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# 12

# Groundwater Quality Degradation in Obrenovac Municipality, Serbia

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## 1. Introduction

Water has no definition. Any interpretation, explanation, its formula or description, does not actually represent anything of what it really is. Although much is written about it and we think to know all, yet, it remains a great mystery to us. The water is like religion. Everywhere around us, does not impose, used as needed, usually mechanically, we are unable to recognize the salvation role in it. When we have enough water and turn it into a "servant" (means of use), we relate to it with negligence, just like we do with the faith in times of welfare. Only the lack of water and the need for it create a sense of ontological connection to us. And then we devote ourselves to prayer. And the greater the need for it becomes, the more zealous the prayer is.

In any well-organized society people's attitude toward water has a special status. If the need for quality water is greater, and its availability is lesser, awareness of the need to preserve and nurture this resource is also greater. During the medieval subsistence economy, the water quality problem did not exist and it was used in its natural state without any special treatment. By social division of labor, development of cities and urbanization, industrialization and intensive agricultural production, a man comes into conflict with the water. Although the conflict was inevitable, it seems that in many communities (societies) a good chance to keep it under control was omitted. So, from a natural ally, we have created ourselves an opponent to whom we are not worthy rivals, nor will we ever be. And all we needed to do was to show just a little respect.

In Serbia, we have long lived under the delusion that with 6000 $m^3/s$ of water flowing off from our territory and 10 million inhabitants, which is 52 $m^3$/inhabitant/day, we fall into countries with the high-water supply. At the end of the last century, the intensification of climate oscillations brought frequent and long drought periods, which pointed to the weaknesses of our water management systems. Then we have remembered that a water crisis is threatening, because, in fact, only 8 % of all waters that flow off are the domicile

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waters (4 $m^3$/inhabitant/day). And with a shortage of water we have also found out that its quality is very bad, considering both surface and groundwater. In the meantime, the need for water has been growing, used resources have been diminishing, and our awareness of the water has not changed a bit since the eighties of the last century.

Although the groundwater participates with 70 % in water supply of the population, its importance is not nearly dedicated enough attention. All the advantages that this resource has over the surface water are often ignored, especially at the time of the river reservoirs construction. One of the indicators that proved poor treatment of the groundwater is considerably more modest monitoring that is carried out over it in comparison with the surface water. Perhaps because the last mentioned is in the sight of every one of us and because the impact of public opinion is extremely important and present in every society, especially ours. Thus, the control system of water quality, or monitoring in general, unfortunately, is a sensitive issue, a subject of finances in a great deal, and thus gets a political connotation as well. In cases of extreme phenomena of water degradation, as it is in the Borska River Basin (one of the largest copper mines in Europe), even the most terrible consequences that are visible, cannot change anything because this issue is under State jurisdiction. The situation is similar with the Topciderska River that flows through the urban core of Belgrade. Although it is known to be one of the most polluted in the country, as demonstrated by regular monitoring, little is changing in a positive way because in the background of the problem, bigger interests are at stake. A constant exceeding of the maximum permitted concentration of mercury and heavy metals, phosphorus and nitrogen compounds (Dragicevic et al., 2010) is occurring throughout the whole length of this river. In addition, the university experience indicates that students of natural sciences such as geography, biology, forestry, agriculture, come to study with a very superficial knowledge of the groundwater, accumulated in previous education. And this is also a sign that this issue is on the social margins.

Quality studies of well and spring waters in Serbia include only limited territory, insignificant compared to the total area. Continuous monitoring is performed by state institutions (Environment Agency and its services), and includes only the observation well stations, and the certain sources of the wells. It does not include the quality of well and spring waters in inhabited areas; the quality is usually monitored when it is already too late, only in cases of health problems of the population. Basic idea of this study is to show the quality of the groundwater on the territory that is under permanent anthropogenic pressure. The Municipality of Obrenovac was selected as the one of those that had a larger number of the springs and wells for the population water supply, and which were not part of the monitoring, more exactly the space with recorded environmental problems.

## 2. Research area

The Municipality of Obrenovac is an integral part of Belgrade region and is located in its western part. The two most striking morphological shapes of this area are the River Sava, which makes its northern border and the right tributary of the Sava, the Kolubara River, with its broad valley bottom. The Municipality consists of the town Obrenovac (24 000 inhabitants) and 28 villages with a total of 74 000 inhabitants. The town acquires particular attention in the seventies of the last century when two power plants (Nikola Tesla 1 and 2) were put into operation, which under the current conditions produce about half the electricity in Serbia. These two systems operate on the basis of the exploitation of lignite from the Kolubara basin that provides 70 % of coal in the country. The basin is located next to the Municipality of Obrenovac, its area is of 600 km$^2$, and the estimated reserves of lignite in it are 2.2 billion tons.


Fig. 1. Position of the Obrenovac Municipality in Serbia

Testing of the groundwater quality was conducted in the south-western, rural part of the Municipality which still does not posses water supply network and which is out of permanent monitoring. The central point of this area belongs to the plane of Dubrava, which is, compared to the surrounding terrain, raised about twenty meters and where the agricultural production is performed. This activity is highlighted as an important cause of degradation of the groundwater quality due to uncontrolled use of fertilizers and other agro-chemical substances. Next, even more important cause is very poor municipal sanitation. Namely, the construction of the septic tanks was carried out without any approval and necessary documentation, often in a primitive way without any insulation enabling contact of feces and groundwater. In addition, most households own livestock and that means collecting manure for fertilizing crops as well. We are convinced, however, that the disposal is not done in hygienic manner and that these plots are not secured, so smooth infiltration of the manure into the soil is carried out. Also, neither the collection nor disposal of municipal waste is regulated in this area which adds to the pollution. Unfortunately, despite the clear environmental degradation of Dubrava and its environment, it will not be easy to fight for a more favorable status. It is quite clear that, for example, each and most compelling criticism of the power plant does not force changes because its harmful effects require huge investments for rehabilitation. And in the time of general lack of money and in the knowledge that such power plants are the "engine" of the half of Serbia, it is not hard to see who will have an advantage in public. What influence they may have gives the fact that only 2 km from Dubrava there is the ashes disposal site where about 2.5 million tons of coal ash is disposed each year.

In addition to waters from the Dubrava area, this study has included the spring horizon, unique in Serbia, which drains the same groundwater zone at the foot of the scarp. The aforementioned spring series, represented by sixty hydrological springs is a rarity that needs state protection and in that sense, this research should be the driver of a broad campaign of its revitalization.

## 3. Previous studies

Environmental problems in Obrenovac Municipality are evident for many years. However, only in recent years the systematic observations are carried out, the data are collected in order to put monitoring in service of plan making to solve the problems (Dragicevic et al., 2008). Although pollution has been observed in all spheres, the existence of thermal power plants has caused water and soil to be of secondary importance, and that special attention is paid to the air. Therefore, since 2006 there has been a station for automatic measurement of air pollution in Obrenovac, which detect values of 5 parameters (NO, $NO_2$, $NO_x$, $SO_2$, $PM_{10}$). According to preliminary results of the environmental situation in Obrenovac (Municipality Press, 2010), it is stated that the concentration of the first four parameters has not seriously threatened the people's health, but the content of fly ash and particles with a diameter smaller than 10 μm ($PM_{10}$) are very high and there was several days period when it was constantly above the allowable limit. According to Nenadovic S. et al. (2010) the air pollution is significantly affected by weather conditions, where the situation is much worse in winter. Contamination of the air by nitrogen and sulfur compounds is very important for water as well, because their dissolution in the atmosphere create acid rains that are very harmful to soil and groundwater, and contributes to the mobility of heavy metals from soil to water. Wind flow in this area is such that Dubrava is the first targeted.

The only study to date, covering all aspects of environmental degradation in Obrenovac Municipality was published in 2007 titled: "The intersection of the current status of the presence of hazardous and harmful substances in the environment in the Municipality of Obrenovac" (CIP, 2007). Identification of pollutants of air, water and soil has been carried out and then by sampling from different locations, the composition of these areas has been analyzed. In the Dubrava area, 8 locations (wells) were selected for the groundwater quality analyses. Of these, 5 had the physical-chemical incorrectness (increased turbidity, ammonia, nitrates, nitrites, $KMnO_4$ consumption), while the bacteriological tests showed 6 incorrect samples (mainly the presence of coliform bacteria of fecal origin). The general conclusion was that environmental problems are most often a result of emission from power plants, the existing ash disposal sites, inadequate use of agro-technical products and poor sanitation utilities. This study did not analyze the spring water, nor was it anywhere referred to as groundwater resources.

The aim of this study was to check a much larger sample of well water condition of Dubrava, as well as the springs in its foothill. The first reason is that these are the only sources of water supply for about 6500 inhabitants of the related settlements, and the other is an attempt that, as part of water protection measures, the spring series gets the status of natural resource and restores the functions it had till the end of the eighties of the last century.

## 4. The origin and morphological characteristics of the terrain

Dubrava is the part of a large Vukodraz-Tamnava plane that binds to post-lacustrian phase of the Pannonian Basin. Loose sediments at the bottom and the rim of the Pannonian basin have a great distribution and great thickness, which indicates the long-term marine-lake period in the basin. The original lake phase of the basin was replaced by the marine phases, which lasted from the middle Miocene to middle Pliocene. The last marine phase of the basin was in the lower Pliocene, and after the middle Pliocene lake-continental phase in the southern rim of the basin resulted in the last lake phase, which lasted from the Upper Pliocene to Middle Pleistocene (Markovic, 1967). Disappearance of the lake and draining its bottom created the modern network of the flows unified in the Danube River system. The youngest flow has become the main stream (the Danube), and the older flows, the former tributaries of the sea and the lake (the Sava, the Kolubara) have become the direct and indirect tributaries of the Danube. Only with the advent of the Sava and its cutting into the central lake level, its tributaries have been activated which turn the former lake riparian landscape into fluvio-denudational shape.

Vukodraz-Tamnava plane is 140-115 m high and points to the more persistent erosive base, relatively tectonic state of rest and the favorable climatic conditions during its formation. Part of this area, which is important for this study (Dubrava), is a local divide, low tump between the Sava and the Kolubara in the length of 12 km, southwest-northeast direction extension and the surface of 97 $km^2$. The greater part of it, 65 $km^2$, slightly tilted to the south, southeast and east is intersected by shallow valleys that converge to the Tamnava and over a dozen sources drain in Ljubinic, Trstenica and Stubline. The smaller part, 32 $km^2$, is oriented to the north and ends with the Posavski scarp. It is one of the more outstanding forms of the lower Posavina. This scarp is both the right valley side of the Sava and the part of famous South-Pannonian scarp consisting of the Posavski and Podunavski scarp. At the rim of Dubrava, this scarp is twenty meters high, although in the west is higher, up to 38 m. Built by the River Sava while intersecting along the Sava trench, and the side moving toward the south taking off the soft lake sediments. Between the current Sava and the scarp there is a distance of ten kilometers, and in that zone a younger form exist, the Sava scarp, 7.5 m high, which follows the course of the Sava River through its entire length. It is the younger one, of the Holocene age, while the Posavski scarp is predominantly of the Virm age. There is a lot of evidence among them showing the building of the terrace plateau made by the Sava. These are its oxbow lakes which are nowadays still clearly observed in the relief (Velika Bara, Mala Bara, Jazmak).

A characteristic feature which distinguishes this area in the geological sense, and is important for the formation of groundwater, is almost exclusively represented by Neogene and Quaternary formations. They have a large surface and lie over the Paleozoic and Mesozoic rocks. These older ones are created at the bottom of the Pannonian Sea, and are mostly made of marl, sand and clay. The youngest sediments in the form of sand and gravel fill the lowest areas of the Sava and the Kolubara valley bottoms.

## 5. Lithological composition and hydro-geological properties

Hydro-geological conditions at Dubrava are showed best by the profile of the drill made in Vukicevica (130 m above the sea level) up to 373 m depth (Milojevic et al., 1975). The dominant layer is made of marly clay, thickness of 220 m and starting from 55 m of depth. Below it, clay, marl, sandstone and limestone take turns in different varieties, and usually mixed with each other. Above marly clay layer, there is a layer of gray sandy clay, about 20 m thick, whose upper limit is the lower limit of phreatic aquifers. Groundwater zone is composed of fine-grained quartz sand about 7 m thick, which on the given profile appeared at 26.6th meter. Yellow clayey sand, also water-bearing (3 m), gravelly clay (4 m) and yellow clay on the surface (19 m) are deposited over it.

The first water-bearing horizon in this zone is located in small-grained quartz sands at a depth of 23 to 33.5 m, and the absolute elevation of 97 to 107 m. Clayey sediments of limestone beginning at a depth of 273 m prevail below this series of sediments. Upper series of sand is formed of yellow clay which is pebbly in places. This clay cover has a wide distribution, so that it extends eastward from Vukicevica, through Trstenica to Stubline, then to the village of Grabovac, in the area of the village of Dren and elsewhere. In a series of thin sands there are intercalations of coal. This sand and gravel come to the surface of the terrain in the village of Dren, in the River Vukicevica itself, and then appear on a steep section of Drenovacka Voda at a level of 95 m, where a powerful spring also appears.

Formed aquifer is of freatic type. Upper clay aquifers are formations that are saturated when the water is practically water impermeable, so the aquifer is poorly fed with water from precipitation. Therefore, the amplitude fluctuations of the groundwater levels are low and usually amount to 1 m. During intense rainfall the terrain gets wet, and water is collected in the hollows and large swamps are created. Such phenomena are very common in the zone Grabovac-Vukicevica. Shallow surface water flows collect and drain the surface water, so that a little water is retained on the terrain and infiltrate the underground. In dry periods the clay is dried, cracks are formed which, in the first stage, could receive a certain amount of water and partly pass it further. Phreatic aquifer is of a large expanse. Depth to water level in some parts of the terrain is different, but typically ranges from 18 to 22 and even up to 25 meters.

Spring series under the Posavski scarp is probably unique according to numerousness in Serbia. As per our study, 60 springs have been noted, and it seems that there are even more of them (inaccessible, neglected springs...). They all feed from the same phreatic aquifers formed in Dubrava. The aquifer is tilted to the north and has no a great fall, and all drainages are at altitudes of 90 to 95 meters.

Southern rim of the area (Dubrava) is poorer in springs and they are tied to shallow valleys of the Josevica (one spring in Ljubinic) and the Trstenica (ten springs in Trstenica and Stubline), and four springs have been recorded on the eastern border in Stubline in the foothill of the scarp towards the alluvial plain of the Tamnava and the Kolubara. All of them belong to the same water-bearing horizon as the springs of Grabovac-Dren scarp, considering that the aquifer from the Dubrava peak profile is oriented to the south. Western rim of the Municipality belongs to the convergent area of the Vukicevica basin. Its underground is part of the same hydro-geological collector as well, and the spring series can be traced back from the spring bend of the river to the place where it breaks the scarp between Grabovac and Dren (16 springs).

## 6. Analysis of the well water

Well water at the site of Dubrava was studied in ten villages located on the area or around it. Sampling was conducted on two occasions and both times in the autumn of the years of 2008 and 2009. Selection of wells was such as to cover the largest possible area of Dubrava and discover possible directions of the pollutants movement. The organization of this research is reflected in carefully guided records of all wells. In that sense, the great number of information has been collected in order to provide all the relevant indicators of the current situation, but also to establish the proposals for possible remediation. In addition to basic data about the owner, a sketch of the position of wells in relation to housing and auxiliary facilities has been made. Each well has been photographed and the GPS coordinates have been recorded. The depth of the well, its diameter and the depth of water in it have been measured. Then the manner of how the water is drawn has been described, whether it is done mechanically or manually. The data on whether a well is dug or drilled, when it was built, when it was last cleaned, what is its coating and the condition of retaining wall are also important. The number of households served by each well has been recorded and also the total number of the well consummators. The distance from the septic tanks has been calculated and each facility that may affect water quality has been noted.

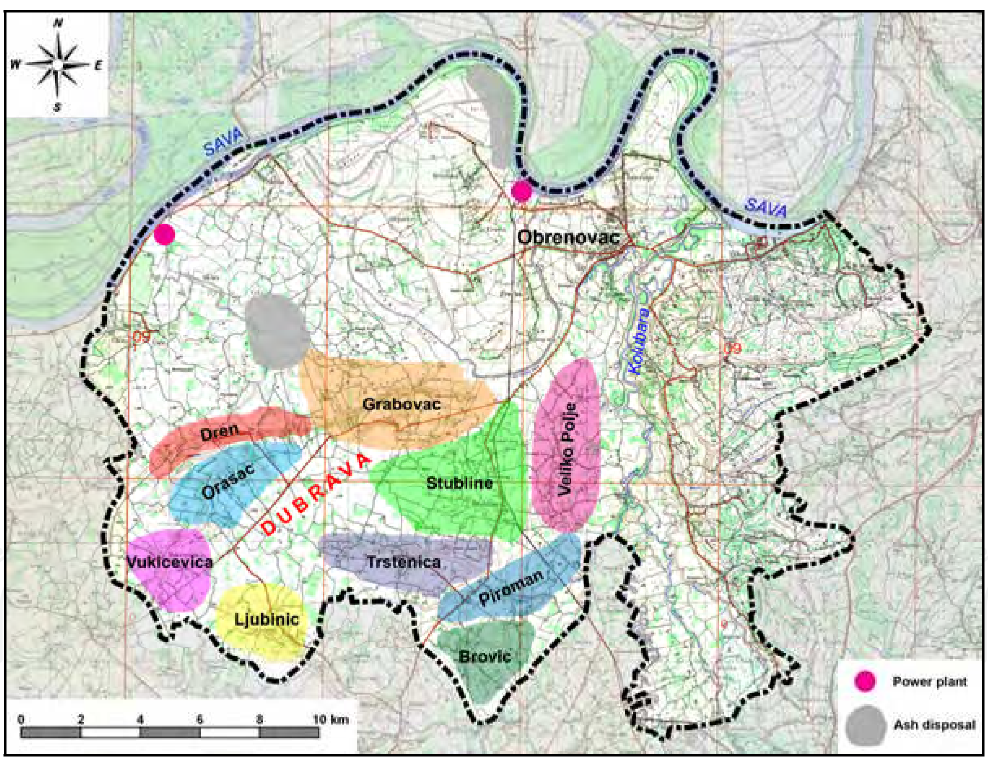


Fig. 2. The locations of wells in villages of Dubrava (Topographic Map 1:50000, VGI, 1970)

On the occasion of the on-site sampling, we have measured the parameters that can be easily changed by standing and during transport: conductivity, pH, temperature and oxygen content. Two samples were taken from each well, one of which was used for bacterial and the other for chemical analysis. Microbiological analysis for total mesophilic bacteria has been carried out using the method of membrane filtration and seeding on a suitable substratum for the total microorganisms. Determination of coliform bacteria and *E. coli* has been also done using the method of membrane filtration and seeding on specific substrata. Besides this, the analysis has included 22 parameters for which the maximum allowable concentration was regulated. These are: turbidity, color, odor, conductivity, pH, $KMnO_4$ consumption, ammonium ion, nitrates, nitrites, chlorides, sulfates, phosphates, calcium, magnesium, iron, anionic detergents and heavy metals (As, Hg, Pb, Cu, Cd , Cr). Analyses of all parameters are derived and aligned with national and international regulations (SZZZ, 1990; USEPA, 1983; Rump & Krist, 1988).

### 6.1 Physicochemical analysis

The total number of wells where the water quality has been tested is 351. The number of samples in the settlements is such that reflects their size (number of inhabitants) and spatial representation on Dubrava. Table 1 gives an overview of the results by settlements.

| Settlement | Num. of samples | Acc. to one param. | Acc. to several param. | Defective samples | | Correct samples | |
|---|---|---|---|---|---|---|---|
| | | | | Num. | % | Num. | % |
| Piroman | 27 | 2 | 13 | 15 | 56 | 12 | 44 |
| Brovic | 23 | 5 | 1 | 6 | 26 | 17 | 74 |
| Trstenica | 32 | 12 | 15 | 27 | 84 | 5 | 16 |
| Ljubinic | 22 | 9 | 7 | 16 | 73 | 6 | 27 |
| Vukicevica | 18 | 8 | 7 | 15 | 83 | 3 | 17 |
| Stubline | 89 | 45 | 37 | 82 | 92 | 7 | 8 |
| V.Polje | 28 | 8 | 3 | 11 | 39 | 17 | 61 |
| Orasac | 23 | 1 | 2 | 3 | 13 | 20 | 87 |
| Dren | 33 | 11 | 10 | 21 | 64 | 12 | 36 |
| Grabovac | 56 | 18 | 19 | 37 | 66 | 19 | 34 |
| Sum | 351 | 119 | 114 | 233 | 66 | 118 | 34 |

Table 1. Deviation from the MCL (maximum contaminant limit) according to physico-chemical parameters

Shown collectively, the correct (proper) 118 wells make only 1/3 of the total number. There is great disparity among settlements in terms of physicochemical correctness of water. The worst situation is in Stubline with only 8 % (7 of 89) satisfactory results, while in Orasac it is 87 % (20 of 23). Only three settlements have more than a half number of proper samples and it is a clear indication of poor water condition. In addition, half of the incorrect samples deviated in terms of quality by just one parameter, while the other half were invalid on multiple parameters. Such a relationship is more or less represented in the settlements as well.

Of all undesirable substances contained in water, the most common are nitrates. They were detected for 220 times, which means that in 63 % of the tested wells they exceed the MCL. Their presence is not of a local character, because they were found in all settlements. In addition to the spatial representation, what concerns is much greater presence than allowed. The mean value of nitrates among the improper samples is 182 mg/l, which is 3.6 times more than the MCL. In addition, 65 samples were with over 200 mg/l, and 8 with more than 500 mg/l.

| | Turb. | E.C. | pH | $NO_3^-$ | Ca | Mg | As | $SO_4^{-2}$ | $NH_4^+$ |
|---|---|---|---|---|---|---|---|---|---|
| NºD.S. | 3 | 97 | 1 | 220 | 26 | 43 | 1 | 10 | 1 |
| MCL | 1 | 1000 | 6.8-8.5 | 50 | 200 | 50 | 0.01 | 250 | 1 |
| Avg. | 11 | 1195 | 5.2 | 182 | 224 | 64 | 0.04 | 366 | 1.16 |
| Max. | 15 | 1860 | 5.2 | 739 | 285 | 99 | 0.04 | 683 | 1.16 |

NºD.S. - number of defective samples, Turb. - turbidity (NTU), E.C. - electrolytic conducti-vity (μS/cm), Cations and Anions in mg/l, Avg. - average

Table 2. Analyses results of the parameters that overstepped the MCL

According to the number of samples that exceed the MCL, the next parameter is the electrolytic conductivity. There were 97 of such samples, that is, 28 %. Overruns have occurred in all settlements and usually in those wells where the nitrate excess was detected. Calcium and magnesium ions are present in 26; that is, in 43 wells in unallowable concentrations. This excess is not large, although it is evident that the calcium concentration in all wells is slightly increased in comparison to natural water and is usually above 100 mg /l. Increased presence of sulfates is noted in 10 wells, but it is important that all samples were detected in only two settlements on the eastern rim of Dubrava. Of all the other physicochemical parameters analyzed, the turbidity was problematic in three samples, and the pH, ammonium ion and the increased content of arsenic by one sample. Higher concentration of arsenic than allowed was detected in one well water in the village Brovic. It was found that it originated from the rodent control products and the well was immediately placed out of service, and the competent services were also informed about that.

### 6.2 Microbiological analysis

Microbiological analysis of well water in the area of Dubrava has showed that the situation is no better in comparison to the hydro-chemical analysis. There ware a total of 282 of the improper samples, which is 80 % of the total number of the wells. The vast majority of them (232) was contaminated with only one type of bacteria. How worrisome is the situation highlights the fact that in 7 of 10 settlements the number of incorrect samples is greater than 80 %, and that there was no proper sample in three settlements.

The most common of all are the aerobic mesophilic bacteria that existed in 279 wells, which is 79 % of the total number of the samples. The average number exceeding of these bacteria is very high and amounts to more than 4 times (431) compared to the number allowed in drinking water (100/1ml). In several settlements that number is even higher, and the worst situation is in Veliko Polje, where the average per improper well is 1060 (the maximum is 3500).

Total coliform bacteria are less common, in 53 wells with an average of 59 bacteria per contaminated well. This means that in those wells the average was 6 times larger than the allowed number set (regulated) for drinking water (10/100ml) - the maximum was 300.

In Orasac and Dren, under the Dubrava scarp, the average amounted to even more than a 100, while in two settlements in the southeast of the area these bacteria were not detected. The most dangerous of all parameters, *E. coli* was found in 15 wells. They are represented in the five settlements with an average of 21 bacteria per well.

| Settlement | Num. of samples | Acc. to one param. | Acc. to several param. | Defective samples | | Correct samples | |
|---|---|---|---|---|---|---|---|
| | | | | Num. | % | Num. | % |
| Piroman | 27 | 9 | - | 9 | 33 | 18 | 67 |
| Brovic | 23 | 6 | - | 6 | 26 | 17 | 74 |
| Trstenica | 32 | 17 | 1 | 18 | 56 | 14 | 44 |
| Ljubinic | 22 | 19 | 3 | 22 | 100 | 0 | 0 |
| Vukicevica | 18 | 15 | 1 | 16 | 89 | 2 | 11 |
| Stubline | 89 | 55 | 21 | 76 | 85 | 13 | 15 |
| V.Polje | 28 | 24 | 4 | 28 | 100 | 0 | 0 |
| Orasac | 23 | 15 | 4 | 19 | 83 | 4 | 17 |
| Dren | 33 | 29 | 3 | 32 | 97 | 1 | 3 |
| Grabovac | 56 | 43 | 13 | 56 | 100 | 0 | 0 |
| Sum | 351 | 232 | 50 | 282 | 80 | 69 | 20 |

Table 3. Deviation by the microbiological parameters

| Typ.of bact. | Mark | S | T | V | P | B | Lj | V.P. | G | O | D | Sum |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | N°wells | 89 | 32 | 18 | 27 | 23 | 22 | 28 | 56 | 23 | 33 | 351 |
| Colif. | Avg. | 47 | 60 | 60 | - | - | 20 | 55 | 55 | 103 | 117 | 59 |
| | N°D.S. | 23 | 1 | 1 | - | - | 2 | 4 | 13 | 6 | 3 | 53 |
| | %(D.S.) | 26 | 3 | 6 | - | - | 9 | 14 | 23 | 26 | 9 | 15 |
| Meso. | Avg. | 272 | 159 | 221 | 201 | 220 | 342 | 1060 | 515 | 532 | 476 | 431 |
| | N°D.S. | 75 | 18 | 16 | 9 | 6 | 22 | 28 | 56 | 17 | 32 | 279 |
| | %(D.S.) | 84 | 56 | 89 | 33 | 26 | 100 | 100 | 100 | 74 | 97 | 79 |
| *E. coli* | Avg. | 18 | - | - | - | - | 10 | 10 | 32 | 20 | - | 21 |
| | N°D.S. | 5 | - | - | - | - | 1 | 2 | 5 | 2 | - | 15 |
| | %(D.S.) | 6 | - | - | - | - | 5 | 7 | 9 | 9 | - | 4 |

Letters in the first row are the first letters of the settlements, Colif. - Coliform bacteria, Meso. - Aerobic mesophilic bacteria, E. Coli - Escherichia coli, NoD.S. - number of defective samples

Table 4. Structure of bacteriological incorrect samples by settlements

## 7. Analysis of the spring water

Research of the springs on the territory of Dubrava was conducted in two phases. The first included their location, description and hydrological characteristics, and the other water sampling and determination of their hydro-chemical and microbiological characteristics. To achieve this previously needed to collect, systematize and analyze existing technical documentation to make the Cadastre of the springs. In that sense, the geo-referencing of topographical, geological and hydro-geological background was executed. This was the basis for further research and development of GIS.

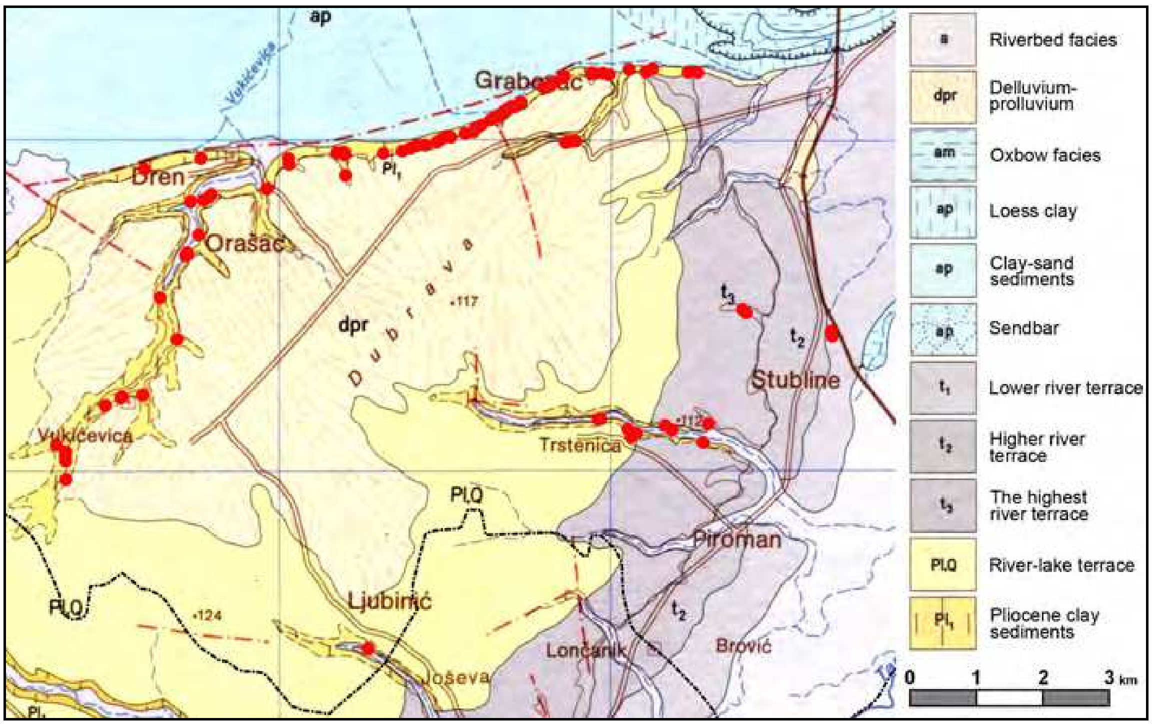


Fig. 3. The location of springs (red spots) (Geological Map 1:100000, Geozavod, 1976)

The first task in the field was to find the springs, and here we affectionately received the assistance of the settlement residents on Dubrava. The problem was that many of the springs were neglected and ingrown with weeds and it was impossible to locate them without the people who knew the terrain. After that, the baseline data about them have been collected, systematized in the "identity card" of each spring. These are the data on the settlement, the owner of the land on which the spring is located, brief description, geographical coordinates and altitude. Its steadiness during the year has been noted, and its purpose as well (water supply, livestock watering, irrigation). The description has also included the access to the spring, derived capping and its condition, the spring type (jet, diffuse). Their current yield has been measured; each spring has been photographed and located on geological map.

### 7.1 Biochemical analysis of the spring water

After processing all the physical indicators and assessments of their condition, out of the total of 88 springs, 30 were selected for which the biochemical analysis of water was done. Water sampling procedures and methods used for biochemical analysis fully meet the existing standards and are identical to those applied to the wells. Because of the special interests for the spring series under the Grabovac-Dren scarp, the largest number of samples was derived from Grabovac, 24 of them. Three samples are from Vukicevica, two from Stubline and one from Orasac. Hydro-chemical analysis has showed that all the indicators are good except the one for nitrate. This parameter deviates (varies) in 14 cases, which is about 50 % of the springs. Its mean value in the contaminated springs is 75 mg/l and it is 25 mg/l higher than the allowed value for drinking water. Regarding the bacteriological analysis, all the samples showed to be incorrect. The number of mesophilic bacteria everywhere exceeded the allowable number (100/1ml). Their average value was 303, which is three times more than the one usable for drinking, while the maximum reaching 450.

## 8. Discussion

Preceding analyses of well and spring waters on Dubrava have made the first step in the establishment of monitoring that will lead to groundwater conservation as one of the most valuable resources in this area. What have the analyses showed? First of all, it was known even before our study that the water is of a dubious quality, because the biochemical analyses were carried out occasionally and on demands of individuals. However, what has been unknown is the spatial definition of contamination, as well as the possibility of comparing the results of time-matched water sampling. Adhering to the strictly regulated values on drinking water quality standards, the groundwater situation is very bad.

| Settlement | Num. of samples | Chem. param. | Bacter. param. | Defective samples | | Correct samples | |
|---|---|---|---|---|---|---|---|
| | | | | Num. | % | Num. | % |
| Piroman | 27 | 15 | 9 | 19 | 70 | 8 | 30 |
| Brovic | 23 | 6 | 6 | 11 | 48 | 12 | 52 |
| Trstenica | 32 | 27 | 18 | 28 | 88 | 4 | 12 |
| Ljubinic | 22 | 16 | 22 | 22 | 100 | 0 | 0 |
| Vukicevica | 18 | 15 | 16 | 17 | 94 | 1 | 6 |
| Stubline | 89 | 82 | 76 | 88 | 99 | 1 | 1 |
| V.Polje | 28 | 11 | 28 | 28 | 100 | 0 | 0 |
| Orasac | 23 | 3 | 19 | 19 | 83 | 4 | 17 |
| Dren | 33 | 21 | 32 | 33 | 100 | 0 | 0 |
| Grabovac | 56 | 37 | 56 | 56 | 100 | 0 | 0 |
| Sum wells | 351 | 233 | 282 | 321 | 91 | 30 | 9 |
| Springs | 30 | 14 | 30 | 30 | 100 | 0 | 0 |
| SUM | 381 | 247 | 312 | 351 | 92 | 30 | 8 |

Table 5. Deviation from the MCL by biochemical parameters of the well water

From a total of 381 water samples, only 30 of them meet the required quality for drinking water. These are mostly the wells in the southeastern part of Dubrava, in Piroman and Brovic. These settlements are on the border of the studied area and under the stronger influence of the groundwater of the River Tamnava alluvium.

In other settlements, besides the slightly better situation in Orasac, the situation is such that clean water is a real rarity. According to relation of the physical-chemical and bacteriological indicators, it is clear that the well and spring water are of the same water horizon. However, comparing the water quality of the wells in Grabovac and the springs at the foothill of the scarp in the same settlement, there is a difference. Specifically, the average value of aerobic mesophilic bacteria in the wells is 515, while in the spring water it is 294. Also, the content of nitrates in the well water is on the average 166 mg/l, and amounts to 75 mg/l in the springs. Anyway, the horizontal distance from the spring to the nearest wells is about 200 m and about 2 km to the farthest analyzed wells. Similarities in the water quality between the wells in Grabovac and their differences in relation to the spring water have two meanings. The first is that there is a constant source of pollution on Dubrava that contaminates the groundwater to a level of the slightly higher amount than these parameters show in the springs themselves. And second, that almost all the wells are in very poor condition and that there is strong local infection of the water. Existing differences in the quality of well and spring waters are a sign that slowly trickling through the groundwater zone from the collector center (center of Dubrava) to the place of flowing out (springs), leads to the natural filtration of water and lowers the pollutants. This is also referred by the fact that the coliform bacteria were found in 13 wells in Grabovac, and *E. coli* in 5, which are indicators of fecal waters and are not present in spring waters.

### 8.1 Nitrate contamination

It is obvious that the water chemical improperness is mostly affected by increased nitrate content. They represent the final stage of a known process of nitrification, and are an important step in the cycling of nitrogen in the soil. Nitrates themselves are not particularly toxic; however, by transferring to nitrites in the organism (body) and a number of other conversions they can create serious health problems (e.g. methemoglobinemia). The normal daily intake of nitrates in the organism (body) in any way should be about 75 mg, and their recommended MCL in drinking water is 50 mg/l (SZZZ, 1990). Therefore, it is clear that the constant presence of nitrate as it exists in the groundwater of the investigated area, with the concentrations that exceed the allowed values, can harm the health of these people.

The origin of nitrates in the water, their transport and effects on humans are a subject that is most present in the studies of drinking water quality in recent decades (Keeney, 1989; Spalding & Exner, 1993; Kovar & Krasny, 1995; Goss, Barry et al., 1998; Foster et al., 2002; Visser, Dubus et al., 2009; Vaux, 2011). Groundwater nitrate contamination stemming from longstanding agricultural practices remains a worldwide and increasing problem with serious economic and health effects (USEPA, 1990). Of all agricultural contaminants, nitrate is the most widespread in exceeding national water standards. In agricultural areas of North America, for example, between 5-46 % of domestic wells in aquifers exceed the 45 mg/l $NO_3$ drinking water standard (Hamilton & Helsel, 1995; Goss, Barry et al., 1998, as cited in Wassenaar & Baisden, 2011).

How is the nitrate contamination formed on Dubrava? First of all, their presence in the surface and ground waters in Serbia is a normal occurrence, particularly in rural areas and local wells. However, this content can vary during the year, usually not exceeding 50 mg/l and only rarely reaches any excess values. In contrast, a spatially large and constant contamination has been established on Dubrava. There are several sources of pollution. They can be divided into dispersed and pointed (concentrated). The uncontrolled treatment of agricultural land by artificial fertilizers and manure, and the impact of thermal power plants as well, belong to the first group. Local (pointed) sources of pollutants are numerous and are related to the septic tanks, pit latrines, open sewer leakage, inappropriately stored animal manure, municipal waste, local landfill.

On the surface of Dubrava, out of 97 km$^2$, the agricultural land is represented at 95% of the area. All land is privately owned with the plots of an average size of about twenty acres. The most common crops are cereals (maize, wheat), clover and little less industrial plants. Much less land is under orchards and vineyards, until the vegetables are grown mostly in the housing estates. All these crops require additional nutrition by mineral and organic fertilizers. However, the agricultural production in Serbia is far away from the yield that was usually achieved in eighties of the last century. Starting from the nineties, the circumstances in which life took place were such that the society maintained only a basic existence. Investments in many areas ceased, so as in agriculture. Consumption of mineral fertilizers was around 1.45 million tons in 1985, and then fell to 220 000 tons in 2000, that is, 300 000 tons in the year of 2003. That is why the yields were also drastically reduced. The last ten years were not any better. The yield of wheat was reduced by 20% (from 4.5 to 3.7 t /ha), or sugar beet by 27% (from 47 to 37 t/ha). Mineral fertilizer consumption is nowadays about 36 kg per hectare, and in order to achieve the European yields, the consumption should be increased as many as eight times. All these findings support the preservation of groundwater quality on Dubrava, especially as agricultural production there has never had an intense character. Irrigation of large parcels has never been practiced and water supplies have been collected from precipitation. What is the actual impact of scientific farming methods (modern farming) today on the increased content of nitrates in groundwater is difficult to say, but this influence is certainly not negligible. Lack of funds for the purchase of nitrogen-based mineral fertilizers has been compensated by animal manure that the vast majority of the land owners in the Dubrava have. The fact that both sources of nitrate in groundwater are not present in quantities as before does not mean that their influence is less. In fact, there are studies that proved that the weather conditions, especially with frequent fluctuations in precipitation in semi-arid areas may encourage intake of nitrates into the groundwater (Lagerstedt, 1994). Precipitation in this part of Serbia is exactly of such characteristics with an average of 650 mm (Zivkovic & Dragicevic, 2003).

### 8.2 The impact of the thermal power plants on the water quality

Thermal power plants Nikola Tesla 1 and 2 which are in a direct proximity of Dubrava dually affect the quality of its waters. Both ways are in relation to atmospheric contamination; the first is pollution from the chimneys, and the other from the ashes dumping sites. The section “Previous studies” shows some effects that the thermal power plants have on the Obrenovac Municipality environment. In the absence of our own research of air pollution, we can only supplement the existing comment. Average emission values of the thermal power plants flue gases in the period of 1990-2002 were (in $mg/m^3$): $SO_2$ - 14 588 (allowed 650), NOx - 3479 (450), CO - 1363 (250) (CIP, 2007). This shows the extent to which the exceeding of the harmful gases allowable emissions was done in the long term period. The same publication shows the total emission of particles and gases in 2005 (in tons): particles 17 000, $SO_2$ - 124 000, NOx - 25 000, $CO_2$ - 20 million. Although the analyses carried out in the spring of 2007 showed that at some distance from the thermal power plants there was no excess of the harmful gases (apart from suspended particles), the conclusion was that the environment was seriously threatened (CIP, 2007). Here, we should bear in mind the long term period, as well as those weather conditions when wind and rain deposit huge amounts of harmful substances on the land cover. A consequence of lignite combustion leads to emissions of nitrogen oxides, sulfur and carbon, hydrocarbons, dust, soot, smoke and other suspended particles. "Acid rains" are formed under the influence of nitrogen oxides ($N_2O$, NO, $NO_2$), which have good solubility and corrosion in the presence of sulfur dioxide, gas without color and odor. This creates a permanent environmental degradation.

The ashes dumping site of the thermal power plant Nikola Tesla 2 is located in a direct proximity of Dubrava. Solid phase after the burning of coal is deposited here, and the quantity is from 12 to 14% of the primary mass of coal. Most of all elements, that are present in coal, remain in the solid phase, i.e., in the ash and smoke residue. Of particular concern is the significant proportion of heavy metals and radioactive elements. How all this affects the groundwater of Dubrava will remain a mystery for now, but one detail from the field has remained in our memory. According to narration of many local residents of Grabovac (nearest to the landfill), it happens that the wind from the north direction brings a huge cloud of ash and soot that deposit in the settlement. On that occasion, anyone who happens to be in his house immediately closes the doors and windows and removes all valuables from the yard. The cloud leaves, as they say, a layer of ash thick like a finger which cannot be removed long after.

### 8.3 Pointed sources of pollution

It may seem that these sources of pollution are not as dangerous as the first ones, but having in mind the microbiological analyses, it must be concluded that their role is very important. They all occur as a result of extremely poor communal sanitation. Lack of water supply network forces the residents to use local sources of drinking water (wells, springs), and the absence of a common system of the used water drains makes every household to solve the problem itself. Although there is the legislation on the facilities construction for the local water supply and drainage, it is not respected. Irregularities occur most often during the construction of septic tanks, pit latrines and manure disposal sites. First of all, the required distance of a septic tank to the well is not respected, so they are often a few meters apart. The next disadvantage is irregular retaining wall of the septic tanks and pit latrines where there is no isolation of fecal matters from the surrounding land. The same applies to the manure disposal sites, which are unsecured and subject to external influences long during the year. Because of all the above mentioned, the fecal waters penetrate the aquifers and make them constantly contaminated. This contamination is usually both, chemical and bacteriological.

Ammonia and organic nitrogen, mostly from the human urinary system, are commonly present in wastewater within septic tanks. Typically, almost all ammonia is converted into nitrate before leaving the septic-tank soil-absorption system drain field. Once nitrate passes below the zone of aerobic bacteria and the roots of plants, negligible attenuation occurs as it travels through the soil (Franks, 1972, as cited in Lowe et al., 2010). Once in ground water, nitrate becomes mobile and can persist in the environment for long periods of time. Areas having high densities of septic-tank systems risk elevated nitrate concentrations reaching unacceptable levels. In the early phases of ground-water quality degradation associated with septic-tank systems, nitrate is likely to be the only pollutant detected (Deese, 1986, as cited in Lowe et al., 2010). As the effluent from a septic-tank soil absorption system leaves the drain field and percolates into the underlying soil, it can have high concentrations of pathogens, such as viruses and bacteria. Organisms such as bacteria can be mechanically filtered by fine-grained soils and are typically removed after traveling a relatively short distance in the unsaturated zone. Pathogens can travel up to 40 feet (12 m) in the unsaturated zone in some soils (Franks, 1972, as cited in Lowe et al., 2010). Some viruses can survive up to 250 days (USEPA, 1987), which is the minimum ground-water time of travel for public water-supply wells or springs to be separated from potential biological contamination sources.

Therefore, neither by the depth of bacteria penetration into the soil, nor by the retention time in it, the groundwater on Dubrava can be immune to this contamination. If we count the longest path that the groundwater passes on Dubrava (from the hydro-geological divide to the spring horizon, about 3 km), it would need about 600 days (5 m/day). However, since the vast majority of the wells is located along the border areas and densely grouped, their interactions are very distinct. So, the eventual increased presence of bacteria in some part rapidly expands to all downstream wells. Apart from penetrating the soil, on Dubrava there is a problem of inadequate protection of the wells causing pollution directly to the groundwater. This type of contamination is usually bacteriological. It should be also noted that even in the settlements in the area of Dubrava there is no organized waste disposal site, so the illegal dumps of solid waste that have a local impact on the groundwater quality are very frequent.

### 8.4 Springs

All that leads to the contamination of the well waters on Dubrava is largely reflected in the spring waters as well. Concentrations of pollutants are not as drastic, but for nitrate and especially total aerobic mesophilic bacteria, they are beyond the allowable limits. If we followed the rules of drinking water properness, no spring would be usable. The survey conducted among owners of the parcels that these springs belong, has led to the data that out of the 88 tested, even 34 are used for drinking, and 43 also for watering livestock. And only a few of them use the basic disinfectants. Most of these springs were in operation in the seventies of the last century. What kind of a quality the water was, we would not know, but the springs were maintained and served as the pride to their owners. Many of them were tapped and equipped and, on weekends and holidays, "the whole village came down to the springs" (referring primarily to Grabovac and Dren). The current situation is such that most are hardly reachable, neglected and almost forgotten.

## 9. Conclusion

Before receiving the results of water quality on Dubrava, there have been some indications that the situation is not satisfactory. Therefore, at the same time with the field work, a wide action that will put the entire Dubrava under a certain degree of protection has been initiated. The implementation should involve, besides the local community, Obrenovac Municipality, also the professional services of the region of Belgrade administration, as well as those of the state level. It was concluded that the site of Dubrava is a unique combination of natural and anthropogenic values and with its environment is a challenge for everyone involved in environmental protection.

It has already been mentioned that the current spring series (from Grabovac to Dren), as part of the same water horizon, does not exist anywhere in Serbia in a similar form. Although the springs are of low yield (together with about 350 liters per minute, constant throughout the year and without oscillations), they are a real hydrological jewel. Besides the intention to try and help people on Dubrava when the water is in question, this research is also largely focused on the protection action of the springs and their revitalization.

Where should we start? In 58% of the examined (tested) local wells, the significant construction-technical and sanitary-hygienic deficiencies that affect the quality of drinking water have been observed. The sanitary protection zone has not been established in most of the wells, and there is no investment-technical documentation as well. So, the first step is training of the people who, by their carelessness, endanger all the residents of Dubrava, and then follows the action of the professional and inspection services in order to eliminate the local sources of contamination. This is primarily to check the condition and rehabilitation of the septic tanks, pit latrines and manure disposal sites that were improperly constructed. As for the wells themselves, it is sometimes enough to clear them from mechanical impurities and to hyper-chlorinate them. This also applies to the springs that were tapped. In the case of air pollution that originates from the thermal power plants, it can not be eliminated, but the regular control and filter installations replacement, as well as the prescribed rehabilitation of the ashes disposal sites, could be maintained at an acceptable level.

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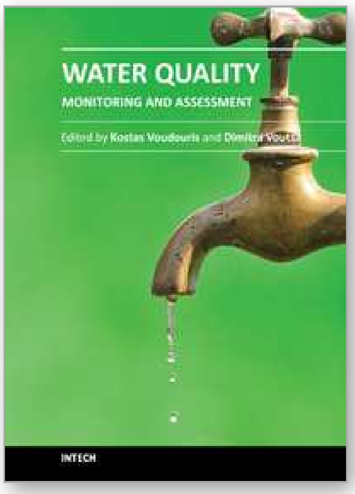


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The book attempts to covers the main fields of water quality issues presenting case studies in various countries concerning the physicochemical characteristics of surface and groundwaters and possible pollution sources as well as methods and tools for the evaluation of water quality status. This book is divided into two sections: Statistical Analysis of Water Quality Data;Water Quality Monitoring Studies.