ($\text{CaMg}(\text{CO}_3)_2$), anhydrite (CaSO_4), halite (NaCl) and in low proportions sylvine (KCl).

The deep aquifer structure is well protected at the upper base by impermeable clay deposits. They provide good protection against infiltrated surface water. As a result, nitrogen compounds such as nitrates (Bellia et al. 2015) and nitrites are found in very low concentrations ($<0.5 - 2.3 \text{ mg/l}$ and respectively $0.01 - 0.04 \text{ ml/l}$), indicating a very low pollution risk. However, in the Siculeni - Ciceu area, the analysis of water samples revealed concentrations of ammonium ranging between 0.9 to 3.5 mg/l .

The ammonium origin

The analysis of the ammonium origin in groundwater is a complex process (Scheiber et al. 2016), involving chemical and

hydrogeochemical knowledge, uncovering the possible pollution sources, understanding the structural and hydrogeological factors related to the groundwater

flow, contouring the recharge areas, risk area assessment, etc. In the aqueous environment, ammonia (NH_3), compared with ammonium (NH_4^+), has high toxicity (Bucur 1999). In natural waters, for a pH between 5.7 and 8.3, the ionic form of ammonium is found. For a pH of 9.3 in the aqueous solution, the NH_3 form is found, (Varduca 1997, Bucur 1999) in a percentage of 50%, and when the pH falls below 8, the amount of ammonia drops to 4.5%. The nitrogen compounds in the form of the nitrates, nitrites and ammonium appear in the aqueous medium as a result of the decomposition (Böhlke 2002, Caschetto 2014, Caschetto & Winner 2017) and mineralization of the protein substances, that penetrate water either in the form of waste water, industrial ones such as waters from the coke plants, benzene, water from slaughter houses, used water from dairy or fertilizer factories, livestock farms, distribution of the chemical fertilizer, etc. Separately from the decomposition of proteinaceous products, ammonia or ammonium may also have mineral origin or from the decomposition of vegetal matter. The mineral origin occurs by the action of denitrifying bacteria in the ferruginous waters. Under such conditions (Varduca 1997), the presence of ammonium is not noxious, as in the case of the decomposition of the vegetal matter.

A special case of the presence of ammonium and ammonia in the earth's crust is represented by the volcanic manifestations. Like the hydrogen, the nitrogen is a characteristic component of the volcanic manifestations. At contact with water, nitrogen is released in the ammonium form. For the fixation of 73 g / cm^2 of fossil nitrogen, oxygen in quantity of 125 g / cm^2 was released, which represents more than half of the oxygen from the atmosphere. (Hutchinson 1944 quoted by Rankama and Sahama 1970). These areas contain ammonium salts, such as ammonium chloride (NH_4Cl), boron nitride (BN) that can easily break down in the presence of aqueous solutions. In most of the volcanic areas, ammonium salts can occur upon contact with the boiling water vapours under the action (Berbeyer 1947 Rankama and Sahama 1970) of the ferromagnetic minerals from the volcanic lava.

The nitrogen compounds can also be found (Lingle 2013, Lingle et al. 2017) in the earth's crust in sedimentary deposits. These are the "caliche" formations, being associated with chlorides, sulfates, borates, perchlorates and iodates. The "caliche" formations environment has (Rankama and Sahama, 1970) the highest redox potential known on Earth. The nitrocalite (KNO_3) and nitronatrite (NaNO_3) are the most abundant nitrates in the "caliche" formation, but the nitrogenous salts are in a low proportion in relation to the saliferous and gypsiferous levels from this geological formation. In Ciceu - Siculeni area, in order to reveal the origin of the ammonium from the mineral waters, in the period of 2018 and 2019, field works were carried out. They aimed to identify the potential sources that can produce ammonium pollution from the ground, as well as water sampling from the shallow aquifer that could have been polluted from the ground. For the mineral water samples collected from the deep aquifer, the laboratory analysis indicate that ammonium concentrations vary between 0.87 and 1.023 mg / l (FH Ciceu well), 1.03 mg / l for F 513 Racu well and 3.38 mg / l for FH Siculeni well.

In the domestic wells from Ciceu and Barzava, which investigate the shallow aquifer, the ammonium ion has concentrations up to 0.047 mg / l. The analysis of the water collected from Olt River indicates an ammonium concentration of 0.119 mg / l. The nutrient analysis of the carbonated mineral water does not indicate significant concentrations (figure 6). Thus, the results of the chemical analysis of groundwater samples from the well FH Ciceu, indicate that the nitrites have concentrations between 0.014 and 0.072 mg / l, while the nitrates have concentrations ranging from 0.05 to 2.33 mg / l. Taking into consideration that in the Ciceu - Siculeni area the deep aquifer is naturally protected from the shallow aquifer by a 15 - 20 m thick impermeable rock deposit, the results of the ammonium and nutrients chemical analysis, as well as the fact that in the Ciceu - Siculeni area there

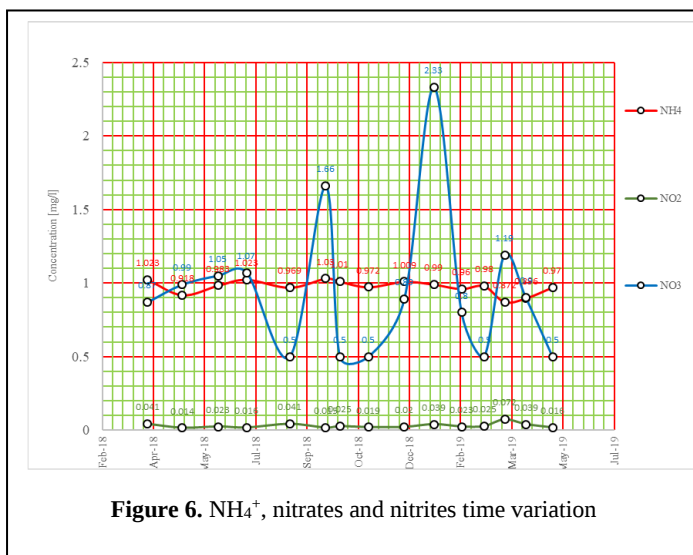


Figure 6. NH_4^+ , nitrates and nitrites time variation

are no industrial or agricultural units that generate organic nitrogen compounds, the origin of ammonium as the degradation of the organic matter of protein type from ground is excluded.

In the geological context of the Middle Ciuc Depression, the region is located in the area of the neogene volcanism. While the volcanoes are no longer active, post volcanic events are extremely common, especially in the crustal fracture areas, generating CO_2 gases, but also other gases such as ammonium. Taking into account the chemical facies of the mineral water and considering that the wells from Siculeni and Ciceu are near a deep fault, in the direction of Racu - Miercurea Ciuc, the origin of ammonium ion is found in the depths of the magmatic chamber. On these tectonic accidents, the carbon dioxide and aqueous solutions circulation can mobilize ammonium from its salts.

Considering the geological and the hydrogeological factors, the possibilities of groundwater contamination from the surface, accentuating the risk areas, the chemical analysis and taking into account the parageneses and the association of

chemical species, etc., it can be concluded, that the ammonium cation occurrence in the mineral waters from Ciceu – Siculeni area is endogenous.

Numerical model

For the simulation of groundwater flow and ammonium transport in porous medium, the numerical model with finite differences (Bear 1972 and 1979, Cretu 1980, McDonald and Harbaugh 1988 - i.e. MODFLOW) was applied. In case of the steady groundwater flow, the finite differences method (FDM) consists in the numerical solving of the explicitly written hydraulic diffusivity equation (McDonald and Harbaugh, 1988) in the form:

$$\frac{\partial}{\partial x} \left(K_{xx} H \frac{\partial h}{\partial x} \right) + \frac{\partial}{\partial y} \left(K_{yy} H \frac{\partial h}{\partial y} \right) + \frac{\partial}{\partial z} \left(K_{zz} H \frac{\partial h}{\partial z} \right) - W = 0 \quad (1)$$

of finite dimensional approximation $\mathbf{V}_{\tau\lambda}$ of the space (Albu & Enachescu 1985, Albu et al 1989) $\mathbf{V} \equiv \mathbf{C}^2(\bar{C}_T) \cap \mathbf{C}^0(\bar{C}_T)$, using the next notations K_{xx} , K_{yy} , K_{zz} the hydraulic conductivity [m/day] in the direction x , y and z , h the hydraulic head [m], H aquifer thickness [m] and W is the leakage flow rate [m³/day].

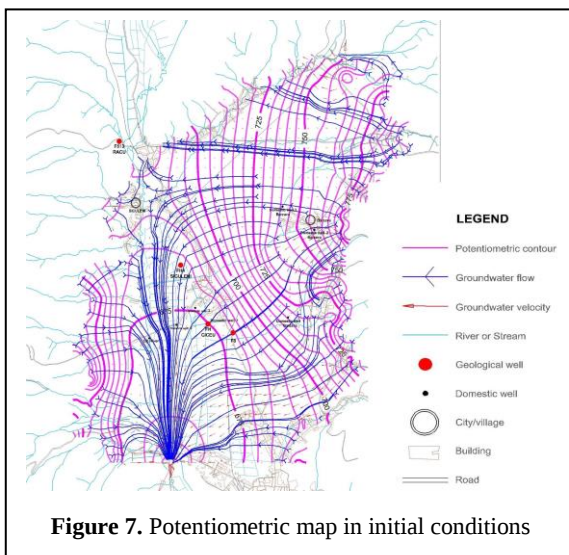


Figure 7. Potentiometric map in initial conditions

The numerical solving of the hydraulic diffusivity equation according to the finite difference scheme implies the partition of the aquifer into representative sub-domains, within which the satisfactory solution for the imposed boundary conditions are found. Thus, the main aquifer was meshed into a network of 70 lines in the x axis direction and 70 columns in the y axis direction, resulting in a number of 4900

elemental cells with a dimension of every cell of 153.8 m on the X - axis and of 181.8 m along the Y - axis.

The parabolic equations associated with the groundwater flow give the possibility to find an infinity of solutions. The solution corresponding the studied case is that which verifies the boundary conditions corresponding to a particular process. In numerical modelling, the main conditions on the boundaries can be (Dassargues 1993) the imposed constant head (Dirichlet type), the imposed groundwater flow rate (Neumann type) and the flow rates conditions dependent by the potential (mixed type). In the steady state groundwater bidimensional flow, the constant head has the expression $h = h(x, y)$. The imposed constant heads were chosen at the contact between the aquifer and the river, lake or precipitation, equipotential lines parallel to the boundary (Gheorghita 1966, Albu and Enachescu 1985), and outcrops of permeable deposits. In the modelling process, the constant heads conditions were imposed on the eastern, southern, western and northern aquifer limits as constant time (figure 8), varying between 730 and 820 m on the eastern limit, 665 - 685 m on the southern border, 705 - 725 m on the western part and 685 - 760 m on the northern boundary.

In the case of non-zero flow, on the boundary S with the surface element ds , for the bidimensional space and in the conditions of the steady states, the required flow condition (Dassargues 1993) is:

$$\int_s k \frac{\partial h}{\partial r} ds = q(x, y). \quad (2)$$

In the modelling process, Neumann type boundary conditions (fig 8) were imposed in the area of carbonate mineral water extraction through the well FH Ciceu with the flow rate of 1.5 l / s. (129.6 m³/day).

In the steady state conditions of groundwater flow, the calibration of the flow model consists in solving the mixed problem in the initial stage, without water

recharge or extraction, requiring only constant heads conditions. By adjusting the values of the hydraulic conductivities (figure 9) and of the storage coefficient, taking into account the hydrodynamic testing of FH Ciceu well, the piezometric heads were calculated, so that between the measured and the calculated values is not a difference greater than 10%.

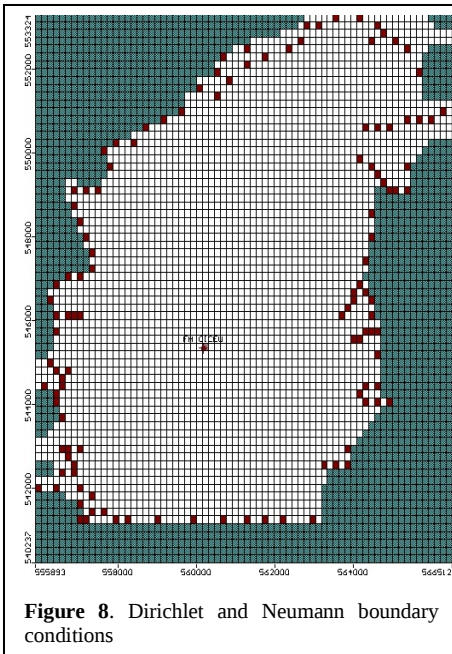


Figure 8. Dirichlet and Neumann boundary conditions

The transporting equation of the chemical solutions through porous media (Bear and Verruijt, 1987, Fetter 1993) is resembling the groundwater flow equation. Thus, the transport of the miscible chemical species through the porous media represents the coupling of groundwater flow and the transport equations. For the aquifers where the concentrations C [mg/l] in a chemical species changes over time, applying Fick's second law, one equation can be written in one direction:

$$\frac{\partial C}{\partial t} = -D_d \frac{\partial^2 C}{\partial x^2} \quad (3)$$

in which $\frac{\partial C}{\partial t}$ represents the variation in concentration over time, and D_d is the molecular diffusion. In the saturated porous media, excepting the concentration changing by molecular diffusion, the dissolved chemical species are transported in the direction of the groundwater flow. This process is called transport by advection, in concordance to the equation:

$$\frac{\partial C}{\partial t} = -\mathbf{v} \text{ grad} C \quad (4)$$

where $\mathbf{V}$ [m / day] represents the groundwater flow velocity tensor. The variations of the velocities along to the stream lines cause the dilution of the chemical species concentrations. The transport variation by advection is achieved by mechanical dispersion of longitudinal

$D_L = \alpha_L V_i + D_d$
and transversal

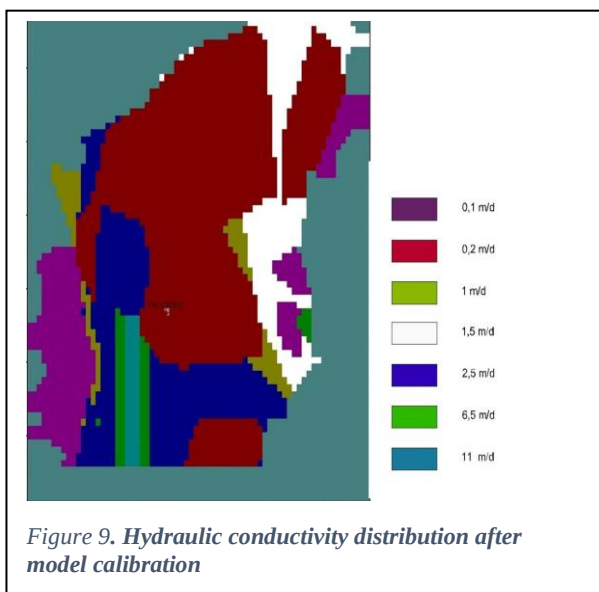
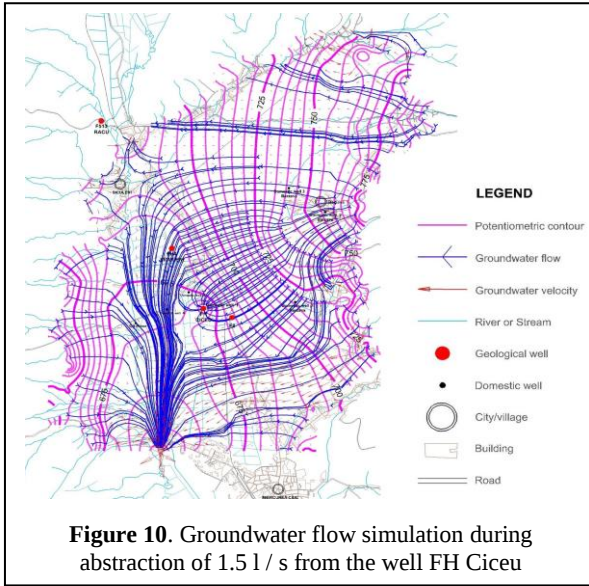


Figure 9. Hydraulic conductivity distribution after model calibration

$D_T = \alpha_T v_i + D_d$ [m²/day] type.

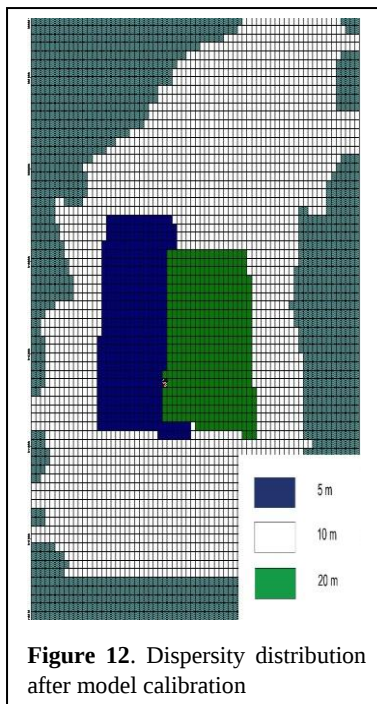
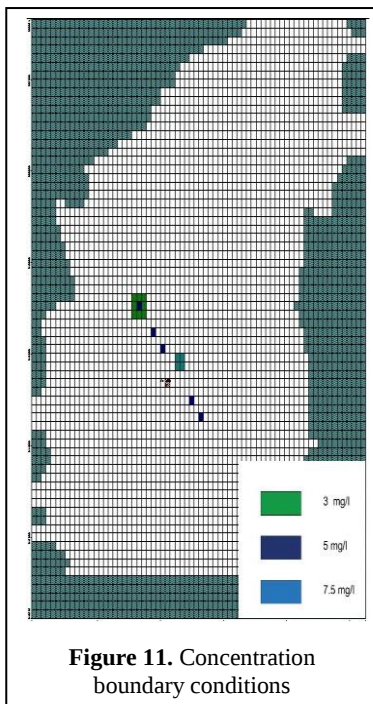


The mechanical dispersions represent a linear combination of the flow velocities V_i and molecular diffusion D_d by the means of the proportionality coefficients α_L and α_T , representing longitudinal and respectively transversal mechanical dispersivities. In the bidimensional space, using the mass conservation law, in an elemental volume, the variation of the massic fluxes occurs in accordance to the coupled equation,

$$\frac{\partial C}{\partial t} = \left[\frac{\partial}{\partial x} \left(D_x \frac{\partial C}{\partial x} \right) + \frac{\partial}{\partial y} \left(D_y \frac{\partial C}{\partial y} \right) \right] - \left[\frac{\partial}{\partial x} (v_x C) + \frac{\partial}{\partial y} (v_y C) \right] \quad (5)$$

which represents the transport equation of the chemical species through the saturated porous media, with the notations C the concentration in a soluble chemical species, D_x , D_y and v_x , v_y the mechanical dispersions, respectively the groundwater flow velocities in the direction x and y .

For the numerical solving of the equation (5), it is necessary to impose both the boundaries conditions and the adjustment of the mechanical dispersivities. In the case of the ammonium migration, the boundary conditions consisted in imposing ammonium constant concentrations in a point manner, along a crustal fracture. The concentrations imposed were considered constant over the time, with higher values than the analysed samples of carbonated water from the wells. In this regard, the imposed concentrations (figure 11) have values between 3 and 7.5 mg / l.



The calibration process of the ammonium transport through the saturated porous medium implies knowledge (Wang et al. 2013) of the mechanical processes associated with groundwater flow, coupled with those of molecular diffusion and the hydrodynamic dispersion, accompanied by chemical reactions and the retardation processes. For the simplification, and considering the absence of information concerning the parameters of some chemical reactions inside the aquifers system and data of the retardation processes, only the mechanical dispersivities fields (figure 12) were taken into consideration. These dispersivities have a variation of 5, 10 and 20 m. In relation to the period of physical – chemical processes related to the ammonium presence in groundwater, the monitoring time in the well FH Ciceu is very short. Thus, the calibration process, was realized so that the calculated values are as close as possible to the measured ones (figure 13).

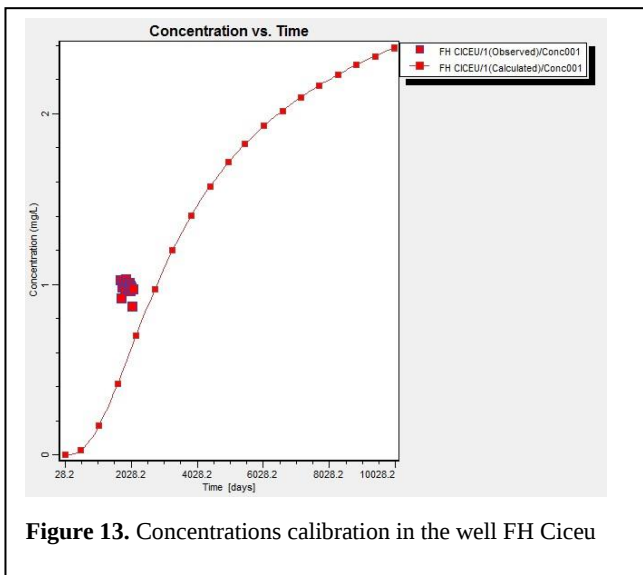


Figure 13. Concentrations calibration in the well FH Ciceu

Results and Discussion

Results referring to the conceptual model

The present study calls attention to more new information. These relate to the geology, hydrogeology and hydrochemistry of the area, with special regarding to the ammonium origin and the transport of this cation through the saturated porous media. The conceptual model construction has brought to light new information referring to the spatial configuration of the deep aquifer in which are stored the carbonated mineral waters, the generating mode of these groundwater's type (figure 5), their chemical facies, as well as the relation between the deep aquifer, the shallow aquifer and the surface waters. In the presented context, the extents of the deep aquifer were defined, it's recharging areas, the groundwater flow and the discharge conditions (figures 2, 7, 14), as well as the aquifer's main hydraulic parameters. Considering the hydrochemical facies of the underground water (figure 5), the aqueous solution is setting up on the basis of the dissolution of the dolomite ($\text{CaMg}(\text{CO}_3)_2$), anhydrite (CaSO_4), halite (NaCl) and silvine (KCl).

Considerations concerning ammonium origin

Between 2018–2019, field investigations and laboratory analysis show that ammonium cations in the domestic wells have concentrations less than 0.047 mg/l for shallow aquifers and less than 0.119 for the surface waters. These results, correlated with field observations, which indicate the absence of economic activities with ammonia production in the area, exclude the origin from the surface of the ammonium cation. Moreover, the concentrations between 0.87 and 3.38 mg/l of ammonium are found only in the carbonated groundwater from the deep aquifer. This cation has concentrations of $0.87 - 1.023 \text{ mg/l}$ in the groundwater from FH Ciceu well, 1.03 mg/l in F 513 Racu well and 3.38 mg/l in FH Siculeni well. In

the case of FH Ciceu well, following the correlation of the ammonium and nutrients concentrations, it results that this cation has deep origin.

Results of the groundwater flow and ammonium transport modeling

In the case of the deep aquifer, after the calibration of the model, were simulated both the groundwater flow processes (figure 7) and the transport of ammonium through the saturated porous medium (figures 10, 13, 14), in the conditions of extracting a 1.5 l / s ($129.6 \text{ m}^3 / \text{day}$) flow rate from the well FH Ciceu. The simulations objective, were to elucidate the groundwater flow process, by confirming the recharge and discharges areas, by configuring the piezometric groundwater surface, in the conditions of a pumping well, observing the produced drawdowns, the direction of groundwater stream lines, hydraulic gradients, distribution of the aquifer hydraulic properties, and the position and the magnitude of groundwater flow velocities.

The coupling of the groundwater flow and ammonium transport was materialized (figure 14) in finding the possible area of ammonium impregnation, originated in the depth, by elucidating the calibration conditions and the underground transport mechanism and, in time observing the evolution of the ammonium plumes. Also, the result of the simulation (figure 14) accentuated the evolution in time of the ammonium plumes, depending on the hydrodynamic spectrum modification due to pumping the FH Ciceu well.

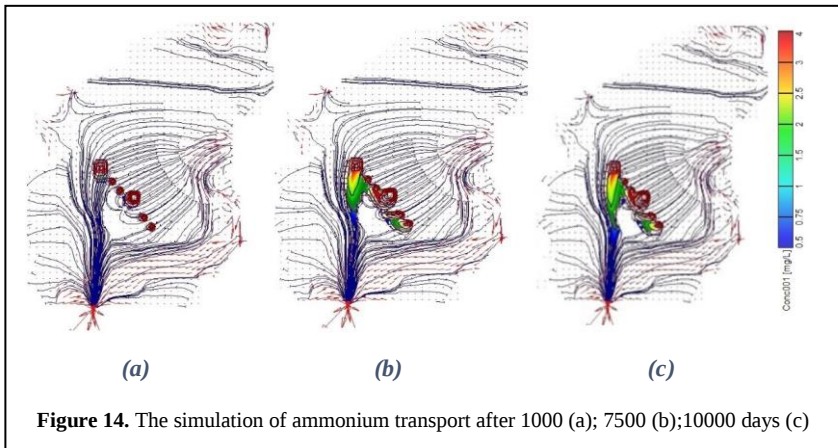


Figure 14. The simulation of ammonium transport after 1000 (a); 7500 (b);10000 days (c)

Discussion referring to the conceptual model

The conceptual model has taken into account the entire data concerning the geomorphology, climatology, hydrology, geology, hydrogeology, using data from the drilling works, water wells, domestic wells, direct field observations, laboratory analysis, etc. Even if the base of the conceptual model is consisting in a great number of data, for the current stage, due to objective limitations, the conceptual model has been transposed only in bidimensional format. In the future, by developing other new complex researches, the current image of the conceptual model can be substantially improved.

Ammonium origin

Concerning the ammonium origin, it can be concluded that it originates from the depth, being transported together with the carbon dioxide on the deep tectonic fractures due to the postvolcanic manifestations. The base of these considerations consist in the ammonium absence in the shallow aquifer, in a good natural protection of the deep aquifer regarding groundwater contamination from the surface, as well as the setting of the studied area being in a postvolcanic manifestations zones. As limits of the hypothesis regarding the ammonium origin, can be considered both the high precision to identify the crustal fractures, representing the gases circulation ways towards the granular aquifers, as well as the ammonium concentration direct data in the crustal faults zones.

Groundwater flow and ammonium transport modeling

The groundwater flow simulation in the deep aquifer has shown (figure 14) that the recharge areas are located to the eastern, northeastern, northern and to the western boundaries, at elevations between 820 m in the north - east and 685 m to the north. The groundwater flow is produced from the east north east to west south west on the aquifer eastern part and from the west to the east in the western part. In the western central area of the aquifer's structure, the groundwater flow is radially converging and the flow has the direction from the north to the south, along the Olt river floodplain. The hydraulic gradients reach their maximum value of 0.09 in the marginal areas of the aquifer's structure, having low values of 0.0004-0.0009 in the Olt floodplain. According to the permeable lithology variation and to the flow conditions, the hydraulic conductivity varies from 0.1 to 11 m / day, in conformity with an inhomogenous and anisotropic aquifer. The pumping of the well FH Ciceu at a flow rate of 1.5 l / s (129.6 m³/day), induces the modification of the hydrodynamic spectrum (figure 10), having 26 - 30 m drawdowns. This process changes not only the piezometric contour layout, but also the direction of the groundwater stream lines, increasing both the hydraulic gradients and the flow velocities. Overall, the groundwater flow velocities vary from 0.1 to 0.2 m / day and 1.5 to 2.9 m / d, in the direction of the southern boundary of the main aquifer.

In the vicinity of the crustal faults, by imposing the ammonium concentrations of 3 to 7.5 mg / l (figure 11), as a result of the transport process simulation, after 10 000 days, the ammonium cation can reach the concentration of 2.4 mg / l in FH Ciceu well. On the surface, the dissolved ammonium plume is expanded from 7.8 x 10⁵ m² in the initial stage to 3.9 x 10⁶ m², after 10 000 days. Largely, the ammonium impregnation area of carbonated groundwater extends southwards, in the direction of the groundwater flow. The axis of the impregnation plume increases from 790 m at 1 000 days (figure 14 a) to 2100 m, after 7 500 days (figure 14 b), and according to the 10 000 days' simulation time (figure 14 c) this axis will increase to 3000 m. On the lateral, the ammonium plume axis increases with much lower values than in the direction of the groundwater flow.

Conclusions

In the Middle Ciuc Depression, the study performed to define the ammonium origin and its migration through the saturated porous media, in the basin area, has a contribution to the improvement of the spatial image of the aquifer structures. This study calls attention for the first time, to the main aquifer heterogeneity and anisotropy, to the groundwater storage and flow conditions, to the genesis of

carbonate waters, and to the ammonium cation origin. In the basin area, in case of the deep aquifer, the groundwater flow is influenced not only by the recharge elevations, but also by the aquifer hydraulic properties variation. The groundwater flow is produced from the marginal areas, being dominantly drained in the area of the Olt river floodplain.

In the sedimentary basin, being located in a post volcanic manifestations area, the ammonium cation has its origin in the magmatic chamber. It runs from the depths to the aquifer generated in the pliocene - quaternary rocks on a crustal faults system. At the present stage, using the existing data, it is difficult to specify with accuracy both the spatial position of the tectonic fractures, and the ammonium concentration in the close proximity of the fault areas. The transport modelling of this chemical species indicates the ammonium plume impregnation areas and their evolution over time. This process is dominantly influenced by the advective factors and less than the convective components. In relation with the revealed information, as a knowledge developing process, the presented model can be improved by answering many unexplained questions.

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