

Basin Water Management in a Coastal Karst Area

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Abstract

The mediterranean's karst basin waters is the topic of this research paper. The aim of the research is to help protect the karst underground waters through wastewater management of the basin's area.

The main difficulty for our research was a shortage of knowledge in the identification of the karst's hydrological system, such as in the case of a researched system where the system's inlet and outlet are not completely known and the whole system is only partially explained from hydrogeological and hydrological aspects. For the research spot we chose a particular karst basin. Municipal wastewaters are discharged into the basin without any purification and, after being held in the underground, they appear at the spring that supplies water for the biggest lake in the Balkans.

Correlation data between low water and the characteristics of the basin (i.e. hydrological balance analysis data of specific capacity) do not exist. A series of hydro-chemical measurements at low water were undertaken in parallel at the inlet and the outlet in order to determine this correlation by an input-output balancing of pollutants' load calculating their mass flow.

The hold time of pollutants in the underground karst water was determined by correlating the particular water quality indexes. Hold time amounts to 55 to 78 hours, depending primarily on the water ingredient features.

Keywords: karst, water, management

Introduction

Numerous literature data exist on the behaviour of contaminants in surface waters, while in underground waters it is hard to understand the ways of transmission of contaminants, as well as the caused processes. Therefore, control of karst system contamination as a natural phenomenon becomes one of the newest and most important aspects of water wealth protection, because it can be easily contaminated (constantly or occasionally) but hardly "cleaned" in a relatively short period of time [1-3]. The quality of karst water has important differences compared to the water quality from other hydrogeological environments, not only because of its natural state, but also because of the contam-

ination. The high-flow karst waters frequently introduce organic and other contaminants from the surface directly into the springs, which depends on the autoperification abilities of karst underground flows [4, 5].

Karst water is a very sensible and balanced system, and its balance constant can be changed even by the smallest amount of contaminant [6]. The difficulties in usage and protection of karst waters are present even in Montenegro. One of the reasons is that the majority of its territory (>75%) is karst. The other reason is the dominant use of underground waters for drinking, mostly of unknown origin, without purification and optimal sanitary protection zones. Furthermore, there are no basic documents on water economy, like the contaminants list and others, that should contain basic elements of management. Therefore, numerous tasks are imposed upon the researchers.

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Considering the inappropriate method of discharge of wastewaters from residential areas, special attention was dedicated to the demands of the standards in this area. The demands do not concern the contamination levels determined in advance or other technical demands, but they stimulate contaminants to show a high level of operation and, therefore, to protect the environment using a consistent and documented management system. Therefore, the standard ISO 14001 [7] should be considered a tool that helps make decisions on the basis of the information related to environmental protection. Finally, the standard always enables us to move beyond the legal obligations.

For many reasons, including: insurmountable difficulties in interpretation and description of karst water flows [5], differences between domestic and European laws, the absence of optimal hydrological and hydrogeological databases, the undefined Crnojevica River basin (and the absence of a list of contaminants present in the basin), and analysis of the character of contaminants from the land surface of the basin as well as the evaluation of their influence on the quality changes in the natural properties of the waters of the basin downstream of the analysed source of contamination, using surveys and terrain inspections.

The planned investigations will provide better knowledge of reactions of the basin in question, from the aspect of contamination, which will also enable us to propose the appropriate measures for the protection of the waters of that karst system, as an invaluable water treasure.

Experimental Procedure

The basin of the Crnojevica River (Fig. 1), taken as an example of coastal karst, belongs to a highly holokarstic area, with typical surface and underground karstic forms. These terrains have high differences in height, and the cotes range from 1,600 to 20 m a.s.l. The geological material of the basin is dominated by limestone, dolomite limestones, and dolomites from the upper trias and lower Jurassic ages. Intense karstification has destroyed the surface river net and moved it underground. Therefore, now only short surface flows temporarily exist, during the rainy period of the year. On the other hand, the precipitations and outflows are closely correlated. The investigations show that the reaction of the watercourse on precipitation impulses is higher than 10 l/h in just two hours, regardless of the previous condition of the hydrological system. The precipitation impulse is relatively quickly amortized by the discharge through the recipient, especially at the end of the system exhaustion season when the stationary condition is established.

The named factors influence the high sensitivity of previously quality waters of the Crnojevica River basin [8] to the influence of artificial factors. Deterioration of the quality of water from the basin in question, with a surface of about 175 m², has been caused by the lack of purification of communal and industrial wastewaters in towns, as well as of sanitary landfills and other diffuse sources.

Connections of the swallet in karst polje (P_0) with the spring measuring points V_0 have been proved several times

by means of markers [9] and determined travel times between swallet and spring of about 55-78 hours.

Modest data on geological, hydrological, and hydrochemical properties of the catchment area, insufficient knowledge of swallets characteristics in karst field, and characteristics of the underground area and conducting zones – especially lacking knowledge of relations of quantities and water speeds – imposed the need for previous voluminous examinations of physical-chemical properties of wastewaters and surface waters for the purpose of detailed definition of the area of connections and effects.

In these investigations the hydro-chemical measurements were performed, in small waters, in order to define the wastewater load in the residential areas. The untreated wastewaters of the residential areas mostly flow into the karst swallet (entrance, P_0), and after a certain period of retention time in karst underground, it appears as a part of concentrated waters from the basin, at the spring of the water flow (exit, V_0).

The dynamics and range of the investigations were appropriate for the investigation of karst hydrological systems [10], while physical and chemical investigations and bacterial examinations were performed using standard methods [11].

During a period of 7 days the “instantaneous” samples were taken every two hours at measuring points P_0 and V_0 in July 2008. Sampling at point V_0 was in each series moved in time for the predicted period of retention time of wastewaters in karst underground.

The terrain measurements include water flow (Q), temperature (t), turbidity, electrolytic conductivity (χ), and dissolved oxygen (O_2), while other parameters, i.e. biochemical oxygen consumption during a 5-day period (BOD_5), consumption of potassium permanganate ($KMnO_4$), pH, total hardness, sodium (Na^+), potassium (K^+), calcium (Ca^{2+}), magnesium (Mg^{2+}), ammonia (NH_3), nitrates (NO_3^-),

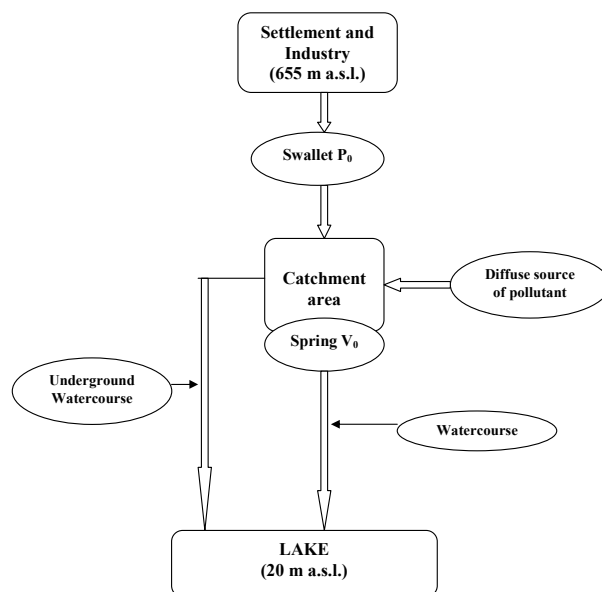


Fig. 1. Location of higher pollutants, watercourses, lake and measuring points.

nitrites (NO_2^-), total coliform bacteria, and fecal coliform bacteria in 100 ml and their identification, were determined in laboratory.

Statistical data analysis, as well as the analysis of the importance of reciprocal dependence (correlation coefficient r) of measured parameters at the points P_0 and V_0 was performed using statistical package EXCEL.

The results are shown in Tables 1-4 and in Figs. 1 and 2.

Results and Discussion

Flow measurement and sampling every two hours enable good observation of the changes in the wastewaters inflow and concentration of the contained unknown components. The data obtained in this manner technically include all the oscillations in the contamination load, therefore their summary can present objective data on the average contamination load during the day.

The data obtained by terrain and laboratory investigations of the wastewaters at measuring point P_0 are presented in Table 1. Because of their quantity, the obtained data are statistically processed and then shown in the mentioned table.

Regardless of the annual period and poor condition of the system for the drainage of communal and atmospheric waters into the major swallet, the obtained investigation data show relatively balanced quantities of water discharged into the swallet. However, the supply of industrial wastewaters has an important role whether for the quantity or for the content of the ingredients in question. High concentrations of the contaminants, mostly of industrial origin, are mostly reflected within the value range of the water temperature, pH, electrolytic conductivity, sodium, phosphates and others, presented in the paper.

The water temperature change can be related to climate conditions, but in our case it is the consequence of the interference of waters of different origin, which is illustrated by *min* and *max* values during the investigation period. The water temperature ranged between 10 and 20°C, while pH value was within the range 6.95-8.85, which indicates the unbalanced inflow of industrial waters, i.e. an unbalanced part of the industrial wastewaters in the wastewaters that flow to the major swallet. This is also proved by the values obtained for electrolytic conductivity, whose min and max values were 260-840 $\mu\text{S}/\text{cm}$. The maximum value for electrolytic conductivity during the investigation period was 840 $\mu\text{S}/\text{cm}$ and it was registered at 10 o'clock. Furthermore, it can be noticed that the maximum values of most components, i.e. of their contents, are more expressed during the a.m. working hours, while after 24 hours, when technical and technological daily processes finish, lower values of these components are noticed.

Min and max values for Na^+ (min 13.5 mg/l, max 310 mg/l) and Cl^- (min 10 mg/l, max 95 mg/l) indicate the "impact" releases of industrial wastewaters into the Major karst swallet together with communal wastewaters, to whom the swallet is dedicated. It was confirmed by the

Table 1. Values of statistically processed data for the wastewaters at the entrance to the major swallet.

Parameters	Statistically processed data				
	average	min	max	st. dev.	median
Flow, l/s	25.7	3	63	13.8	30
Temperature, °C	13.8	10	20	2.3	14
Turbidity, SiO_2 mg/l	171.9	50	400	73.5	180
El. conductivity, mS/cm	470.9	260	840	102.1	466.5
Dissolved oxygen, mg/l	3.9	0.2	7.9	2.1	4.1
BOD ₅ , mgO ₂ /l	120.9	15	315	62.3	112.5
KMnO ₄ , mg/l	173.9	35	480.3	91.5	158.4
pH	7.42	6.95	8.85	0.37	7.35
Total hardness, °dN	10.07	4.02	12.74	1.49	10.28
Na^+ , mg/l	54.81	13.5	310	57.62	42.5
K^+ , mg/l	9.1	4.5	15	2.1	9
Ca^{2+} , mg/l	40.50	8	62.4	10.05	41.6
Mg^{2+} , mg/l	19.43	7.78	36.98	5.35	19.46
Fe, mg/l	88.5	30	400	57.9	75
Cl^- , mg/l	29.44	10	95	16.93	25.25
SO_4^{2-} , mg/l	32.32	12.8	75	12.51	33.3
PO_4^{3-} , mg/l	12.7	0.8	51.8	13.9	6.4
NH_3 , mg N/l	18.39	0.77	38.85	9.13	15.54
NO_3^- , mg N/l	0.14	0.11	0.69	0.07	0.11
NO_2^- , mg N/l	0.01	0	0.24	0.04	0
Zn, mg/l	0.6	-	-	-	-
Cu, mg/l	0.2	-	-	-	-
Pb, mg/l	0.05	-	-	-	-
Ni, mg/l	0.03	-	-	-	-
Cr, mg/l	10	-	-	-	-
F, mg/l	1.2	-	-	-	-

unspecific mol ratio between alkaline ($\text{Na}/\text{K}=7.95$) and alkaline earth metals ($\text{Ca}/\text{Mg}=1.98$), salts of which were used in the treatment of galvanic wastewaters, as a part of wastewater that flows into the swallet. The values of the calculated ratios indicate the possibility of the presence of the ingredients of water, which can inhibit the biodegradation process of the organic materials in underground karst water.

The content of potassium was within the range of 4.5 to 15 mg/l, and calcium from 8 to 62.4 mg/l, whose minimum values are explained by their precipitation caused by phosphates.

Among anions, the highest variation is in phosphates, which come from communal wastewaters (detergents) as well as from industry according to the obtained data. It is proved by the determined range of 0.8 to 51.8 mg/l. The maximum was registered at 10 o'clock, which confirms the "impact" inflow of industrial waters. The quantity of sulphates was within the range of 12.8 to 75 mg/l, which indicates their origin from industry as well, but it was lower than the quantity of phosphates, because of the average value of sulphates of 32.32 mg/l.

Nitric compounds are mostly expressed in the form of ammoniac and nitrite, while the content of nitrate is relatively low (min. 0.11 mgN/l, max. 0.69 mgN/l). The content of ammoniac varied from 0.77 to 38.85 mgN/l. The values for nitrate were from 0 to 0.24 mgN/l, while the average value was 0.01 mgN/l. The nitrogen balance indicated a small amount of oxygen. The values obtained for dissolved oxygen in wastewater were within the range of 0.2 to 7.9 mg/l. Naturally, the obtained data can be used only conditionally, mostly because of the presence and determined concentrations of nitrites, which in fact represent the interfering substances in the determination of dissolved oxygen according to Winkler [11].

BOD₅ values were determined by water dissolution method [11], so the obtained values can be taken into consideration and commented on regardless of interfering factors. The values for BOD₅ varied from 15 to 315 mgO₂/l, where max values were usually registered before noon, at 8, 10 or 12 o'clock. The average value for the consumption of KMnO₄ was 173.9 mg/l. The minimum value of 35 mg/l was determined in the afternoon, while the max value for the consumption of KMnO₄ was determined at 10 o'clock. Such variation of the consumption values of dissolved oxygen lead to the assumption that its important part was spent on the transformation of the contaminants of industrial origin. In order to better explain this phenomenon, the total number of bacteria in 100 ml of the wastewater sample was also determined, and it varied from 9,600 to 2,400,000. The range between extreme values is explained by the influence of inorganic toxicants that inhibit the processes of bacterial self-purification.

On the basis of the results obtained by the investigation of wastewaters that flow into the major swallet, it can be concluded that, apart from sodium, ammoniac, nitrite and phosphate, there is a presence of synthetic organic substances, as well as heavy metals such as inhibitors (Fe, Zn, Ni, Pb, Cd), which are considered the biggest water contaminants of the karst basin [8].

The investigated wastewaters, after a relatively short period of retention in the underground from 55 to 78 hours [9] (depending on hydrological conditions), flow to spring V₀. As presented in the experimental procedure, in the same hydrological situation and at the same time as the measurements at the major swallet (entrance P₀), the measurements

Table 2. Values of statistically processed data for waters at the exit from the karst underground, spring.

Parameters	Statistically processed data				
	average	min	max	st. dev.	median
Flow, l/s	460	460	460	0	460
Temperature, °C	10.6	10	12	0.8	10
Turbidity, SiO ₂ mg/l	11.9	5	20	4.2	10
El. conductivity, mS/cm	275.12	245	300	14.43	279
Rastvoreni O ₂ , mg/l	9.8	3.1	13.3	1.9	10.2
BOD ₅ , mgO ₂ /l	2.3	0.6	5.7	1.1	2.1
KMnO ₄ , mg/l	7.3	3	17.6	3.2	6.4
pH	8.16	7.8	8.6	0.18	8.15
Total hardness, °dN	9.66	8.71	11.17	0.62	9.83
Na, mg/l	4.29	2	9.6	1.49	3.7
K, mg/l	1.6	1	3.9	0.4	1.5
Ca ²⁺ , mg/l	46.30	40	62.4	3.90	46.4
Mg ²⁺ , mg/l	13.48	2.19	18.49	2.38	13.62
Fe, mg/l	17.9	5	90	13.6	10
Cl ⁻ , mg/l	7.79	7	9.1	0.53	8
SO ₄ ²⁻ , mg/l	15.45	8.98	26.9	4.79	14.1
PO ₄ ³⁻ , mg/l	0.4	0.1	1.3	0.2	0.3
NH ₃ , mg N/l	0.004	0	0.19	0.02	0
NO ₃ ⁻ , mg N/l	0.59	0.11	0.96	0.22	0.66
NO ₂ ⁻ , mg N/l	0.001	0	0.004	0.001	0

with the nominated time delay were also performed at the spring of the water flow of the Crnojevica River (exit V₀), with Skadar Lake as a recipient.

As can be seen from the results shown in Table 2, the flow was constant and it had a value of 460 l/s, which is the consequence of the hydrological period of the year. Certain variations in the flow at the swallet and spring are a result of direct rainfall at the basin.

The variations in temperature values during the investigation period do not exceed 2°C, and they vary within the values of 10 to 12°C. At the same time, it's the characteristic of strong and constant karst springs [5, 10], which is explained by the equalization of the temperatures of the water and its environment. The extreme pH values range between 7.8 and 8.6. The registered maximum pH value in the period of small waters is the consequence of biochemical and photochemical processes in the water. This maximum value was followed by the maximum value of electrolytic conductivity of 300 μS/cm.

Table 3. Na/Cl and Ca/Mg mol ratio during the investigation period in the spring water.

Mol ratio	Statistically processed data				
	average	min	max	st. dev.	median
Na/Cl	0.85	0.24	1.80	0.30	0.74
Ca/Mg	2.29	1.47	12.27	1.70	1.99

The values for calcium were from 40 to 62.4 mg/l, while magnesium was found in the amount of 2.2 to 18.5 mg/l. Total hardness varied within the limits of 8.7 to 11.2 °dN, which classifies the waters from the spring of the Crnojevica River as moderately hard waters.

The obtained values show that the content of dissolved oxygen ranges between 3.1 and 13.3 mg/l, as well as in other strong springs in the karst. The lowest values are registered in the period of small waters, while its high concentrations indicate good air-exposure of the underground holes, where the water flows.

Sodium and potassium are significantly increased. The values of sodium were between 2 and 9.6 mg/l, and for potassium 1-3.9 mg/l.

The increased content of nitric compounds and organic materials during the period of high waters is a characteristic of karst springs. This phenomenon is the consequence of the transport of contamination in the karst, where the water does not discharge the organic contamination taken from the surface, considering the limited abilities of filtration and short retention time in the underground [5, 12].

At the spring of the Crnojevica River the situation is different. The increased content of nitric compounds and organic material was registered in the period of small waters. The analysis of the obtained values demonstrates the importance of the differences between the extreme values, for ammoniac 0.00-0.19 mg/l and for nitrites 0.00-0.004 mg/l, which leads to the conclusion that these nitric compounds have industrial origin. On the basis of relatively low values

for nitrates (0.11-0.96 mg/l) it can be concluded either that the ammonifying bacteria are not present in appropriate amount in karst underground or that the retention period of three days in karst underground is too short.

Phosphates are found in almost every sample of the water at measuring point V_0 . The phosphate values varied from 0.1 to 1.3 mg/l. The differences between the extreme values lead to an assumption that the wastewaters that flow into the karst underground are occasionally loaded with higher content of phosphate, which is demonstrated by the data presented in Table 1.

Nitrates and phosphates are very important nutritive salts. The waters of these terrains have low amount of nitrates and phosphates, which is the consequence of a poor pedological base. As a result, particular attention should be dedicated to the protection of the investigated waters so that Skadar Lake, which is fed by these waters, can be protected from negative influences of the eutrophication process [13].

The consumption of $KMnO_4$ varied from 3 to 17.6 mg/l, which is the consequence of the constant organic substances load in the water from this spring.

The values for BOD_5 were from 0.6 to 5.7 mgO_2/l , demonstrating that spring waters contribute to the contamination of Crnojevica River with organic substances, which takes the contamination to Skadar Lake as a final recipient.

The microbiological investigations showed that the spring waters were loaded with bacteria, from their absolute absence to the quantity of 24,000 bacteria in 100 ml of water.

A comparison of the obtained data with previous investigations [13] concludes that the waters of the karst area have significantly worse quality.

The inflow of the industrial contaminants that get into karst underground, whether through the major swallet or smaller swallets, or even through the infiltration of the percolation waters from the industrial and communal hard waste landfills, has important influence on the level of disturbance of the natural calcium/carbonate balance of spring water. This conclusion is based on the change of Na/Cl i.e. Ca/Mg mol ratio value (Table 3) in the spring water.

Table 4. Correlation coefficients between physical and chemical parameters of water quality at points P_0 and V_0 .

V_0	P_0								
	Q	t	χ	O_2	BOD_5	$KMnO_4$	pH	Total P	Total N
Q	-0.1	-0.4	-0.12	+0.1	-0.01	-0.02	-0.11	+0.45	-0.17
t	+0.05	0.4	+0.1	-0.02	+0.14	+0.44	-0.1	+0.11	-0.14
χ	-0.05	+0.7	+0.43	-0.15	-	+0.1	-0.01	-0.1	+0.5
O_2	+0.1	-0.1	-0.12	-0.02	+0.02	+0.04	-	+0.06	-0.1
BOD_5	-0.02	-0.3	-0.13	+0.01	-0.01	+0.04	-0.03	-	-0.2
$KMnO_4$	-0.05	-0.1	-0.01	-0.01	-0.05	-0.1	-0.03	+0.1	-0.03
pH	-0.3	+0.4	+0.34	-0.3	-0.04	-0.1	+0.2	-0.1	+0.13
Total P	-0.13	+0.4	+0.2	-0.05	-0.05	+0.15	-0.02	+0.1	-0.2
Total N	-0.15	+0.5	+0.2	-0.01	+0.03	+0.3	+0.02	+0.2	-0.14

As can be seen from the results presented in Table 3, the calcium-carbonate balance is disturbed, which is proved by the Ca/Mg mol ratio value. The obtained data contribute particularly to the development of the method of usage and protection of karst underground waters as the most adequate for water supply from the aspect of the influence on human health, considering the fact that their natural Ca/Mg mol ratio is 3.

On the basis of the disturbance dynamics of Ca/Mg mol ratio, it can be concluded that the water flow in question, if not constantly then with impacts, contaminates with the pollutants from industry located in the area of the basin of the water flow chosen for observation.

Fig. 2 illustrates the load (in kg per day) expressed through BOD₅, total N, and total P at the major swallet and spring.

The maximum load values at the entrance show impact contaminations that influence the concentrations at the spring. The load corresponds to the load at the spring after 55 hours, which indicates explicitly that the waters from karst underground are contaminated with the pollutants from land surfaces of the basin.

In order to understand the correlation between physical and chemical parameters of water quality at points P₀ and V₀, correlation analysis was performed (Table 4). The correlation level was expressed by simple correlation coefficients (r).

The alternate impacts of the pollutants influence the chemical status of the water system, as can be seen from the correlation coefficient values between certain general limiting quality indicators and some inorganic ingredients. The negative values of the correlation coefficients for Q at the entrance and Q at the exit indicate earlier confirmed presumption that the water released into the swallet does not appear at the spring.

Considering the fact that the obtained results are the results of the measurement performed during an unspecified period from small to middle waters, the chemical quality at the spring caused the deterioration of the ecological water status of the water flow where it has plane character, all the way to the mouth of Skadar Lake, which is in accordance with earlier data [13]. At that section waters are of the beta-mesosaprobic type that prevail during the hydrological year.

Conclusions

The obtained results show the necessity of quantifying the contamination sources that emit various pollutants, including the abandoned factory dump in the settlement, which lately have lower activity. Furthermore, it can be concluded that the wastewaters that flow untreated into the karst swallet, as well as the contamination from different sources in that area, influence particularly the quality of the spring water.

Unconcern for the contaminants in the area of the basin in question is evident, so the question is how the waters of the karst underground need to be protected. The answer can

be obtained by further investigations in order to promote a method for water protection of the presented basin area, in accordance with the aims of the EU Water Framework Directive.

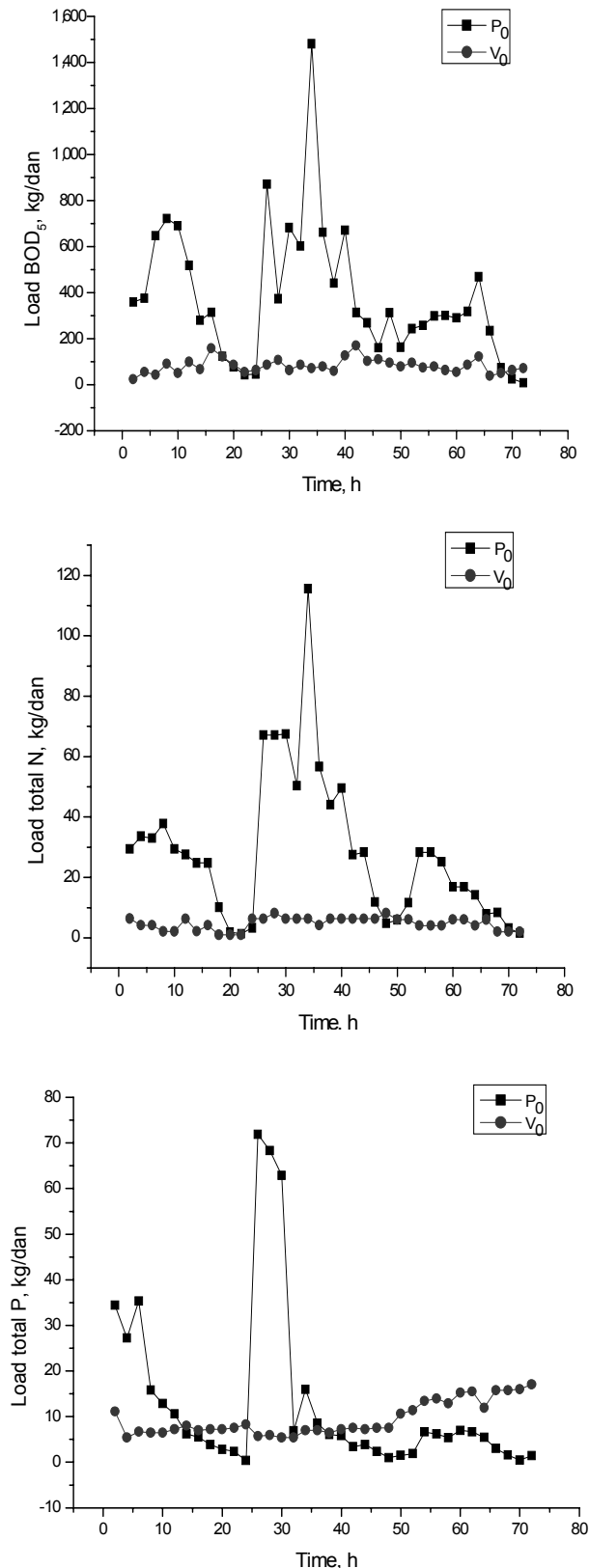


Fig. 2. Load expressed through BOD₅, total N and total P.

The Water Framework Directive aims to achieve good ecological and chemical status of waters by 2015. Therefore, it is necessary to perform a reliable analysis of present and future water conditions. For that purpose, the automatic monitoring stations have a great role and importance, as a reliable management element in definition and implementation of necessary protection measures, especially in situations of accidental water contamination.

For the application of ISO 14001 standard in the catchment area, it is important for each company located at the basin area to apply this standard, because it's related to companies. This standard does not determine absolute demands regarding the results of environmental protection, but only the obligations to adapt environmental protection policy to the law and other regulations, as well as to provide its constant improvement.

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