



WATER CHEMICAL ANALYSIS OF WELLS IN THREE SETTLEMENTS OF SUCEAVA PLATEAU, ROMANIA

*Andrei-Emil BRICIU, Luciana-Alexandra COSTAN (BRICIU), Vasile Adrian IONESEI, Iulian Ciprian GÎZA, Constantin Mihai ŞCHIOPU Department of Geography, Ștefan cel Mare University, Universității 13, Suceava, Romania *Corresponding author: <u>andreibriciu@atlas.usv.ro</u> Received 21th November 2017, accepted 21th March 2018

Abstract: Water from wells in Humoreni, Comănești and Soloneț (Suceava County, Romania) was sampled in order to measure the concentration of ammonium, nitrite, nitrate, orthophosphate and sulfide. The measured values were used to map the spatial variation of each parameter. Relevant spatial resolution was obtained due to the 15 sampling points in each settlement. The water quality was assessed according to the national standards. The worst water quality (deteriorated class) was recorded in Humoreni and Soloneț (for the orthophosphate parameter), while in Comănești the same water quality was recorded for nitrate. Mediocre water quality was recorded for ammonium in Humoreni; the same settlement also had the highest nitrite concentration (as compared to the other settlements in this study), included in the average water quality class. Sulfide was barely present in the analyzed samples and did not exceed the maximum admissible concentration; however, there are higher concentrations in Soloneț village. The main cause of the observed ground water pollution is the lack of sewerage systems in the studied settlements.

Keywords: *pollution, phreatic water, spectrophotometer, water quality.*

1. Introduction

The water chemistry is in a permanent change in the inhabited areas due to changes in human behavior and land use. The dynamic socio-economic processes are equally affecting surface and ground waters.

The water quality in Suceava Plateau is analyzed in numerous papers that focus mainly on surface waters, such as rivers [1-6] or lakes [7, 8]. There is a generally decreasing water quality downstream [8-10]. The changed surface water chemistry (affected by human activities [11, 12]) is often an indicator of ground water pollution. The ground water contamination and quality in Suceava County is directly investigated in recent scientific works [1, 13, 14]. Not only the temporal evolution of contaminant concentration is of interest, but also its spatial/territorial changes, especially on small surfaces such as the built areas of settlements in Suceava Plateau [15-19]. The latter studies show significant variability of ground water pollution within the built areas, depending on population density, economic practices and various land uses. The objective of this study is to contribute to the knowledge of the spatial variation of selected contaminants in the ground water of the built area of settlements in Suceava Plateau. The analysis is centered on nutrients found in ground water, as they are the main indicators of the social and environmental problems caused by the extensive usage of cesspools/soak pits in rural areas [20].

2. Study area

The study area is located in NE Romania, in Suceava County. The three studied settlements are Humoreni, Comănești and Solonet. These are villages that belong to 2 communes, Comănești (Comănești and Humoreni villages) and Todiresti (Solonet village). According to the 2011 census [21], the population number of Comănesti and Humoreni is similar: 1068 inhabitants and, respectively, 1026 inhabitants. Solonet population village had a of 1527 inhabitants, according to the same source. The total population of the studied area has diminished over the last 25 years, but the on environment human impact has increased due to the higher standards of living. The higher standards include water supply networks for some inhabitants.

The three settlements are completely included in the middle catchment of Soloneţ River. Their built areas are crossed by Soloneţ River and its tributaries (most main tributaries flow from the western hills: Ruşcanul, Cajvana, Botoşana etc.). The hilly landscape is a succession of cuestas with the gentle slopes on the left side of Soloneţ River catchment and the steep slopes on the other side (Fig. 1a). The surface lithology is represented by layers of sands, clays, sandstones, marls, gravel and loess.



Fig. 1. Details of the studied area: a. geographic position and terrain elevation; b, c, d. location of the sampling points within the built area of Humoreni, Comănești and Soloneț respectively

Soloneț and Comănești lie on homoclinal geological strata and their ground water flows according to the geological strata

slope (NW-SE) and to the terrain elevation (eg. towards Soloneț River). In the floodplain of Soloneț River, the ground

Andrei-Emil BRICIU, Luciana-Alexandra COSTAN (BRICIU), Vasile Adrian IONESEI, Iulian Ciprian GÎZA, Constantin Mihai SCHIOPU, Water chemical analysis of wells in three settlements of Suceava Plateau, romania, Food and Environment Safety, Volume XVII, Issue 1 - 2018, pag. 87 - 96

water flow is influenced by the horizontal strata, the river water level and the streamflow direction. The ground water flow in Humoreni on the left side of Solonet River and in its floodplain has the same principles as in the other 2 settlements. In the eastern side of Humoreni administrative area, there are deluvial deposits that generate generally impredictible ground water flow. Also, according to a recent study, there could exist folded geologic strata in Suceava

3. Materials and methods

Water samples from the selected wells were collected in 2015 as part of a broader sampling campaign that analyzed the ground water quality in the western part of Suceava Plateau [18, 19]. Water was sampled on August, 28th from Comănesti and on August, 29th from Humoreni and Solonet. There were 45 sampling points equally distributed within the built areas of the three setlements (Fig. 1b-d).

The water from wells was collected in polyethylene bottles and analyzed within 1 day from sampling. The water chemistry was analyzed by using a Hach 2800 spectrofotometer with specific reagents and methods based on USEPA regulations [24]. Detection limits of the reagents used in this study are: 5-800 µg/l (S²⁻), 0.015-2 mg/l (NH₄⁺-N), 0.002-0.3 mg/l (NO₂⁻-N), 0.1-10 mg/l (NO₃⁻-N), 0.02-2.5 mg/l (PO₄³⁻).

The water quality of the analyzed samples was established by using the classification in Order 161/2006 of the Romanian government. The spatial distribution of the water quality classes within the studied built areas was calculated by using the interpolation between the values of the sampling points in ArcGIS software, resulting in water quality maps.

Plateau [22] and that would directly alter the ground water flow intensity and direction, with implications on contaminant dispersion.

The climate of the study area is temperate continental with an average annual air temperature of ~8°C (with negative temperatures in the cold season) and an average annual sum of precipitation of ~600 mm (with main rainfalls during the warm season) [23].

Synthetic maps of general water quality were obtained by applying the principle used by "Apele Române" National Administration - marking each sampling point with the worst quality recorded by the various analyses (in our case, the worst quality recorded by any nutrient indicator (sulfides do not have quality classes)). On the same maps, an alternative general water quality was estimated by using the arithmetic mean of all quality classes recorded in each sampling point (of each parameter); this calculus method was also implemented in previous studies [17-19] and assumes the value of 1 to the best water quality class and 5 to the worst one.

The methodology in this study is identical to that used by Oprea et al. [18, 19] for assessing the water quality in settlements neighbouring our study area and, therefore, the results are comparable, especially because of the localization of all settlements in the Solonet River catchment. More information regarding the sampling environment and methods is found in dissertation theses of some authors of this study [25-27] (unpublished works that analyzed the ground water quality in the study area).

Andrei-Emil BRICIU, Luciana-Alexandra COSTAN (BRICIU), Vasile Adrian IONESEI, Iulian Ciprian GÎZA, Constantin Mihai SCHIOPU, Water chemical analysis of wells in three settlements of Suceava Plateau, romania, Food and Environment Safety, Volume XVII, Issue 1 – 2018, pag. 87 – 96



Fig. 2. Territorial distribution of the ammonium concentration (values and proportional columns) and the corresponding water quality classes (coloured areas between isolines) in the built area of: a. Humoreni, b. Comănești, c. Soloneț

4. Results and discussion

Sulfide contamination of the studied water wells is not a threat. Thus, only one point per built area with concentration above the lower detection limit was recorded in Humoreni. Comănesti and These concentrations were recorded at point no. 1 $(17 \ \mu g/l \ S^{2-})$ and at point no. 11 (6 $\mu g/l \ S^{2-})$, respectively.

In Solonet village, on the other side, there were 6 points with detectable sulfides. These points (no. 6-11) are grouped on the western side of the village, possibly having a common source of contamination. The found concentrations for points 6-11 are 6 $\mu g/l$, 8 $\mu g/l$, 22 $\mu g/l$, 23 $\mu g/l$, 20 $\mu g/l$ and, respectively. 10 μg/1. In all three settlements, the sulfide concentrations were below the Maximum Admissible Concentration (MAC). which is conventionally set at 100 μ g/l.

The western neighbour of Solonet village is Cajvana town. A previous study of Oprea and Savu [18] detected certain sulfide contamination only in the easternmost sampling point of the town's built area. An aerial or satellite view of Solonet and Cajvana settlements reveals that the short road linking their official built areas is also sparsely constructed with individual houses and properties that link the built areas with a corridor having significant human activities which may lead to ground water pollution. The spatial extension of the common sulfide contamination area, spreading between the eastern part of Cajvana and the western part of Solonet, is most probably favoured by its superposition on the drainage divide that separate Ruscanul and Cajvana River catchments.

The ground water contamination with ammonium is weak as can be observed in Fig. 2 (the water quality is good and very good). A significant exception is only in the sampling point no. 12 of Humoreni (2.95 $mg/l N-NH_4^+$, mediocre quality).

Andrei-Emil BRICIU, Luciana-Alexandra COSTAN (BRICIU), Vasile Adrian IONESEI, Iulian Ciprian GÎZA, Constantin Mihai SCHIOPU, Water chemical analysis of wells in three settlements of Suceava Plateau, romania, Food and Environment Safety, Volume XVII, Issue 1 – 2018, pag. 87 – 96 90



Fig. 3. Territorial distribution of the nitrite concentration (values and proportional columns) and the corresponding water quality classes (coloured areas between isolines) in the built area of: a. Humoreni, b. Comănești, c. Soloneț

The high nitrite pollution in the same point (Fig. 3a) and its weak contamination with nitrate (Fig. 4a) suggest that an important ground water pollution with ammonium occurred in the ground water surrounding the water well or in the well itself short time prior to the water sampling for analysis.

The average ammonium concentration in all settlements is lower than the MAC (0.5)mg/l). The average concentration in Humoreni is 0.058 mg/l N-NH4⁺ (the outlier is not included in calculus); it is 0.070 mg/l N-NH4⁺ in Comănești and 0.043 mg/l N-NH₄⁺ in Solonet.

One can observe that there are high ammonium concentrations around sampling point no. 12 in Humoreni: these concentrations are 2-5 times higher than the modal value in Humoreni. This contamination behavior may be indicative of a buffer zone or of a broader area with mechanisms similar to those that generated the high ammonium pollution in sampling point no. 12.

Compared to other settlements in Solonet River catchment where the water quality in wells was assessed (ammonium - very good water quality exclusively [18, 19]), the water quality in our study area is worse (for ammonium concentration), with some areas having good or worse water quality.

There is no significant water contamination with nitrite excepting point no. 12 in Humoreni (Fig. 3). That contamination is the result of ammonium conversion into nitrite through biological oxidation done by various microorganisms.

most frequent causes of The nitrite contamination are the in-situ dejections and organic manure disposal through the usage of cesspools/septic tanks in the absence of a sewerage (no settlement in the studied area has a sewerage network or a wastewater treatment plant) and the animal husbandry in the built area, in spaces that lack proper buildings and practices.



Fig. 4. Territorial distribution of the nitrate concentration (values and proportional columns) and the corresponding water quality classes (coloured areas between isolines) in the built area of: a. Humoreni, b. Comănești, c. Soloneț

The nitrite contamination is similar to the one observed in nearby settlements [18. 19]. The average concentrations measured in the study area are: 0.008 mg/l N-NO₂⁻ in Humoreni, 0.005 mg/l N-NO₂in Comănesti and 0.007 mg/l N-NO2⁻ in Solonet. The MAC for nitrite (0.5 mg/l) is not exceeded in the monitored water wells. There is a widespread nitrate pollution in the three settlements (Fig. 4). The main causes of nitrate pollution in this rural area is the nitrite oxidation and the usage of nitrogen-based fertilizers (even the organic fertilizers generated animal from husbandry).

Fertilizers are frequently used in the large gardens or agricultural fields that surround the streets along which the houses are built. The studied villages have a complex mosaic of pervious and impervious surfaces generated by the streets network. This complexity incurs the nitrate pollution of the water wells when fertilizers are used in the local agriculture for increased farm output.

The pollution with nitrates is similar to the pollution of the same type observed in settlements of Solonet other River catchment [18, 19]. The average values of the measured concentrations are: 2.6 mg/l N-NO₃⁻ in Humoreni, 3.4 mg/l N-NO₃⁻ in Comănești and 3.1 mg/l N-NO₃⁻ in Solonet. The MAC for nitrate (50 mg/l) is not exceeded in the water samples of the monitored wells.

The ground water polution with orthophosphates is the worst pollution with nutrients in the analyzed area. It has the biggest surfaces occupied with water in the degraded and deteriorated classes (Fig. 5). The water pollution with phosphorus in this area is caused by fertilizers containing phosphorus and by wastewaters rich in detergents. As part of the increasing standards of living, water supply networks are built in Humoreni and Comănești, even if there is no sewerage network.



Fig. 5. Territorial distribution of the orthophosphate concentration (values and proportional columns) and the corresponding water quality classes (coloured areas between isolines) in the built area of: a. Humoreni, b. Comănești, c. Soloneț

According the Suceava County to Masterplan [28], there is a $\sim 10\%$ population coverage with water supply network in Humoreni, with a future perspective of 80%. The population coverage with a water supply network in Comănesti is ~15%, with a 100% future perspective. There is no water supply network in Solonet, but there are plans to offer such a service to the entire population of the village.

The average concentrations of the measured orthophosphates are 1.5 mg/l PO_4^{3-} in Humoreni, 0.12 mg/l PO43- in Comănești and 1.1 mg/l PO₄³⁻ in Solonet. The MAC for orthophosphate (50 mg/l) is not exceeded in the water samples taken from the selected wells.

The environmental problems caused by the lack of a sewerage network and a wastewater treatment plant is not specific only to rural areas with low purchasing power. Even in countries with the highest gross domestic product per capita, important ground water pollution with nitrogen and phosphorus occurs from septic systems of any kind [29].

According to the "Apele Române" National Administration methodology for determining the general water quality by using the existing analyses, there are deteriorated waters in all three built areas (Fig. 6). The worst water quality is recorded orthophosphate for the parameter in Humoreni and Solonet and for nitrate parameter in Comănești.

However, according to the mean water quality obtained through the arithmetic mean, the most polluted points in Humoreni are not no. 13 or 6, but the sampling points located north of them (Fig. 6a). Also, there is a continuous belt of the highest water pollution that divides Solonet village on a west-east direction. The general water quality in Comănești is the same irrespective to the methodology used for classification.



Fig. 6. The worst water quality classes (colour palette for: 1 – very good, 5 – deteriorated) and the arithmetic average of all recorded water quality classes per each sampling point (displayed numeric values on map): a. Humoreni, b. Comănești, c. Soloneț

4. Conclusion

The implementation of water supply networks in rural areas of Suceava Plateau leads to increased ground water pollution because of the missing sewerage networks and wastewater treatment plants.

The most intense and territorially frequent types of ground water pollution are the and orthophosphate pollution. nitrate originated from human and animal manure and dejections, from fertilizers for the built area agriculture and from detergents found in wastewaters.

The contamination of water in wells of Humoreni, Comănești and Solonet has a similar profile to that of other settlements in Solonet River catchment.

The existing water supply networks in the studied area use water from local sources, but, if the observed ground water pollution extends out of the built area due to increased human activities, there is a risk of contaminating the tap water.

supply networks As the water are progressively extending in the built areas of the studied settlements (as planned and implemented strategy), the ground water pollution will increase because of the missing sewerage systems, which means that the entirety of the provided drinkable water becomes polluted ground water.

5. Acknowledgments

We thank Dinu Iulian Oprea (Department of Geography, Stefan cel Mare University) for the templates used in producing maps.

6. References

BRICIU A.-E., MIHĂILĂ D., MIHĂILĂ D., [1]. Short, medium and long term stochastic analysis of the Suceava River pollution evolution in the homonymous city, SGEM2012 Conference Proceedings, 3:809-816, (2012) DOI: 10.5593/SGEM2012/S13.V3039

- [2]. FILOTE C., CIUFUDEAN C., ALACI S., MARUSIC G., COZGAREA A., The spline analysis of parameters and pollutants dispersion in river surface water, *14th WSEAS International Conference on Mathematical and Computational Methods in Science and Engineering*, 1: 243-246, (2012)
- [3]. NISTERIUC C., Study of Siret River and its tributaries water pollution on the territory of Suceava County (Studiul poluării apelor râului Siret și afluenților săi de pe teritoriul județului Suceava), *Abstract of PhD Thesis*, Alexandru Ioan Cuza University, Iași, (2012)
- [4]. ROMANESCU G., CREŢU M. A., SANDU I. G., PĂUN E., SANDU I., Chemism of streams within the Siret and Prut drainage basins: water resources and management, *Revista de Chimie (Bucureşti)*, 64(12): 1416-1421, (2013)
- [5]. MĂNESCU A., MIHAIL L., MIHALACHE R., Identifying pollutants in the Siret River basin by applying new assessment tools on monitoring data: the correlation of land use and physicochemical parameter of water quality analysis, *Present Environment and Sustainable Development*, 8(2): 5-19, (2014)
- [6]. ROMANESCU G., HAPCIUC O. E., SANDU I., MINEA I., DASCALIȚA D., IOSUB M., Quality indicators for Suceava River. *Revista de Chimie (Bucureşti)*, 67(2): 245-249, (2016)
- [7]. ROMANESCU G., SANDU I., STOLERIU C., SANDU I. G., Water resources in Romania and their quality in the main lacustrine basins. *Revista de Chimie (Bucureşti)*, 65(3): 344-349, (2014)
- [8]. BRICIU A. E., Urban hydrology study in Suceava municipality area (Studiu de hidrologie urbană în arealul municipiului Suceava), *Ștefan cel Mare University Press*, Suceava (2017)
- [9]. BRICIU, A.-E., TOADER, E., ROMANESCU, G., SANDU, I., Urban streamwater contamination and self-purification in a central-eastern European city. Part I, *Revista de Chimie (Bucureşti)*, 67(7): 1294-1300, (2016)
- [10]. BRICIU, A.-E., TOADER, E., ROMANESCU, G., SANDU, I., Urban streamwater contamination and self-purification in a central-eastern European city. Part B, *Revista de Chimie (Bucureşti)*, 67(8): 1583-1586, (2016)
- [11]. DIŢOIU V., IOSEP I., Quantifying pollution level of Suceava River in Suceava-Liteni sector (Cuantificarea nivelului de poluare a râului Suceava în sectorul Suceava-Liteni), Annals of

Ștefan cel Mare University, Geography Series, 12(1): 95-100, (2003)

- [12]. MIHĂILĂ D., DIŢOIU V., BISTRICEAN P.-I., The current state of municipal solid waste landfills in Suceava county and their impact on water and soil, *Annals of Ștefan cel Mare University, Geography Series (Georeview)*, 22: 106-128, (2013)
- [13]. HREȚCANU C.-E., LEAHU A., GHIVNICI I., ROPCIUC S., Statistical studies on water quality parameters from two underground sources from Suceava County, Annals of University of Oradea, Fascicula Ecotoxicologie, Zootehnie şi Tehnologii de Industrie Alimentară, 12(A): 249-258, (2013)
- [14]. ZAHARIA C., Evaluation of water pollution status in siret hydrographical basin (Suceava region) due to agricultural activities, *Chemistry Journal of Moldova*, 9(1): 42-52, (2014)
- [15]. BRICIU A.-E., OPREA-GANCEVICI D., Studiu privind calitatea apelor în perimetrul localității Berchişe,ti (Study concerning the waters quality in Berchişeşti Area), Annals of Ştefan cel Mare University, Geography Series, 19(2): 43-56, (2010)
- [16]. BRICIU A.-E., OPREA-GANCEVICI D., Rural hydrology study regarding the phreatic water quality in Dragomirna Plateau, Romania, *Present Environment and Sustainable Development*, 5(2): 279-293, (2011)
- [17]. BRICIU A.-E., OPREA-GANCEVICI D. I., The effect of rural settlements on water quality in northern Suceava Plateau, *Food and Environment Safety*, 10(2): 88-96, (2011)
- [18]. OPREA-GANCEVICI D. I., SAVU C., Ground water quality of domestic wells in Cajvana town, *Food and Environment Safety*, 15(1): 36-45, (2016)
- [19]. OPREA-GANCEVICI D. I., GEMĂNAR A.-I., Girigan A., Assessment of the water quality of some wells in Todireşti and Părhăuți settlements, Annals of University of Oradea, Geography Series, 26(1): 94-106, (2016)
- [20]. WITHERS P. J. A., JARVIE H. P., STOATE C., Quantifying the impact of septic tank systems on eutrophication risk in rural headwaters, *Environment International*, 37(3): 644-653, (2011)
- [21]. I.N.S.S.E., Anuarul Statistic al Județului Suceava 2014 (Statistical Yearbook of Suceava County 2014), *Revista Română de Statistică Publishing House, București*, (2015)
- [22]. OPREA-GANCEVICI D., Folded structures in the homocline deposits of Suceava Plateau (Structuri cutate în depozitele monoclinale ale Podişului Sucevei), Annals of Ştefan cel Mare University, Geography Series, 18: 35-44, (2009)

- [23]. TĂNASĂ I., Climate of Suceava Plateau Risk phenomena. Implications in sustainable development (Clima Podişului Sucevei -Fenomene de risc. Implicații în dezvoltarea durabilă), Abstract of PhD Thesis, Ştefan cel Mare University, Suceava, (2011)
- [24]. <u>https://www.standardmethods.org</u>, last accessed 01.09.2017
- [25]. IONESEI V. A., Phreatic water quality in the territory of Soloneţ settlement (Calitatea apelor freatice pe teritoriul localităţii Soloneţ), Undergraduate Thesis, Ştefan cel Mare University, Suceava, (2016)
- [26]. GÎZA I. C., Phreatic water quality in the territory of Humoreni settlement (Calitatea apelor freatice pe teritoriul localității Humoreni), Undergraduate Thesis, Ștefan cel Mare University, Suceava, (2016)

- [27]. ŞCHIOPU C. M., Phreatic water quality in the territory of Comănești settlement (Calitatea apelor freatice pe teritoriul localității Comănești), Undergraduate Thesis, Ștefan cel Mare University, Suceava, (2016)
- [28]. http://www.cjsuceava.ro/documentenou/MP%20Jud.%20Suceava/Parte%20scrisa/C apitolul%202/Capitolul%202-Analiza%20situatiei%20existente.pdf, last accessed 01.09.2017
- [29]. LUSK M. G., TOOR G. S., YANG Y.-Y., MECHTENSIMER S., DE M., OBREZA T. A., A review of the fate and transport of nitrogen, phosphorus, pathogens, and trace organic chemicals in septic systems, *Critical Reviews in Environmental Science and Technology*, 47(7): 455-541, (2017)