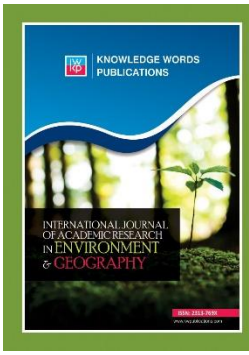

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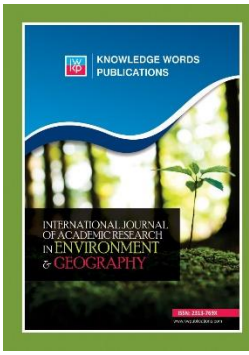

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Geochemical Considerations - Chemical Considerations in the Environmental Impact Assessment for Areas Affected by Industrial Activity. Case Study - Slobozia Aquifer Area, Ialomita County

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Abstract

Pollution caused by anthropic activity (agriculture, industry, non-compliant domestic activities) affects water quality in the long run, especially when the causes of the pollution source are not correctly identified, so remedy measures will be ineffective. This is the situation of the aquifer system Strate de Fratesti through the water bodies ROAG 11, ROAG 12 and ROAG 13, located inside the Arges-Vedea Hydrographic Space.

Due to the economic importance of these bodies of water for the municipality of Slobozia in Ialomita County, numerous studies have been conducted that have analyzed the quality of water in the aquifer (ROAG 12). These studies identified the frequent exceeding of the ammonium ion concentration in the aquifer, but the processes through which it enters the aquifer were not highlighted. The contradictory information presented in the studies and the lack of correct scientific explanations regarding the presence of ammonium ion in groundwater led to the approach of this issue from a geochemical point of view.

The conclusions based on geochemical considerations show that the source of ammonium ion pollution cannot be attributed to the geological substrate, so the source is certainly anthropic,

without proving the source of the pollutant. It is recommended to continue studies on the exact identification, on a scientific basis, of pollution sources, their cessation and the urgent remediation of the affected environmental factors.

Keywords: Aquifer, Pollution, Ammonium Ion, Chemical Hypotheses, Geochemical Hypotheses, Chemical Industry

Introduction

The pollution that occurred many years ago - from intensive agriculture, industry or non-compliant domestic activities - affects water quality today and will continue to do so in the future, if remedial measures are not corroborated with the cause/source of pollution. Experience over the last 30 years in remedying pollution has shown that the measures taken have not been effective, and the sources of pollution, even partially removed, have continued to release pollutants for a long time.

The aquifer is the main source of drinking water, and pollution prevention and rehabilitation is a difficult issue to address, as a clear distinction must be made between contamination-enrichment caused by natural geological factors and anthropic pollution caused by non-compliant industrial and/or domestic activity. In addition, groundwater is a "hidden resource" to which accessibility is much lower than in surface water.

According to the methodology developed by NIHWM (National Institute of Hydrology and Water Management) in accordance with the provisions of the Water Framework Directive 2000/60/EC Aquifer System – Strate de Fratesti is the most important groundwater reservoir in Romania and has an area of 42,423 km2, between the Olt River to the West and the Trotus River to the Northeast. This aquifer crosses the Subcarpathian Dingle, the Romanian Plain and Southern Moldova (Liteanu, 1961). The most important identified water bodies are ROAG 11, ROAG 12 and ROAG 13, being located inside the Arges-Vedea Hydrographic Space, these water bodies are under pressure, being located in Pleistocene sedimentary deposits.

Due to the economic importance of this aquifer, studies were conducted that analyzed the water pollution of said aquifer. All these studies showed the frequent exceeding of the ammonium ion concentration in the aquifer, but did not highlight the process/phenomenon through which it enters the aquifer. Natural causes - geological and/or anthropic – agricultural were mentioned as identified sources of pollution. The contradictory information presented in the studies and the lack of scientific explanations regarding the presence of ammonium ion in groundwater, led to the approach of this issue from a geochemical point of view.

Methodology

The main aim of this research project was the quantitative determination of the chemical species dissolved in the drinking water from the water network of Slobozia city, Ialomita County. To achieve this goal, the sampling program was designed to take samples from both the supplier and the population, and for the highest accuracy of the results obtained, 5 samples were processed for each sampling point, so that the processing or reading error of the results would be reduced.

The processing of the samples and their analysis was carried out within a student project, at the Environmental Quality Laboratory, within the Faculty of Ecology and Environmental Protection, UEB. The CECIL 4004 spectrophotometer was used for the chemical analysis of the

water samples, for laboratory work and the portable oximeter, turbo meter and pH meter, for testing at the site.

For the secondary purpose, that of identifying the real cause of the exceeding concentration of certain chemical species in drinking water, we correlated the results and conclusions of several studies conducted by other researchers, thus highlighting the importance of geochemical factors.

The Importance of Geochemical Characteristics of Groundwater. Ammonium Ion – Ammonical Water

The aquifer is a dynamic system that has the function to storage (storage capacity); the conductive function (transfer of dissolved water and mineral substances from the supply area to the drainage area); the exchange function: physical/thermal, chemical/dissolution-precipitation of mineral substances from the geological and biological environment/self-purification by degradation of organic matter. Therefore, the geochemical exchange function must be corroborated with the geological environment/regional substrate, as it will control the geochemistry of said groundwater.

Therefore, the geological substrate percolated/leached by groundwater is defining, because the dissolved mineral salts are determined by the content of the respective rocks. At the same time, the important role of the geological environment in terms of the conductive function must be highlighted, because by increasing the degree of porosity, the diffusion capacity of chemical species contained in water will also increase, by draining them from the surface to the interior.

The ford area is a buffer between the soil surface and groundwater, acting as a filter (Gastescu *et al*., 1975). The penetration of pollutants into the groundwater is done through the ford area either in an unsaturated regime - dry season and infiltration – or diffusion in a saturated regime - rainy season. Solid state pollutants reach groundwater in the form of dissociated ions, dissolved by a solvent - water, or in the form of fine particles - sediments. Thus, pollutants with high solubility will be entrained by the infiltrated meteoric water, and the suspensions will be deposited along the layers of sedimentary minerals, which have the role of physical filtration. The microorganisms and the lack of oxygen from the deep starts will develop reducing conditions of the respective environment, therefore they will achieve a biochemical filtration through degradation and transformation processes, only reduced species being chemically stable.

Nitrogen salts, both nitrates/nitrites and ammonium are completely soluble in water, thus having a very high geochemical mobility and will rarely precipitate from solutions (Benciu *et al*., 2016). This geochemical behavior is the basis for the formation of nitrogen deposits, explaining their rarity and reduced extent. The only natural nitrogen deposits being in Chile and India, with the useful minerals NaNO3 - called Chile Saltpeter and KNO3 - called India Saltpeter, having a very small surface they are currently depleted by exploitation.

Thus, from a geochemical point of view, in Romania there are no deposits or nitrogen minerals (Urda *et al*., 2002), so even in the studied area, we will remove from the hypothesis the existence of a contamination - enrichment with nitrogen salts caused by the geological environment / substrate.

The ammonium ion is present through a dissolution of ammonia in water, resulting in an ionized solution of NH_4^+ cations and OH- anions, which being an ionic compound, cannot be

isolated as a stand-alone molecule. The term is rather used to show the property of ammonia to dissociate the water molecule in solution (Benciu *et al*., 2016). Ammonia water is water that contains free ammonia or ammonium salts, the content varying between 5-10 g/l, it can also contain hydrogen sulfide, carbon dioxide etc. (Urda et al., 2002).

According to the environmental authorization of SC Chemgas Holding SA, domestic and technological wastewater discharged from the industrial platform contains the following pollutants: suspended solids, ammonium, nitrates, nitrates, phosphorus, detergents, chlorides, sulfates, fluorides, calcium, copper, etc. Wastewater from the chemical industry has a high load (ammonium ions and nitrates) from the installations of ammonia, urea, ammonium nitrate, nitric acid and from the cooling cycles related to the facilities, pre-treated locally is discharged into the wastewater treatment plant biological stage, and after purification, they are discharged into the general collector, where the treated domestic wastewater, including meteoric water, also ends up. From the general collector, the treated wastewater is discharged into the Ialomita River.

Case Study - Ammonium Contamination of the Water Source of Slobozia Municipality

The groundwater body from which the water that supplies the municipality of Slobozia is extracted is coded ROAG 12 and belongs to the Strate de Fratesti aquifer. The body of deep groundwater has a very extensive development on almost the entire surface of the Romanian Plain. The water body is assigned to the Arges - Vedea Water Basin Administration (figure 1) and is located in the Fratesti and Candesti formations. From the point of view of water quality, this deep aquifer provides water that meets the drinking parameters according to the analysis made by ABA Arges-Vedea. The aquifer is under pressure with a low vulnerability to pollution, but has the risk of clogging the boreholes due to the structure of the geological layer in which it was formed and which contains fine sands that are easy to entrain.

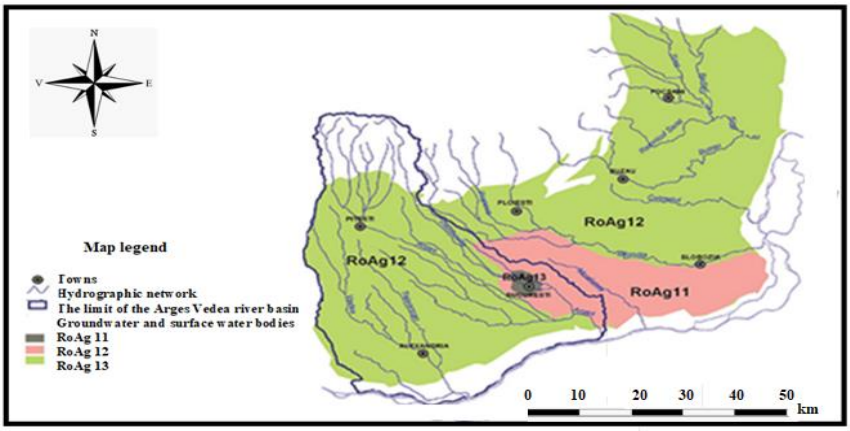

Figure 1. Groundwater bodies attributed to the Arges-Vedea Water Basin Administration
Source: http://www.rowater.ro/daarges/continut%20site/directive%20europene/planul%20de%20management.aspx

From a geological point of view, the bed of the Strate de Fratesti aquifer sinks towards the center of the studied perimeter in the Tandarei - Saveni area (INHGA, 2003). The flow direction is towards the Danube and the hydraulic gradients have values of 3-5‰. The quality of the waters on the left bank of Ialomita (the part on which the municipality of Slobozia is located)

differs completely from the quality of the drillings on the right bank (the part on which the catchment front is located).

The Ialomita Valley is in depth a major tectonic line that determines the change of the hydrochemical character of the waters of the Strate de Fratesti in the Northern part of the river compared to the Southern part (INHGA, 2003). The depth at which Strate de Fratesti is found increases from 20-25 m in the South, to 40-70 m in the North. The aquifer is under pressure and the piezometric level was highlighted between the depths of 20-50 m in the field area and 7-15 m in the meadow area of Ialomita, thus the flow direction is made on the VE direction (Gastescu *et al*., 1975).

At the level of Ialomita County, the source of water supply of the groundwater in this region is the meteoric supply/atmospheric precipitation for Baraganul Central and Baraganul Sudic. This opinion is based on the analysis of numerous boreholes from which emerged the parallel between the groundwater mirror and the topographic surface, the biggest differences being in the areas with sand dunes (Gastescu, 1971).

The deep aquifer located in the Strate de Fratesti was analyzed by exploring 14 drilling wells that exploit water from depths between 55-120 meters. The tests revealed the existence of ammonium ion in concentrations that frequently exceed the CMA (maximum allowable concentration). In five boreholes, respectively Perieti, Slobozia, Cosambesti, Tandarei, Draglina (in the immediate vicinity of the capture front) the ammonium concentration was in the range of 1-2.2 mg/l.

The tests also showed the presence of H_2S, the source being the Dacian/Levantine coal deposits that are associated with pyrite, therefore the source is natural, strictly dependent on the geological substrate.

From an economic point of view, in the studied area economic activities take place that decisively influence the environmental factors. The groundwater catchment front from the groundwater Strate de Fratesti is located along DN 21 Slobozia - Drajna. The land is used for intensive agriculture, being subjected to a continuous process of fertilization with synthetic nutrients. In the same area, a few kilometers away, there is a chemical plant for synthetic fertilizers. The chemical platform is located in the southern part of Slobozia, on the road Slobozia - Calarasi at kilometer 4. The main products are: ammonia, nitric acid, ammonium nitrate, urea and liquid agricultural fertilizers. Wastes from the manufacturing process include ammonia water.

Next, the studies that were carried out both before the implementation of the Slobozia municipality water supply project from the underground source and after the investment will be presented.

• 2001, Romproed SRL, in the "Hydrogeological Study for the Extension of the Underground Water Source of Slobozia Municipality" - shows frequent exceedances of ammonium ion and hydrogen sulfide, ammonium ion - anthropic origin caused by non-compliant drillings/wells, which connected the deep aquifer with groundwater infested with nitrogen compounds used in soil fertilization. Therefore, the cause of ammonium ion pollution is the non-compliant anthropic activity in intensive agriculture corroborated with the non-compliance of the water supply boreholes of Slobozia municipality.

• 2003, the National Institute of Hydrology and Water Management, in the Annual Report, details the quantitative and qualitative characteristics of groundwater in the area of Slobozia

municipality, Ialomita County. Thus, from a hydrochemical point of view, the presence of ammonium above the allowed limit in the perimeter determined by the Slobozia - Dragalina axis (area where the capture front was located) is found. The specialists' conclusion was that according to the piezometric map, the concentration of pollutants (hydrogen sulfide and ammonium ion) decreases in the direction of flow of the aquifer.

Based on the hydrogeological and hydrochemical characteristics, the Strate de Fratesti ensures water flows (200 l/s) at a very good quality, and the location of the catchment front, drilling must be done at a depth of 100 m, respectively 5 m after crossing the last layer sand intercepted to this depth. It is recommended to use a cemented protection column in the back to a depth of 25-30 m to prevent surface infiltration.

• 2005, Geototal SRL - in the study "Supply of drinking water from underground sources of Slobozia and Calarasi municipalities", shows that from a hydrochemical point of view, the water from the Strate de Fratesti aquifer has favorable characteristics for exploitation in order to supply water to the population and it is within the potability limits established by Law 458/2002, except for the parameters: ammonium ion (NH_4^+) and hydrogen sulfide H_2S. It was concluded that the NH_4^+ origin would be of anthropic origin, the source being the water supply boreholes, from the north of the studied perimeter (Perieti - Slobozia – Cosambesti - Tandarei alignment), which do not have adequate insulation, so water is contaminated by nitrogen fertilizer infiltrations, used in intensive agriculture. The study recommends the location of the capture front on the N-S Slobozia - Calarasi alignment, emphasizing the need to place it "as perpendicular as possible" on the flow direction.

• 2006, the National Institute of Hydrology and Water Management - in the Hydrogeological Expertise Report at the Preliminary Hydrogeological Study on Drinking Water from Groundwater of the Municipalities of Slobozia and Calarasi - supports the conclusion of the study conducted by SC Geototal SRL for the location of the front north of the Bucharest - Constanta railway on the NS Slobozia - Calarasi alignment, contrary to the previous study, 2003. It also recommends the sanitary protection perimeter in accordance with the Water Law - 107/1996, by performing two exploitation drillings to establish the water quality and treatment methods.

• 2010, Ialomita Public Health Directorate - in the Triennial Report 2008-2010 on drinking water quality in Ialomita County, following monitoring tests, repeated exceedances of ammonium and hydrogen sulfide concentration, which they associate with "natural geological causes".

•2010, Technical University of Constructions of Bucharest - in the study Assessment of possible risks to change the quality of water at the source, treatment plant and distribution network of Slobozia, highlights the frequent exceedances of ammonium ion, free chlorine and iron. The source/cause of the pollution identified by them being precisely the water treatment attempts for the removal of ammonium, through excessive chlorination processes, which led to interactions between water and distribution pipes. This also led to a change in color and turbidity. The average concentrations for the ammonium ion parameter determined by laboratory analysis is represented in the graph below (Figure 2).

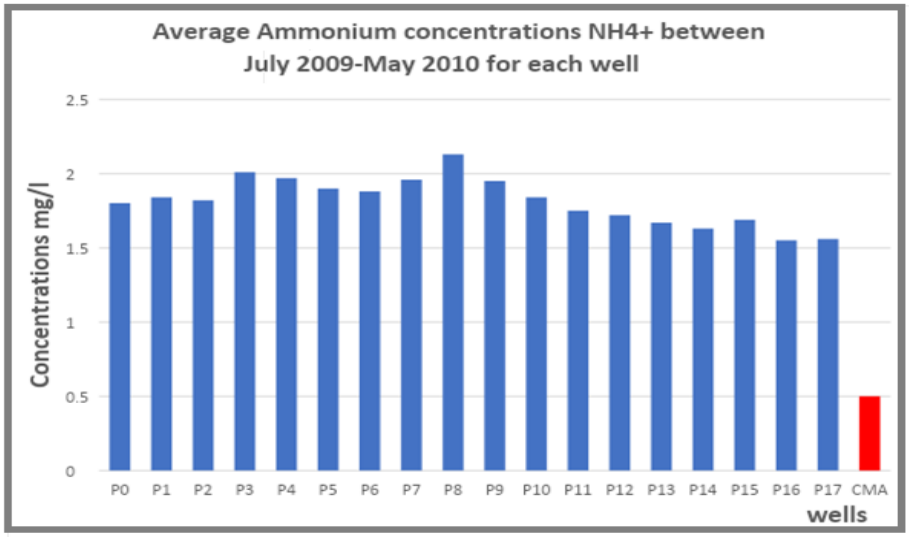

Figure 2. The variation of NH_4^+ in the sampling points
Source: UTCB

The study concludes that: "This phenomenon of ammonia ion aquifer pollution may be explained by its communication with the surface aquifer or contamination of the aquifer upstream, in the direction of flow, in its feeding areas" (UTCB, 2010).

• 2014, Ecological University of Bucharest, in the study ”Drinking Water Quality in Slobozia Municipality, Ialomita Conty” shows significant exceedances to the ammonium ion, both at the entrance to the treatment plant and at the samples taken at the exit of the station and the distribution network. As can be seen in the graph below (figure 3), the results obtained are close in value to the results obtained by the study conducted by UTCB, 2010.

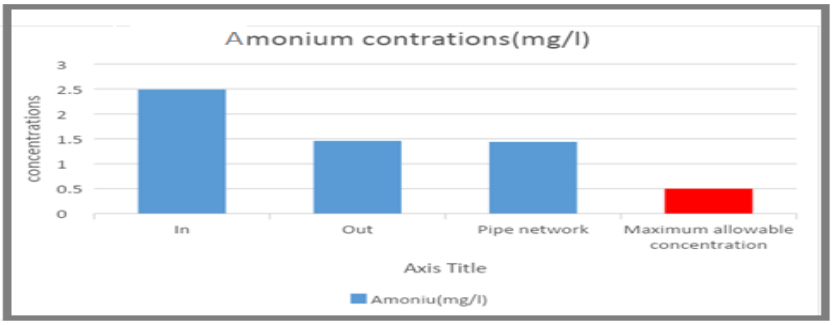

Figure 3. The variation of ammonium concentration during the monitoring period
Source: UTCB

The conclusions drawn on geochemical considerations highlight the fact that the source of ammonium ion pollution cannot be the geological substrate, because regionally/locally there is not a nitrogen deposit, so the source is certainly anthropic.

At the same time, the source - intensive agriculture is excluded, because from a quantitative point of view it would not be possible to have such large quantities present in the deep aquifer.

Conclusions

All studies on water quality in the Strate of Fratesti aquifer, which supplies the municipality of Slobozia, identified the pollution of the capture front with ammonium ions and hydrogen sulfide, but did not correctly identify the source of pollution and the way in which the contamination takes place.

Specialists were unanimous in assessing that groundwater pollution has anthropic causes and concluded, without proof, that the source of the pollutant would be the downstream water wells drilled in the past that have been abandoned and have deficiencies in the isolation from surface layers.

In order to identify the possible sources of pollution, two hypotheses remain to be analyzed:

1 - *The first refers* to contamination due to abandoned or operational drilling rigs that lack layer insulation. According to previous studies, there are no such wells in the perimeter of the front. The only mining drilling is located in Dragalina commune, about 20 km north of the studied area. The drilling feeds the commune with drinking water, and the water quality parameters comply with the legal drinking conditions except for the NH_4^+ parameter, which registers exceedances similar to those found at the studied catchment front.

Taking into account the structure of the Strate de Fratesti aquifer, of which the ROAG 12 groundwater body that supplies the municipality of Slobozia is part, the ammonia pollution from surface sources is excluded. The marly complex that covers the aquifer throughout the studied perimeter prevents the infiltration from the surface of water from precipitation or irrigation that could be contaminated.

The geochemical behavior of marls is that of semipermeable rocks, so they can store various chemical species from the surface, but will not be able to release them, acting as trap rocks for fluid deposits.

2 - *The second hypothesis* is that the groundwater aquifer in the Ialomita meadow located south of the catchment area, in the terrace area, communicates in various ways with the deep aquifer. The hypothesis is refuted by several arguments.

The distance to Slobozia, where there are exploitations of the groundwater aquifer and where there are significant exceedances of H^2S and NH_4^+ concentrations is over 8 km, the distance to the south to Borcea Arm, which is the discharge area, is 18 km and to the direction east of the same point is 40 km. These elements do not justify the consideration of the ROAG 12 water supply from other polluted groundwater aquifers.

The conclusion of the study of the Public Health Directorate, that ammonium pollution would have natural geological causes is not scientifically correct. The presence of ammonium ion in groundwater can have natural geological causes, when there are geochemical premises, in the environment/geological substrate to contain nitrogen deposits/minerals, which is not the case in Romania. Therefore, the causes that lead to the pollution of the aquifer are anthropogenic, the only problem to be clarified being the source of the pollutant and the way it reaches the groundwater.

The analysis of the H_2S - NH_4^+ torque present in the groundwater near the catchment front is another argument for which the pollution of the underground water source is not achieved by the communication between the aquifers. In the area of the capture front H_2S is present in concentrations between 2-8 mg/l in the Slobozia area or 6.4 - 11.5 mg/l in the Perieti

area and the NH_4^+ concentration varies very little, between 1.8-2 mg/l. If the aquifer in the Ialomita terrace communicates in any way with the deep one from which the water for extracting the municipality of Slobozia is extracted, the H_2S pollutant should also be found in the water from the catchment front. Monitoring analyzes conducted between July 2009 and May 2010 by UTCB show that H_2S does not exist.

The lack of H_2S in the water at the catchment front is clear evidence that ammonium ion pollution cannot be attributed to contamination of the aquifer exploited by the meadow aquifer. The global analysis of the ROAG 12 groundwater body that supplies the water source of Slobozia municipality shows that the chemical condition of the water body is good and that the chemical risk is low. The presence of ammonium in only 3 of the 28 observation boreholes indicates very precisely that where the contaminant appears we are talking about point causes due to anthropic activities.

A very plausible working hypothesis in the geochemical and hydrogeological context described above, which could explain the presence of NH_4^+ contaminant and its high concentrations is related to anthropic activities in the study area, namely the existence of chemical industry/synthetic fertilizers locally. The economic unit established in 1970 did not have a treatment plant for wastewater-ammonia from the technological flow. Thus, until 1990, as it results from the documentation carried out in the field, through interviews with former employees of the company, the method of greening these ammonia-residual waters was to inject them under pressure in a well drilled at great depth, 120-180 m. As the procedure is illegal, it is not found in the archives of the economic unit, with indications regarding the volumes of water injected. After 1990, the well was closed, and the wastewater treatment was done by diluting with industrial additive water and discharging into the Ialomita River.

Although based only on field documentation, the hypothesis is to be considered because it explains the large quantitative presence of ammonium ion in the deep aquifer.

The case study presented shows very clearly the very serious consequences of historical pollution in view of the fact that the correct causes/sources of pollution have not been identified, so that remedial measures could not be effective, for example extrachlorination has led to severe degradation of the quality of the water supplied to the inhabitants. Degradation of the biofilm on the metal pipes of the distribution system led to changes in water parameters.

The leaching of the material from the pipe walls had the following effects on the water: high turbidity, change in taste, increase in the concentration of Fe and Mn, increase in the number of germ and bacterial colonies.

From an economic point of view, the real causes of pollution, whether accidental or historical, should not be avoided according to the "The polluter pays" rule, the economic unit or organization environment/community/area.

References

Benciu, F., Bujor, L., Bogan, E., Puia, O., Gabor, S., & Enciu, M. (2017). Evaluation of the Physico-Chemical Water Quality Parameters of Lake Branesti, Romania. *International Journal of Academic Research in Environment and Geography*, 4(1): 17-26.

Gastescu, P. (1971). *Lakes in Romania – Regional Limnology*, Academy Publishing House, Bucharest.

Gastescu, P., Zavoianu, I., & Breier, A. (1975). Les particularités hydrogéologiques de la Plaine Roumaine de nord-est et le régime de variation du niveau piezométrique pendant la période d'excès d'humidité (1969-1973). *Rev. roum. Géol., Géophys., Géogr., Série de Géographie*, 19(2).

Liteanu, E. (1961). Geological Research in the Romanian Plain of the Nord-Est. Tehnical and Economic *Studies. Series E, Hidrogeology*, Bucharest.

Urda, A., Angelescu, E., & Sandulescu, I. (2002). *General Technological Chemestry*, part I, University of Bucharest Publising House, Bucharest.

Romanian Waters National Administration. (2011), Synthesis of Updated Management Plans at the Level of Rivers Basins.

Romanian Waters National Administration (ABA) Arges-Vedea. (2013), Updated ABA Arges-Vedea Management Plan.

Romanian Waters National Administration. (2014), Synthesis of Water Quality in Romania in 2013.

SC Geototal SRL. (2005), Drinking Water Supply From Underground Source of Slobozia.

National Institute of Hydrology and Water Management, (INHG). (2006), Preliminary Hydrogeological Study on the Supply of Drinking Water from Underground Sources of the Municipalities of Slobozia and Calarasi.

National Institute of Hydrology and Water Management, INHGA). (2003), Study on the Detailing of the Quantitative and Qualitative Characteristics of the Goundwater in the Area of Slobozia Municipality.

SC Romproed SRL. (2001), Hidrogeological Study for the Extension of the Underground Water Source of Slobozia Municipality.

Tehnical University of Constructions Bucharest. (2010), Assessment of Possible Risks of Changing Water Quality at the Source, Treatment Plant and Distribution Network –Slobozia Municipality.