RURAL HYDROLOGY STUDY REGARDING THE PHREATIC WATER QUALITY IN DRAGOMIRNA PLATEAU, ROMANIA

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Abstract. Six villages are analysed in order to observe their chemical impact on the phreatic waters. Ammonium, nitrite, nitrate and phosphate from the water sampling points are analysed and their results are used to make extrapolation maps for the built area of the villages. For a holistic perception, the maps have the absolute values converted into qualitative values upon a proprietary system of the authors. This study allows the statistical identification of the main characteristics of the phreatic water quality in Dragomirna Plateau. We found that some rural areas have a heavily polluted water and we identified the main causes as being the chaotic water supply and the lack of centralized sewerage.

Introduction

The purpose of this study is to present water pollution from inside the built area of some villages in Dragomirna Plateau, Romania. On July the 30th, 2010 water samples were taken from the administrative area of six villages - Adîncata, Calafindeşti, Frătăuţi Noi, Pătrăuţi, Şerbăuţi, Vereşti - to analyze them qualitatively in terms of ammonium, nitrites, nitrates and total phosphorus concentrations.

The villages were chosen from a relatively uniform geographical area, with little spatial variation of geology, topography and climate as controlling factors of hydrology. The settlements were chosen so that they representatively cover the Dragomirna Plateau: 2 villages are on the border between Dragomirna Plateau and Suceava Valley and 4 are within the plateau (Fig. 1).

The geology is represented by a NW-SE oriented homocline with alternating layers of clay and sand (and, sometimes, layers of sandstone) of Volhinian age covered by a layer of loess of variable thickness, often with

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underlying alluvial gravel of Quaternary age. This allows the existence of multi-layered aquifers which are sometimes discontinuous due to facies variability; these aquifers have similar hydrogeologic behavior throughout the plateau (Pascu, 1983). The landscape of the studied villages built area shows almost the same morphological and morphometric features, having the average altitudes between 200 and 400 m. The climate has low thermal and pluvial variability from N to S and from NW (near the Carpathians) to SE. All localities have equal or higher than 600 mm/year of rainfall, excepting Veresti, which has less than 600 mm/year, because the 600 mm isohyet passes through Suceava). The temperatures have a 7-8°C annual average. The soils in the studied villages are also similar: clay illuvial soils of different subtypes and alluvial soils in the flatplain of Suceava river, in Frătăuții Noi and Verești. Concerning the vegetation, it is not taken into account as an invariable factor because it has wide type variations in the built area and its vicinity, from garden, farmland to pasture and forest. Vegetation is often used as an explanation of the variation of the analyzed water quality.

The issue of pollution by nitrates, nitrites, phosphates and ammonium in rural inhabited areas has been generally studied either in terms of spatial budget for
these chemicals in different villages (Manlay et al., 2004), or as case studies on rural areas included in small and easy to monitor catchments. These latter studies have shown that effluents from wastewater treatment plants have contributed significantly to phosphorus pollution of water, along with agriculture (Drolo and Koncan, 2002).

The studies regarding only water quality in villages are less frequent. A study on water pollution in the UK in some villages has shown that ammonium and phosphates are the dominant pollutants and that nitrite has values above those considered dangerous to fish (0.1 mg/l) where septic tanks are used instead of centralized sewerage (Withers et al., 2011). The authors conclude that septic tanks are an environmental problem for water quality in rural areas especially in ecologically sensitive periods. This study is very important for the analysis of the Romanian villages without water sanitation because it shows, by analogy, that they have the same type of pollution.

The origin of a large part of phosphorus pollution from point sources has been demonstrated by old and new studies (Judová and Jansky, 2005; Withers et al., 2011), which showed that high concentrations of phosphate were observed downstream of large human agglomeration areas. Even if there are treatment plants in the catchment, if they are not equipped with tertiary treatment able to remove phosphorus, pollution occurs (Judová and Jansky, 2005). Point sources of phosphorus pollution from agriculture, rather than diffuse ones, represent the most significant risk for river pollution, even in rural areas with large losses of phosphorus. (Helen Jarvie et al., 2006).

Phosphorus pollution of water is the main common characteristic of cities and villages. The secondary characteristic is the N pollution. In the city of Mikasa, Japan, analysis of water samples showed that 35% of the amount of N are from point sources and is attributed to human and animal dejections, the remaining N being from surrounding agricultural lands. Similar features were found in rural areas of the mentioned city (Liang et al., 2006).

Studies on the quality of groundwater from wells used for drinking water, showed different results: in the village of Al-Mahareth from Assir region, Saudi Arabia, showed average levels of nitrates, nitrites and nitrogen (with reference to the maximum concentration permitted by World Health Organization) varying between 23.09 and 25.06 mg/l, 0.006 and 0.36 mg/l and between 0.008 and 0.179 mg/l, respectively (Khanfar, 2010); from 168 wells in villages in Burkina Faso used in a study, 15% of these exceeded the limit of 45 mg/l recommended by the World Health Organization for the nitrate concentration (Groen et al., 1988); in Rajasthan, India, were monitored 21 wells in rural villages of Sri Ganganagar district and were found values of nitrates between 7.10 and 160 mg/l (with average values of 60.6 ± 33.6 mg/l) having as specified source of pollution nitrogen-based
fertilizers, sewage, animal waste, N-based fertilizers, the local geology, the latrines; the conclusions were that waters are heavily polluted because of human activities and are a serious damage to health for the local residents (Suthar et al., 2009).

In the light of this literature background, the present article aims to detect if the highly populated rural areas in Dragomirna Plateau have a similar behaviour, which are the concentrations of the detected pollutants and the possible sources of water pollution.

1. Methodology

20 points were selected for sampling water from the built area and the nearby for each studied settlement. The choice of points was made from wells and springs so that a. they are relatively homogenously distributed in order to form the basis of a map as close as possible to the truth of the spatial variation of the concentration of various substances dissolved in the analyzed water and b. most of them to be positioned inside the built area and only a minority outside it in order to generate isolines with maximum precision in the settlement and to have the extrapolated values inside more close to reality. Of the total of 20 points per village, 15 were analyzed for ammonium (preserving the same principle of homogenous point distribution) and all 20 were analyzed for nitrites, nitrates and total phosphorus. Water samples used in this study were collected in the absence of rainfall both during the sampling time and during the last 2 weeks before sampling (30th July 2010). Chemical tests were made with a Hach-Lange DR2800 spectrophotometer. DR2800 is a portable spectrophotometer often used to detect pollutants, for example to calculate the concentrations of PO4, NO3, NO2 according to the methods developed by HACHDR2800, based on Standard Methods for the Examination of Water and Wastewater (Gill et al., 2009; Rouvalis et al., 2009). Chemical analysis carried out by other authors with DR2800 showed that in rural areas PO4 ions in the water drained after a rain are in higher concentrations than in urban areas; on the other hand, they showed that the NO3 and NO2 anions concentrations are higher in urban areas (Rouvalis et al., 2009). These studies indicate the good precision of the device for the type of analysis performed in Dragomirna Plateau.

The accurately measured intervals by the device by type of the reagents used in the analysis for this study are: ammonium 0.015 to 2 mg/l, nitrite from 0.002 to 0.3 mg/l, nitrate from 0.1 to 10 mg/l and phosphates 0.02 to 2.5 mg/l. Above and below the specified limits, the device can calculate the value of concentration, but with less accuracy than the maximum, more and more diminished by the increasing concentration. We measured points where the real concentration exceeded the
maximum precision range of the device, but also the range in which the device can determine an approximate value, in 5% of tests. Under these conditions, it was assigned by default the minimum round possible value higher than the maximum amount that can be read by the device, depending on the type of reagent used (because this water sample concentrations are higher than the values that can be measured by the device). All water samples were taken from low turbidity points, analyzed within 24h from sampling and the analysis were done when all samples had the standard temperature of 20°C.

In the transformation of data into maps of water quality, absolute values were converted into values of quality classes (according to regulations on water quality - Order MMGA 161/2006) and were used only nitrates, nitrates and total phosphorus because all values of the ammonium are in the first quality class – except for the sampling point no. 6 in Șerbăuți whose value of 0.472 mg/l is included in the quality class 2, being just below the maximum admissible concentration for drinking water - and the purpose to synthetically represent them on a map is not justified. Quality values for nitrites, nitrates and total phosphorus were transformed for each sampling point into columns and the background map is represented by
the extrapolation, in ArcGIS, of the arithmetic average of the three parameters per point (nitrites, nitrates and total phosphorus). ANAR system was not used to create the mixed quality classes based on the principle of the equivalence between the value of the mixed quality class with the value of the maximum value quality class recorded because it would have resulted a single-class background corresponding to the most polluted water recorded, which is always of 5th quality class, the damaged one, mainly due to phosphorus and secondary to nitrate pollution.

The creation of the mixed quality map for the background with isolines starting from a combination of raster maps with isolines representing the extrapolation of values for each parameter per raster-map was avoided (Fig. 2) because a. the errors of a map with isolines generated according to a limited number of points would be multiplied accordingly by joining that raster with another raster-map and because b. that method creates unrealistic cutting of the areas of quality that cannot be true. The method created to avoid the mentioned deficiencies uses the creation of the arithmetic average of the parameters for each point in tabular format and then the extrapolation of those averages in the final map with isolines (Fig. 3). Later, because the errors increase substantially to the edges of the rectangular map because it extrapolates to the infinite the values nearby the village, we created a crop of the map with isolines which represent the values only inside the built area and the corresponding isolines (Fig. 5). A new system of five classes (combined quality) was created for the final maps made to classify the averages of classes; class limits are 1.5, 2.5, 3.5, 4.5 and have identical names and numerical values with the ANAR classes. The making of the maps with isolines has not taken into account the direction and speed of groundwater flow because there is no sufficient data about them. In the deluvial and the homoclined aquifer layers, the isolines drawn on the maps in this article should be softly elongated in the direction of bed tilt over which are the phreatic waters and/or in the direction of the piezometric surface negative curvature, both cases depending on the speed of underground water flow.

2. Results and discussions

Analyses performed for ammonium, nitrites, nitrates and total phosphorus were found exceeding the CMA (maximum admissible concentration) (Fig. 4) in 68 samples (of 423) and 5 samples had concentrations just below the CMA. Among the values that have exceeded the CMA, 54 were for phosphorus and 13 for nitrites; just below the CMA 1 was for ammonium and 4 for nitrite. The number of CMA exceeding per settlement are: 13 at Adâncata, 22 at Vereştii, 10 at Calafindeşti, 6 at Pătrăuţi, 11 at Şerbăuţi and 6 at Frătăuţii Noi. Immediately below the CMA values were 3 at Vereştii, one at Şerbăuţi and one at Pătrăuţi. In Fig. 4 is presented the average value in mg/l at all sampling points on the local parameter
(for ammonium and nitrite the CMA is 0.5 mg/l, for nitrates it is of 50 mg/l and the amount considered the maximum allowable total phosphorus in drinking water is 50 mg/l – there is no CMA).

Fig. 4 – Complex histogram of mean recorded values per parameter for each settlement

2.1. Adâncata. As sources of water pollution in Adâncata, might be mentioned: in the northern village on the Ciocilor Creek valley there is the former landfill and the former stables from the communist period (these sources of pollution correlate well with the mediocre quality of the waters in this part of village (Fig. 5); nitrite concentration is the largest in the village and is due to animal manure from the former stables). In the south of the built area, the use of nitrogen-based fertilizers for a dense apple orchard explains the mediocre quality of water here (the contribution of nitrate pollution).

The whole village is characterized by high levels of phosphorus pollution (phreatic water quality never decreases below 4 for the loading with phosphorus in the built area), which determines an average quality of water in most of the village. Current water supply of a portion of the population generates a greater volume of wastewater compared to other villages not connected to water supply system (and with good water quality of the built area, by default) and then disposed in the underground because there is no sewerage system here; phosphorous pollution may be caused due to the use of phosphorus-based detergents and phosphate fertilizers in the gardens.
2.2. Frătății Noi. The settlement shows the cleanest phreatic water of the villages in this study, the combined water quality being generally good (Fig. 6). Water pollution is present in the eastern built area because of the former communist farm (combined medium water quality) and in the western part where is a neighborhood of gypsies, with a high density of population, of housing and, implicitly, of the cesspool and with very small green spaces between built areas. When villages or neighborhoods of villages are scattered across a large area, the contamination is more diffuse because it is assumed that the plants between houses consume a substantial part of the load of nitrogen and studies on other villages have found that in the wells downstream from the village, in the direction of groundwater flow and surface, there is a high incidence of contamination with nitrates (Groen et al., 1988).

Both mentioned extremities of the village have poor water quality due to nitrate pollution engendered by the human and animal manure. The combined medium water quality in the central part of the village is due to the infiltration in the built area (downstream and according to the inclination of geological strata) of nitrogen fertilizers used on agricultural land outside the built area, from the north, and to the use of the same type of fertilizer in the gardens.
2.3. Calafinestei. It shows average-good quality waters. The waters are the cleanest in the highest part of the village, in the northeast (Fig. 7) where, on the interfluves, there is also a forest; from here, the waters flow through the village, on the surface and underground, and are gradually loaded with different pollutants.
downstream. In the eastern part of the village there is a pasture where fertilizers are annually used.

2.4. Pătrăuți. In the south-west of the village lies the former landfill, and in the south is the former cooperate farm, now occupied by a mill and a cheese factory; also in the south there are the intensely used arable lands. All these explain the average-mediocre water quality from the south part. Mediocre and degraded water quality in the north of the village is explained by the downstream flow of fertilizers annually applied by hall on the pasture outside the built area at north to the village (pollution by nitrates and phosphorus) and by the existence of a dense gypsy community with the same spatial behavior as in Frătăuții Noi (nitrate pollution from human and animal manure and phosphorus pollution from the use of detergents) (Fig. 8).

![Fig. 8 – Map and histograms of phreatic water quality in Pătrăuți](image)

2.5. Verești. In the western extremity of the built area there is the former C.A.P. which had a pig farm (pollution with nitrites); the pollution in the central-east part is due to the existence of former stables on the northern uphill outside built area nearby, combined with the rainwater flow downstream from the northern
lands where the farmers use chemical fertilizers (nitrate pollution), the area being very productive to agriculture (soils, slopes, underground drainage of terrace). In the north-east of the built area there are working stables which generate nitrite pollution. In the central-west part of the village there is an area that benefits from sewage, marked on the map by the average quality of waters. Most of built area (downtown, especially) centralized water supply, which explains, combined with the much poor sewerage coverage, the high levels of phosphate pollution (secondary coming from phosphorus-based fertilizers used in gardens and the northern arable land) (Fig. 9).

2.6. Șerbăuți. In NE of the village pollution originates from the use of fertilizers in the apple orchard in the outside nearby (Fig. 10) and in SE from the former landfill.

By combining the averages per settlement of nitrites, nitrates and total phosphorus, were obtained averages of classes which were then classified using the same system utilized in the combined classes of water quality (figures 6-10) and the values were graphically transposed in Fig. 11. Note that the cleanest groundwater is in Frătăuții Noi, while in Verești it is the most polluted. Calafindești, Șerbăuți and Pătraști have medium values per locality. Adincata is at the upper limit of the middle class.
Regarding the measures that can be taken to reduce groundwater pollution, very representative is the Honigau catchment (Germany) which was extensively investigated from 1972 to 1974 and from 1996 to 1998 and where were monitored the effects of taking various administrative measures to limit water pollution and where, over time, there was a significant reduction of the pollution through the creation of farm wastewater treatment plants; better leakage management gave less pollution with phosphorus, but remained high concentrations of nitrates due to diffuse pollution sources from the agricultural fields (Deunert et al., 2007). Wastewater treatment plants with chemical treatment and built in rural areas should eliminate the problem of point sources (sewage) pollution by phosphorus (Judová et Jansky, 2005). Another measure often cited in international literature is the creation of wetland buffers in the way of diffuse sources of pollutants from agricultural areas. The effectiveness of small wetlands in the amelioration of water nutrient loading has been proven in a small catchment in a rural area of Australia (Rasin et al., 1997). Regarding the water supply when people cannot control the pollution of the phreatic waters and when there is no centralized water supply from
safe areas, it is recommend to place the drinking water extraction wells in the upstream of the villages and to keep a minimum distance from the settlement center (Groen et al., 1988).

Fig. 11 – Synthetic water quality values per settlement

High concentrations of pollutants in the phreatic waters of Verești and Adîncata villages can cause health problems only to people who use water from their gardens, not to those who use the centralized water supply system. Phosphorus pollution due to the introduction of water supply without sewerage system is a sign of socio-economic chaos. The nitrite pollution in Verești is due to a lack of quality control, in the past and present, of the environmental impact of animal manure. We observe, both in Verești and in other places, how old sources of pollution, now disappeared, create a residual pollution.

Conclusions
We found water pollution cases in summer 2010 in some built areas. The studied built areas have wastewater, mainly, and fertilizer, secondary, as sources of phosphorus pollution, fertilizers as sources of nitrate pollution and animal, mainly, and human manure, secondary, as source of nitrite pollution. Some of the pollution sources are remnants of the disappeared ones. It is necessary to repeat the
measurements in the same season and in other seasons in order to detect the
dynamics of values. The knowing of the position of pollution sources and their
characteristics is necessary to choose the appropriate administrative actions.

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