The effect of effluent on the water quality in the Nišava

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From a general perspective, the sewage system in Niš is a combined-type system. After mixing with fecal and atmospheric water the effluent is directly discharged into the Nišava *via* two main outlets (the left and right collectors). This research studies the influence of untreated wastewater on the recipient's (surface water) quality. The analysis of the samples was done by application of a standard spectrophotometric method, with validation reports and measurement uncertainty evaluation reports. Surface and wastewater quality testing was carried out in accordance with the relevant directives, national and international regulations. Physical (temperature, turbidity, pH and electrical conductivity) and chemical (chlorides, ammonia, nitrites, nitrates, sulfates, iron, manganese and chromium as Cr^{6+} and Cr^{3+} ions) parameters were analyzed as indicators of quality. Yearly sample quality monitoring indicated river water degradation, which necessitates wastewater treatment in the left and right collectors before the discharge into the Nišava.

Keywords: wastewater and surface water, monitoring, spectrophotometry

INTRODUCTION

Wastewater is any water that has been adversely affected in quality by anthropogenic influence. The sewage from communities, as well as the effluent from industrial units have been identified as the main cause of water pollution across our country. Sewage is a water-carried waste in a solution or suspension that is intended to be removed from a community. It is also referred to as wastewater and it is characterized by volume or flow rate, physical condition, chemical constituents, and bacteriological organisms that it contains. During recent years, there has been an increasing awareness and concern about water conservation all over the world. Hence, new approaches towards achieving sustainable development of water resources have been internationally advanced [1].

Due to industrial development, domestic effluent and urban run-off account for the bulk of the wastewater generated in Niš. Based on its origin, wastewater can be categorized as sanitary, commercial, industrial, agricultural or surface runoff. The term wastewater needs to be differentiated from the term sewage. Because pathogens are excreted in feces all sewage from cities and towns is likely to contain pathogens of some type, potentially presenting a direct threat to public health. Putrescible organic matter has posed a different sort of a threat to water quality in recent years. There has been an increasing awareness and concern about water conservation all over the world [2]. Water management poses a major challenge in many densely populated countries throughout the world. In Europe, and due to the WFD [3], stewardship of water resources is of paramount importance now and in the future. The major aim of the WFD is to reach good water quality in all European waters by managing water bodies, i.e., lakes, rivers, groundwater bodies, transitional waters and coastal waters by 2027 at the latest.

In Europe, the state of the aquatic environment is controlled by legislation outlined by the European Commission. Directive 2000/60/EC setting out the framework for community action in the field of water policy has reformed the water quality policy of the community, and is the first attempt to move towards ecosystem-based management that should ensure a good ecological status [3, 4]. Its aim is the prevention of water pollution within the European Union through such steps as identifying the pollutants which pose the greatest risks to or *via* the water environment. A supplementary of WFD is Directive 2008/105/EC of the European Parliament and of the Council of December 2008 on environmental quality standards in the field of water policy and Directive 2013/39/EU of the European Parliament and of the Council of August 2013 amending Directives 2000/60/EC and 2008/105/EC as regards priority substances in the field of water policy which includes a list of 45 priority substances. Requirements for the quality of wastewater discharged from plants are included in Council Directive 91/271/EEC of May 1991 concerning

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urban wastewater treatment. The Directive determines the *inter alia* requirements for discharges from urban wastewater treatment plants, including emission limit values for these [4].

Municipal wastewater is one of the largest sources of pollution, in volume. Therefore, it is necessary to treat any type of wastewater to produce an effluent with good quality. "The higher the level of treatment provided by a wastewater treatment plant, the cleaner the effluent and the smaller the impact on the environment" (US EPA 1999).

To remove soluble organic matter and possibly also nitrogen from wastewater, biological treatment is often the second step and is followed by a disinfection unit (chlorine contact tank) [5, 6].

From a general perspective, the Niš sewage system is a combined-type system. A large section of the city, in particular, the central region of the city on the left and right banks of the Nišava, possesses general (mixed)-type collectors whereas for Niška Banja and certain peripheral and newly-built parts of the city a separation system was constructed. After mixing with fecal and atmospheric water the wastewater is directly discharged into the river Nišava *via* the two main outlets: outlet 1 - the left collector in Ivan Milutinović street and outlet 2 - the right collector in Beograd mahala.

The purpose of this study is to estimate the effect of untreated sewage effluent on the recipient's water (the Nišava) quality *via* physical and chemical water quality indicators.

EXPERIMENTAL

Materials and methods

Water quality was tested according to the corresponding directives and regulations of national and international authorities – regulations (Official Gazette of RS, No: 33/2016; 67/2011, 48/2012 1/2016; 50/2012; 24/2014; 74/2011 and Official Gazette of SRS, No. 31/82).

The Nišava water quality was also monitored following drinking water regulations (EU Council Directive 98/83/EC 1998; Official Gazette SRJ No: 42/1998, 44/1999, 28/2019; WHO 2011a; US EPA 1999a; US EPA 2012) considering that river water (at the entrance to the city) is used as the water intake.

The quality analysis of the wastewater in the left (L) and right (R) city collectors and the Nišava water quality analysis before (N- the water intake) and after the discharge of the left city collector (Nk - around 300 m downstream) (Fig. 1), was carried out at the Laboratory of the sanitary control sector with the JKP 'Naissus' laboratory in Niš. The laboratory is accredited according to the standard SRPS ISO/IEC 17025:2006. Fig. 1 shows Nišava-water intake (locality 3), and Nišava downstream from the left collector (locality 10).

The water samples for physico-chemical examinations were taken by experts in accordance with the standards: SRPS EN ISO 5667-1:2008, SRPS EN ISO 5667-3:2017, SRPS EN ISO 5667-4:1997, SRPS EN ISO 5667-6:1997, SRPS EN ISO 5667-10:1997.

Fig. 1. Nisava River - locality 3 and locality 10.

The analysis of wastewater and surface water encompassed the appointment of the following parameters:

Physical parameters (methods): water temperature (SRPSH.Z1.106:1970), turbidity (EN ISO 7027: 1999); pH value (EN ISO 10523: 2008) and electrical conductivity (SRPS EN 27888:2009).

Chemical parameters (methods): chloride (SRPS ISO 9297/1:2007 revision 1); ammonia (SRPS.H.Z1.184:1974); nitrite (SRPS ISO 26777:2009); nitrate (standard methods for testing hygienic correctness "Drinking water"1990); sulfate (USEPA 375.4:1978); iron (SRPS ISO 6332:2003); manganese (standard methods for testing hygienic correctness "Drinking water"1990); and chromium as Cr^{6+} and Cr^{3+} ions (ISO 11083:1994(E)).

Physical methods

The wastewater and surface water quality analysis was conducted from January to December 2017 with a monthly sampling frequency.

Temperature measurement - the standard SRPSH.Z1.106:1970 method was validated. Measurement uncertainty was determined (2.26%). The measuring apparatus was standardized.

Spectrophotometric determination of color - by the 2120C SMEWW 21 method which is non-standard, validated as confirmed by the validation and measurement uncertainty reports. The limit of quantification was 5 units of Co-Pt scale, the coefficient of variation (CV) was 0.42%, measurement uncertainty was 9.6%. Internal control was conducted and the equipment was standardized.

Determination of turbidity - by a turbidimeter, the lab used the standard EN ISO 7027: 1999 method for ascertaining turbidity. This method was validated, which was confirmed by the validation and measurement uncertainty reports. The limit of quantification was from 0.20 NTU, CV was 0.80%, and measurement uncertainty was 6.37%. Turbidity was measured with a turbidimeter HACH 210ANIS. The laboratory used certified reference materials.

Potentiometric determination of the pH value - the laboratory used the standard EN ISO 10523: 2008 method for ascertaining pH, which was validated as confirmed by the validation and measurement uncertainty reports: accuracy was 98-99%, CV was 0.23%, measurement uncertainty was 3.0%. The measuring equipment was the pH meter WTW Level 1. The instrument was standardized, marked.

Conductometric determination of electrical conductivity - the laboratory used the standard and validated SRPS EN 27888:2009 method. Measurement uncertainty was 3.68%. CV was 0.25%, the limit of quantification was 0.01 μS/cm. The instrument measuring electrical conductivity was the Inolab Cond Level 1 WTW conductometer. The range was from 1 to 1999 μS/cm. The instrument was standardized.

Chemical methods

Chloride determination (Mohr's method) - the volumetric method, SRPS ISO 9297:1997, SRPS ISO 9297/1:2007 revision 1. The laboratory utilized the standard method which has verification and measurement uncertainty estimation reports. CV was 0.64%, measurement uncertainty was 10.02%. The range of chloride detection in water was 5-300 mg/L.

Ammonia determination (Nessler reagent method) - the spectrophotometric method SRPS.H.Z1.184:1974.The laboratory used the standard method with verification and uncertainty reports. A report verified the method's suitability: CV was 2.5%, the limit of quantification was 0.04 mg/mL, measurement uncertainty was 11.4%. The equipment for performing this method was standardized. The parameter was in the range between 0.004-4.88 mg/L.

Nitrite determination - the laboratory used the standard spectrophotometric method SRPS ISO 26777:2009 with validation reports and measurement uncertainty evaluation reports CV was 0.95%, measurement uncertainty was 5.16%. The parameter was measured in the range between 0.005-0.300 mg/L.

Nitrate determination - the laboratory relied on a non-standard (Manual P-V-31/C) spectro-photometric method for nitrate determination which was validated as stated in the validation and measurement uncertainty estimation reports. CV was 0.21%, measurement uncertainty was 10.16%, the limit of quantification was 0.4 mg/L.

Sulfate - the turbidimetric USEPA 375.4:1978 method. Validation and measurement uncertainty reports were issued. CV was 12.5%, measurement uncertainty was 8.86%. The equipment used in the laboratory for this method was a turbidimeter HACH 2100 ANIS. Sulfate measurement range in water was 1.0-40 mg/L.

Calcium determination - the volumetric USEPA 215.2:1978 method and magnesium content determination (by calculation from calcium) VMK. Validation and measurement uncertainty reports were issued. For LGS QCI-715, code 82724, Ca (54±0.5mg/L), Mg (13.2±0.1mg/L); Ca: CV was 2.21%, Mg: CV was 1.28%, measurement uncertainty: for Ca=5.25%, for Mg=6.20%. Calcium

was determined in the range of 0.6-200 mg/L and magnesium – in the range of 0.4-200 mg/L.

Iron determination - the spectrophotometric standard method SRPS ISO 6332:2003. Measurement uncertainty was 6.7%, accuracy 4%, the limit of quantification was 0.010 mg/L, CV was 2.82%. The measuring range was 0.010-2.00 mg/L.

Manganese determination - the laboratory used a non-standard spectrophotometric P-V-26A method for measuring manganese. This method was validated as confirmed by validation and measurement uncertainty reports. Measurement uncertainty was 12.9%, for a sample concentration of 0.025 mg/L (CV 7.9%), for sample concentration of 0.050 mg/L (CV 7.6%), the limit of quantification was 0.025 mg/L. The parameter was measured in the range of 0.025-4.0 mg/L.

Aluminum determination - the standard spectrophotometric ISO 10566:1994 method which has validation and measurement uncertainty reports. A report on method suitability was issued. The limit of quantification was 0.02 mg/L, CV was 1.38%, measurement uncertainty was 10.8%. The parameter was measured within the range of 0.020-0.500 mg/L.

Chromium determination - the laboratory used the standard spectrophotometric ISO 11083:1994(E) method which has verification and measurement uncertainty estimation reports. The limit of quantification was 0.01 mg/L Cr for a sample concentration of 0.0012 mg/L, CV was 2.3%, for CRM 0.050 mg/LCr, measurement uncertainty 7.60%.

Copper determination – the standard method 3113-B-APHAAWWA-WEF 2005, atomic absorption spectrometry, VARIAN, was used.

The apparatus used in the laboratory for spectrophotometric methods was UV/VIS spectrophotometer Analytic JENA.

Statistical analysis

The experimental results were expressed as mean value ± standard error of three replicates. In order to statistically estimate any significant differences among mean values, where applicable, the data were subjected to a one-way analysis of variance (ANOVA) test [7].

RESULTS AND DISCUSSION

The results of the physical and chemical parameters are shown in Tables 1, 2 and 3. The highest surface water and wastewater temperatures were measured in the wastewater samples (R) 23.8°C in August while the lowest water temperature was measured in the samples of surface water at the water intake location (N) 6.4°C in December (Table

1). With a change in temperature, there is a change in the chemical composition of water, the content of gases and especially of oxygen. No national or international standards have been set for the temperature of surface water and wastewater (US EPA 1998 andOfficial Gazette SRJ no 42/98; 44/99) because they don't have an immediate effect on human health, but they influence the chemical and microbiological processes in water. The turbidity values measured in each surface water sample ranged from 1.80 NTU (nephelometric turbidity units) at the water intake area to 30.00 NTU in the Nišava downstream from the wastewater discharge point (Table 1), which points to the deterioration of river water quality. Turbidity is lower than 10 NTU in the water samples (N) from low water level periods, while in rainy periods particles from the Nišava banks get washed away and dissolved in the water. The water becomes muddy and colored and consequently even turbidity at the water intake increases.

The toxicity of many components depends on the pH value. For instance, HCN toxicity increases with the decline of pH values while the toxicity of NH_3 grows with the elevation of pH values. Simultaneously with the elevation of pH values, heavy metals in effluent get deposited in the form of their hydroxides. The measured pH values (Table 1) in all effluent and surface water samples with the highest value of 8.39 were within the recommended values (Official Gazette of RS, No: 50/2012; 74/2011 and Official Gazette SRJ No: 42/1998, 44/1999, 28/2019).

The electrical conductivity of water depends on the geology of the area through which water flows and the ionizing particles in it. It was confirmed that warmer water has higher conductivity. The highest values of electrical conductivity in the wastewater were 1289 µS/cm (the right collector), which did not affect the drastic increase of conductivity in the surface water: from the highest value 471µS/cm at the water intake (N) to the highest value of 522 µS/cm in the river downstream from the discharge point (Nk) (Table 1). The EU directive (1998) limited conductivity to 2500 µS/cm at 20 °C under the condition that the water is not aggressive. In Kanoja, Turkey, in 177 samples of groundwater the electrical conductivity was within the interval of 332 µS/cm to 3004 µS/cm with the average value of 1573 µS/cm [8]. In Lahore, the Punjab, Pakistan, the electrical conductivity in groundwater samples before and after monsoons ranged between 455 µS/cm to 16700 µS/cm and from 315 µS/cm to 13445 µS/cm, respectively, where more than 50% of the samples had a conductivity of about 1000 µS/cm

[9]. Chloride concentrations in all river water samples (N and Nk) (Table 2) were below the maximum allowed concentration values of 100 mg/L (Official Gazette of RS, No: 50/2012; 74/2011). In natural water, chloride is present in low concentrations, usually below 100 mg/L. Chloride concentration increased with the rise of mineral content.

Table 1. Yearly temperature, turbidity, pH values and electrical conductivity of surface and wastewater: (N) Nišava-water intake, (L) left city collector, (R) right city collector, (Nk) Nišava downstream from the left collector.

Month	Temperature (°C)				pH value				Turbidity (NTU)		Electrical conductivity (μS/cm)			
	N	L	D	Nk	N	L	D	Nk	N	Nk,	N	L	D	Nk
January	11,2 ±0.1	14,0 ±0.14	14,1 ±0.04	13,8 ±0.21	7.9 ±0.11	7.96 ±0.09	7.95 ±0.09	8.02 ±0.02	22,1 ±0.22	28,9 ±0.13	352 ±0.75	886 ±0.32	1062 ±0.43	468 ±0.09
February	6,5 ±0.2	13.2 ±0.21	15.6 ±0.24	8.9 ±0.11	8.18 ±0.12	8.00 ±0.08	8.00 ±0.01	8.30 ±0.01	12,6 ±0.08	10,4 ±0.21	375 ±0.24	922 ±0.41	1072 ±0.28	400 ±0.22
March	8.0 ±0.2	14.9 ±0.07	13.8 ±0.09	9.5 ±0.15	7.79 ±0.10	7.60 ±0.10	7.95 ±0.07	7.90 ±0.03	15.2 ±0.24	27.0 ±0.18	354 ±0.15	727 ±0.21	933 ±0.19	412 ±0.25
April	9.8 ±0.1	16.2 ±0.11	15.1 ±0.45	11.4 ±0.31	8.02 ±0.08	7.61 ±0.11	7.82 ±0.12	8.06 ±0.02	5.2 ±0.05	11.1 ±0.04	384 ±0.31	870 ±0.22	1184 ±0.31	398 ±0.42
May	12.0 ±0.3	15.9 ±0.3	16.1 ±0.42	14.3 ±0.7	8.01 ±0.11	7.90 ±0.12	7.50 ±0.07	8.04 ±0.31	17.1 ±0.08	25.0 ±0.31	372 ±0.41	860 ±0.27	1022 ±0.20	407 ±0.19
June	17.2 ±0.5	18.1 ±0.3	17.7 ±0.51	19.1 ±0.4	8.10 ±0.11	7.92 ±0.10	7.52 ±0.05	8.39 ±0.04	16.1 ±0.28	16.7 ±0.14	467 ±0.51	803 ±0.13	1027 ±0.14	513 ±0.33
July	19.5 ±0.1	21.8 ±0.2	22.5 ±0.24	21.7 ±0.5	8.04 ±0.12	7.80 ±0.17	7.87 ±0.01	8.30 ±0.02	11.1 ±0.21	30.0 ±0.17	457 ±0.27	840 ±0.39	1045 ±0.38	522 ±0.10
August	16.9 ±0.7	18.8 ±0.1	23.8 ±0.16	18.2 ±0.3	8.00 ±0.09	7.81 ±0.12	7.94 ±0.11	8.10 ±0.08	6.0 ±0.06	26.0 ±0.08	403 ±0.24	876 ±0.17	1008 ±0.07	464 ±0.24
September	17.4 ±0.3	22.7 ±0.2	23.18 ±0.41	17.7 ±0.4	8.08 ±0.12	7.80 ±0.04	7.94 ±0.10	8.20 ±0.14	1.8 ±0.05	4.4 ±0.12	411 ±0.11	884 ±0.34	970 ±0.35	460 ±0.10
October	13.2 ±0.2	17.6 ±0.6	14.7 ±0.07	13.8 ±0.2	8.05 ±0.08	7.65 ±0.03	7.62 ±0.11	8.06 ±0.10	4.3 ±0.11	4.4 ±0.01	471 ±0.11	886 ±0.24	1289 ±0.25	491 ±0.17
November	8.2 ±0.4	14.4 ±0.12	13.8 ±0.28	8.6 ±0.5	7.96 ±0.11	7.88 ±0.12	7.65 ±0.11	7.72 ±0.22	10.2 ±0.24	15.2 ±0.05	380 ±0.11	823 ±0.16	840 ±0.12	405 ±0.09
December	6.4 ±0.5	12.4 ±0.11	11.3 ±0.17	6.7 ±0.09	7.98 ±0.21	7.85 ±0.25	7.94 ±0.11	8.20 ±0.08	18.3 ±0.34	25.1 ±0.21	307 ±0.11	890 ±0.10	792 ±0.21	328 ±0.13

Table 2. Yearly chloride, ammonia, nitrite and nitrate ion concentration in surface and wastewater: (N) Nišava - water intake, (L) left city collector, (R) right city collector, (Nk) Nišava downstream from the left collector.

Month	Cl⁻ (mg/L)				NH₄⁺ (mg/L)				NO²⁻ (mg/L)	NO³⁻ (mg/L)			
	N	L	D	Nk	N	L	D	Nk	Nk	N	L	D	Nk
January	<5.0	45.8 ±0.74	67.5 ±0.21	12.8 ±0.13	0.2 ±0.12	35.7 ±0.42	30.6 ±0.27	7.9 ±0.11	<0.71	4.7 ±0.13	7.1 ±0.15	10.6 ±0.16	7.5 ±0.31
February	6.6 ±0.15	53.7 ±0.45	62.7 ±0.43	7.5 ±0.14	0.1 ±0.02	26.7 ±0.16	30.1 ±0.31	0.6 ±0.01	<0.65	4.5 ±0.17	4.5 ±0.08	6.3 ±0.12	4.8 ±0.11
March	<5.0	62.6 ±0.32	84.0 ±0.45	5.2 ±0.22	0.1 ±0.01	35.6 ±0.19	28.9 ±0.16	0.5 ±0.02	<0.03	4.5 ±0.11	7.1 ±0.23	11.2 ±0.27	5.4 ±0.06
April	<5.0	46.8 ±0.28	81.9 ±0.46	5.1 ±0.22	0.1 ±0.01	30.8 ±0.24	34.4 ±0.32	6.1 ±0.05	<0.85	3.8 ±0.12	3.6 ±0.24	3.7 ±0.08	3.7 ±0.33
May	6.5 ±0.03	45.5 ±0.31	63.1 ±0.38	7.4 ±0.21	0.2 ±0.01	45.3 ±0.51	60.0 ±0.01	3.9 ±0.02	<0.75	5.4 ±0.13	3.0 ±0.17	4.5 ±0.11	21.3 ±0.47
June	6.7 ±0.35	42.8 ±0.33	50.9 ±0.42	8.5 ±0.14	0.1 ±0.01	24.7 ±0.18	28.3 ±0.15	0.7 ±0.04	<1.15	6.5 ±0.12	2.7 ±0.10	2.5 ±0.06	5.5 ±0.19
July	6.5 ±0.35	40.8 ±0.22	77.5 ±0.55	6.6 ±0.18	0.1 ±0.01	25.6 ±0.18	26.5 ±0.06	6.2 ±0.07	<2.24	5.0 ±0.10	1.1 ±0.08	1.9 ±0.13	4.9 ±0.14
August	5.3 ±0.05	42.0 ±0.19	55.0 ±0.42	14.7 ±0.07	0.1 ±0.03	31.2 ±0.31	35.1 ±0.15	6.7 ±0.06	<0.22	4.9 ±0.09	1.1 ±0.09	0.7 ±0.05	4.5 ±0.13
September	6.5 ±0.09	54.3 ±0.56	59.5 ±0.15	12.2 ±0.14	0.1 ±0.08	23.5 ±0.24	27.4 ±0.12	1.4 ±0.21	<0.17	4.3 ±0.16	1.3 ±0.09	6.3 ±0.13	5.4 ±0.12
October	6.6 ±0.05	57.3 ±0.36	140.5 ±0.72	11.4 ±0.04	0.1 ±0.07	33.5 ±0.29	42.9 ±0.16	2.3 ±0.06	<0.14	7.7 ±0.11	6.0 ±0.11	4.3 ±0.08	7.7 ±0.25
November	5.2 ±0.08	41.2 ±0.22	92.8 ±0.72	5.1 ±0.08	0.1 ±0.19	26.2 ±0.02	36.2 ±0.27	0.4 ±0.04	<0.62	4.8 ±0.08	5.2 ±0.08	6.1 ±0.06	2.2 ±0.05
December	<5.0	44.8 ±0.33	107.2 ±0.52	<5.0	0.1 ±0.11	29.1 ±0.15	39.2 ±0.05	2.3 ±0.09	<0.88	3.8 ±0.05	4.2 ±0.55	8.4 ±0.31	3.9 ±0.23

Chloride increases water's electrical conductivity and thus corrosiveness in water is also increased [10]. In metal pipes, chloride reacts with metal ions forming soluble salts (WHO 1996a) and consequently increasing metal levels in the water. Wastewater samples (L and R) contained chloride in a higher concentration, but lower than 100 mg /L in the left collector (Table 2), while the right collector contained concentrations above the maximum allowed in only two samples (October and December), which is understandable because they are untreated wastewater (Table 2). The increased concentration of chloride in wastewater comes from industrial wastewater, galvanization and other technological processes. In Banat, Serbia, groundwater has low chloride content ranging from 5 mg/L to 50 mg/L [11].

The presence of ammonia in concentrations higher than the geological level is an important indicator of fecal contamination and can be utilized for the assessment of overall water quality [12]. Ammonia nitrogen concentrations (NH^{4+}-N) in all wastewater samples ranged from 23.5 (L) to 60.00 mg/L (R) (Table 2) and this affected the increase of this parameter in the river: from 0.1 mg/L (at the water intake) to 7.9 mg/L in the Nišava after the wastewater discharge, which is considerably higher than the maximum allowed concentration in a river (Official Gazette of RS, No: 50/2012; 74/2011 and Official Gazette of SRS, No. 31/82).

Nitrates and nitrites in wastewater and surface water can appear naturally but anthropogenic processes like the overuse of inorganic nitrogen fertilizers, municipal wastewater, septic tanks, farm runoff, industrial effluent, and others comprise the most common causes. Inorganic nitrogen analysis enables the assessment of these activities' influence on water quality [13]. The highest nitrate nitrogen (NO_3^--N) concentration of 21.3 mg/L and nitrite nitrogen (NO_2^--N) concentration of 2.24 mg/L in the Nišava (Table 2) show water quality deterioration after the discharge of untreated wastewater into the river. These values are above the maximum allowed concentrations for surface water (Official Gazette of RS, No: 50/2012; 74/2011 and Official Gazette of SRS, No. 31/82). In the United States of America, Texas, a region that aside from oil and natural gas production also engages in agriculture, the groundwater nitrate concentration varied from <0.44 mg/L to 149 mg/L whereby in 3 out of 40 water samples nitrate concentration exceeded the national standard of 44 mg/L. Statistics show that nitrate concentration drops with well depth [14].

Sulfates are the least toxic anions (US EPA 1999a). Available literature does not indicate a sulfate concentration in water that may be detrimental to health. Studies suggest that in concentrations between 1000 mg/L and 1200 mg/L sulfates have a laxative effect but without diarrhea, dehydration and weight loss (WHO 2004b). Also, sulfates may contribute to corrosion in distribution systems (WHO 2004b). Sulfate concentration in each sample ranged: (N) (8.4-24.5) mg/L; (Nk) (9.1-28.7) mg/L; (L) (51.8-141.1) mg/L and (R) (16.9-178.7) mg/L (Table 3). The highest concentration of sulfate was measured in (R) (16.9-178.7) mg/L in March while the lowest sulfate concentration was measured in (N) (8.4 mg/L) in September. The increased concentration of sulfate in wastewater comes from industrial wastewater of galvanization, chemical and electrochemical degreasing in the metal industry and other technological processes [14]. Despite the mild increase of sulfate after the wastewater discharge all measured values at this location were far below the maximum allowed concentration of 100 mg/L for surface water (Official Gazette of RS, No. 50/2012). Sulfate concentrations are a consequence of leaching from agricultural land or originate from industrial waste and municipal waters [14]. These are wastewaters and their composition is of variable quality, so the results are varied.

Iron concentration (Table 3) in all surface water samples (the Nišava after wastewater discharge) was (0.05-0.39) mg/L, below the maximum allowed concentration (<0.5 mg/L) (Official Gazette of RS, No. 50/2012). Iron does not pose a risk to human health in concentrations it appears in natural water. However, if the concentration is above 0.3 mg/L it may cause turbidity and coloration, and as a consequence of the increase of iron-oxidizing bacteria pipes are lined with mucous layers. U.S. EPA (2012) considers iron a secondary contaminant and sets a secondary maximum contaminant level (MCL) of 0.3 mg/L in drinking water. The reason behind this limit is its influence on organoleptic features of water: rusty color, metallic taste, red or orange coloration. Iron promotes the reproduction of iron-oxidizing bacteria. These bacteria rely on the oxidation process of Fe^{2+} into Fe^{3+} ions for energy. This leads to clogging and the formation of a mucous layer in water system pipes [15]. On the North of Serbia, in Subotica, iron concentration in groundwater samples ranges from 0.04 mg/L to 0.96 mg/L [11].

Table 3. Yearly iron, manganese, chromium, copper and sulfate ion in surface water: (N) Nišava-water intake, (Nk) Nišava downstream from the left collector.

Month	Fe (mg/L)	Mn (mg/L)	Cr^{6+} (mg/L)	Cr^{3+} (mg/L)	Cu (mg/L)	SO_4^{2-} (mg/L)			
	NLDNk	NLDNk	NLDNk	NLDNk	NLDNk	N	L	D	Nk
January	<0.35	<0.025	<0.010	<0.010	<0.021	13.2±0.41	58.2±0.55	50.±0.05	22.9±017
February	<0.16	<0.025	<0.010	<0.010	<0.026	21.3±0.52	141.6±0.72	178.9±0.72	21.2±0.61
March	<0.06	<0.025	<0.010	<0.010	<0.018	10.0±0.36	34.7±0.21	18.1±0.10	10.9±0.24
April	<0.08	<0.025	<0.010	<0.010	<0.012	9.4±0.31	93.0±0.44	143.0±0.62	16.5±0.06
May	<0.11	<0.025	<0.010	<0.010	<0.017	15.3±0.08	46.3±0.31	71.8±0.47	14.1±0.07
June	<0.12	<0.025	<0.010	<0.010	<0.010	14.9±0.16	46.4±0.32	65.2±0.08	18.9±0.13
July	<0.13	<0.025	<0.010	<0.010	<0.027	24.5±0.34	45.7±0.31	70.1±0.15	28.7±0.08
August	<0.22	<0.025	<0.010	<0.010	<0.010	16.9±0.07	35.7±0.06	47.4±0.16	17.3±0.11
September	<0.15	<0.025	<0.010	<0.010	<0.010	13.6±0.06	29.9±0.26	16.9±0.09	20.4±0.16
October	<0.39	<0.025	<0.010	<0.010	<0.030	16.4±0.15	15.8±0.11	28.9±0.11	13.1±0.03
November	<0.21	<0.025	<0.010	<0.010	<0.010	8.4±0.13	24.8±0.08	19.5±0.29	11.6±0.08
December	<0.05	<0.025	<0.010	<0.010	<0.010	8.9±0.15	31.8±0.52	29.6±0.07	9.1±0.04

Manganese concentration in all samples of analyzed surface water was <0.025 mg/L (Table 3) and thus satisfies the recommended values and the maximum allowed concentration (0.1 mg/L) (Official Gazette of RS, No. 50/2012). Manganese is one of the elements the presence of which is considered natural in water (WHO 2011a). Of course, it can appear in water as a consequence of anthropogenic actions. Manganese in water behaves similarly to iron. It also promotes the proliferation of manganese-oxidizing bacteria. These bacteria rely on the oxidation process of Mn^{2+} to Mn^{3+} for energy which leads to the formation of a mucous layer in pipes. This problem occurs at manganese concentrations that exceed 0.1 mg/L. (WHO 2011a). Although these bacteria are harmless to humans they may cause clogging in water systems [16], WHO 2011a. In the groundwater of the Pannonian Basin (eastern Hungary and western Romania), manganese concentrations vary from <0.001 mg/L to 0.336 mg/L [17].

The Cr^{3+} and Cr^{6+} concentrations in all water samples from the river Nišava was <0.01 mg/L (Table 3) and therefore they meet the recommended values and the maximum allowed concentration (0.05 mg/L) (Official Gazette of RS, No. 50/2012). The distribution of compounds containing Cr^{3+} and Cr^{6+} depends on the reduction potential, pH value, oxidizing and reducing compounds presence, kinetics of reduction reactions, the formation of Cr^{3+} complexes or insoluble Cr^{3+} salts and the total chromium concentration. When chromium concentration is low, Cr^{3+} is present as a monovalent $HCrO_4^-$ below the pH value of 6.5 and divalent CrO_4^{2-} at a pH value between 6.5 and 10 [18]. In water without oxygen or with a very low concentration of it, Cr^{3+} is a dominant particle that occurs in cationic (Cr^{3+}, $CrOH_2^+$ or $Cr(OH)$) or neutral ($Cr(OH)_3$) form depending on the pH value.

Cr^{3+} is insoluble (<20 µg/L) within the pH range of 7 to 10, with the minimum solubility at the pH value of 8 (1 µg/L) [18]. In natural minerals, chromium mostly appears as Cr^{3+}. The results of studies in Croatia have shown that contaminated groundwater (Fe, Pb, Ni, and Cr) becomes a large hygienic and toxicological problem since it considerably impedes groundwater utilization [19]. Even though all of these contaminants have not yet reached toxic levels, they still represent a long-term risk for the population's health [20].

Copper concentration (Table 3) in all surface water samples (the Nišava after wastewater discharge) was (0.01-0.03) mg/L, below the maximum allowed concentration (<0.25 mg/L) (Official Gazette of RS, No. 50/2012). Copper does not pose a risk to human health in concentrations it appears in natural water.

Although the determined concentration values of Fe, Mn and Cr were below the maximum allowed concentrations, an increase in river water turbidity, as well as elevated values of nitrogen (ammonia ion, nitrates) indicated that the untreated wastewater discharge continually deteriorates the Nišava water quality. Due to higher values of ammonia ions, which indicate fecal contamination, there is a risk of pathogenic bacteria. Numerous studies [21] show the efficacy of various technical and technological wastewater treatment processes. They mostly refer to filtration, aeration, disinfection [6] and other processes depending on the degree and type of wastewater contamination. This is certainly applicable to the wastewater in Niš and the result would be the preservation of the environment and river water quality.

CONCLUSION

The physical and chemical analyses of the wastewater and surface water quality indicate deterioration in the Nišava water after the discharge from the city wastewater collectors. Contaminant concentration in the effluent has been a factor in the deterioration of the recipient's water quality. This can be stated because of the elevated turbidity values and fecal contamination indicators (ammonia ion, nitrates) in the river after the discharge from the collectors. These values are considerably increased in comparison to the values before the discharge of wastewater and in comparison to the limit values for a good ecological status according to the regulation on contaminant limits in surface water, groundwater, sediment and the time limit for reaching them (Official Gazette RS no 50/12) - for a good ecological status, i.e. class II - river type 2; natural level.

As the aforementioned regulations stipulate time limits for reaching the threshold values, in the following period it is necessary to adjust the emissions of contaminants to the threshold values. To achieve this, a central wastewater facility must be constructed with the view of preserving water from contamination and maintaining public health.

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