




## Wastewater treatment in the city of Koprivnica

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### ABSTRACT

Based on the concept of sustainable development, water must be stored and protected for present and future generations. This also means saving the water through wastewater treatment. The primary role of the wastewater treatment plants is to treat wastewaters up to a satisfactory level of quality as close as possible to the natural state. The central wastewater treatment plant (WWTP) of the City of Koprivnica treats wastewater including the tertiary wastewater. Due to considerable fluctuations in wastewater volumes and loads, sequential batch reactor (SBR) technology was selected as the best solution for wastewater treatment. The final stage of treatment at the WWTP of the City of Koprivnica is the process of sludge treatment by aerobic stabilization, dehydration and MID-MIX technology, which produces a chemically inert powder – solidificate. Solidificate can be used in civil engineering or it can be disposed to landfill without environmental impact. This paper analyses the physical-chemical indicators of wastewater quality (chemical oxygen demand - COD, biological oxygen demand - BOD<sub>5</sub>, total nitrogen, total phosphorus, suspended matter) on wastewater samples from the WWTP of the City of Koprivnica in a period from 2014 to 2016. The results indicate that the treated wastewater has a satisfactory quality and that the WWTP of the City of Koprivnica works efficiently.

## Introduction

Water needs to be properly managed throughout the entire water cycle: from fresh water sources, pumping, pre-treatment, distribution, use, collection and subsequent treatment, then to wastewater treatment and final return to the environment. With increasing population growth, urbanization and economic development, the amount of treated wastewater and pollution levels are increasing globally. Wastewater management has been seriously neglected, and such waters are undervalued as a potentially affordable and renewable source of water and energy. Knowledge of chemical, physical-chemical and microbiological indicators of water quality is important for the control and management of all water resources, since the ecological status of surface waters is assessed on the basis of these indicators. Monitoring the quantity and

quality of water is a process defined by law and is an integral part of water management procedures (EU Water Framework Directive, 2000; Croatian Water Law, OG 66/19). Considering that a large part of Croatia is a porous karst area (Biondić and Biondić, 2014), wastewater treatment is the only way to conserve the largest and most valuable Croatian resource, large supplies of drinking water. Concerning the fact that Croatia bases its development on tourism and the production of healthy and environmentally friendly food, it is quite clear that the unpolluted sea, rivers, lakes, wetlands and ground waters directly influence the overall economic development. Construction of water utilities, including wastewater treatment plants in Croatia, is financed through European funds (EU Special report, 2015). Urbanization and construction of industrial plants without the construction of municipal wastewater drainage systems and their effective

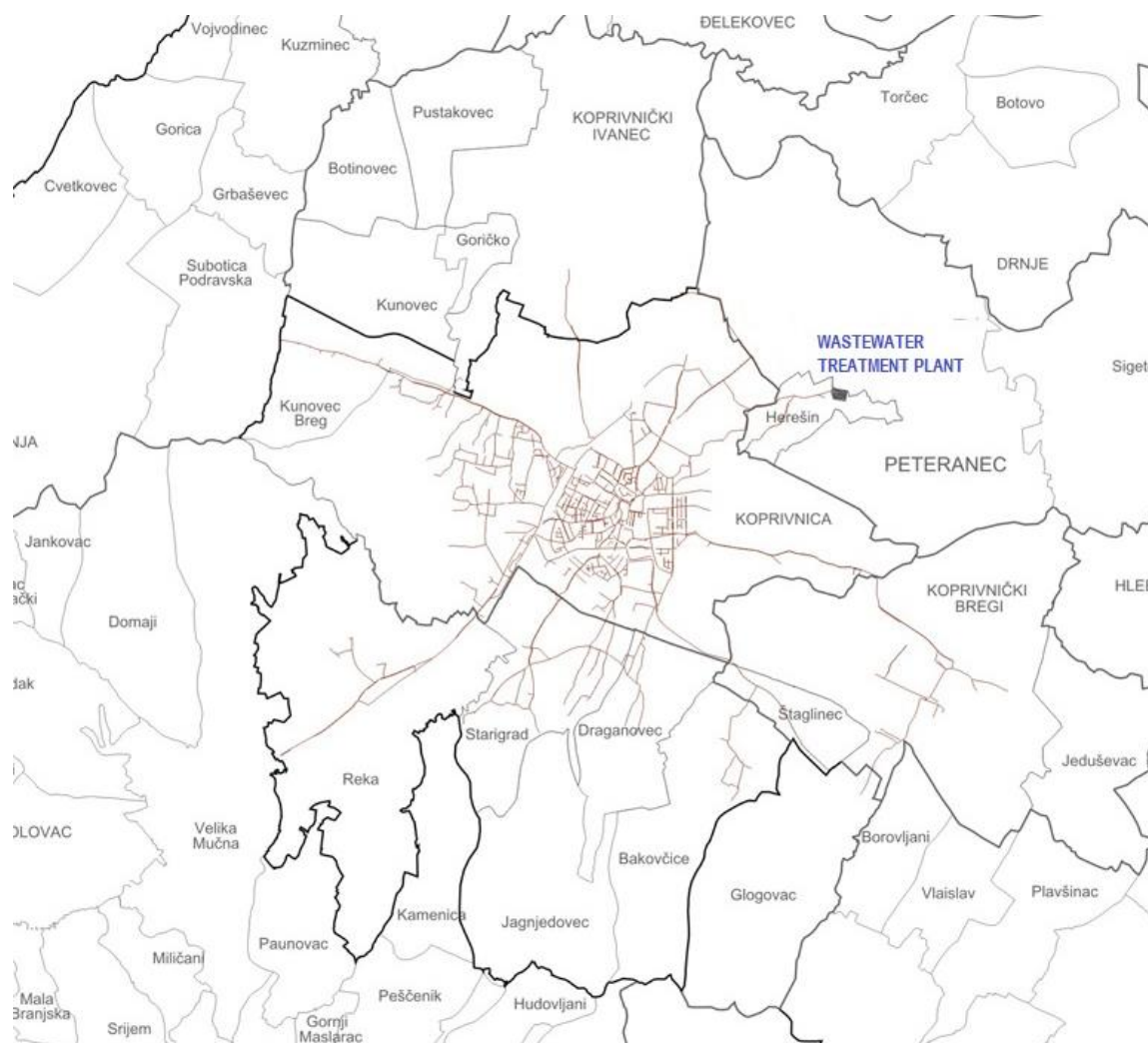
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maintenance, result in an increasing threat to groundwater quality. Significant measures for the protection of aquifers should slow down water pollution processes so that the supply of drinking water to the population remains satisfactory. It is for these reasons that wastewater should be seen as a great potential, not as a burden. Today, there are various treatment processes and functional systems that allow the use of wastewater to meet the increasing needs of the population, agriculture and industry (Samer, 2014; Crini and Lichtfouse, 2019). The aim of this paper was to describe the wastewater treatment at the WWTP of the City of Koprivnica and to analyse the physical - chemical indicators of wastewater, i.e. total nitrogen, total phosphorus, biological oxygen consumption, chemical oxygen consumption and suspended substances.

## Materials and methods

### *Description of the central wastewater treatment plant in the city of Koprivnica*

Drainage system of the city of Koprivnica involves a mixed system, meaning that the common sewage system drains wastewater from households and industry, as well as rainfall waters. The delivery of the mixed wastewater to the location of the WWTP is performed by the main drainage collector Koprivnica - Herešin. The sewerage system is connected to approximately 11,873 households and businesses. A total of about 279 km of sewage network and several dozen special facilities, like pumping stations, overflows and pools for water intake, were constructed.



**Fig. 1.** Drainage system of the city of Koprivnica (source: [www.kcvode.hr](http://www.kcvode.hr))



**Fig. 2.** Biological wastewater treatment plant in the city of Koprivnica (source: [www.kcnode.hr](http://www.kcnode.hr))

The biological wastewater treatment plant, presented in Fig. 2, treats wastewater up to the third stage of treatment, that is, pre-treatment of wastewater, primary treatment, biological treatment, sludge treatment, and further sludge treatment at the MID-MIX plant.

Pre-treatment of wastewater uses a coarse grate that stops large-sized waste such as tree pieces, rags, leaves and plastic objects. Primary or mechanical treatment of wastewater is carried out in an automated compact device consisting of a fine grid, sand trap and grease trap. Procedures for secondary, i.e. biological treatment of wastewater, include the implementation of aerobic, anoxic and anaerobic processes in which microorganisms break down the carbon, nitrogen, and phosphorus compounds from wastewater. Secondary wastewater treatment is carried out by sequential batch reactors (SBR). SBR technology is a discontinuous biological, secondary treatment process where different processes take place in one reactor; such as filling, aerobic reactions, anoxic, anaerobic reactions, sedimentation and decanting of treated water. The biological decomposition process in sequential batch reactors produces excess sludge that is extracted and transported by pressure pipeline to a collector in which it accumulates, thickens, aerobically stabilizes and is dehydrated by centrifuge. Subsequently, the sludge with 25 % dry matter is further treated in the MID-MIX plant to produce the final product, an inert powder called neutral with more than 85 % dry matter. The final product is in the form of a hydrophobic material, which is conveyed to the silo by a conveyor belt and packed in a jumbo bag. Neutral obtained by sludge treatment is a useful material. It is hydrophobic, it has good thermal and acoustic insulation properties

it can be used in the construction industry or dumped into landfills as a fertilizer, or it can be used to make a compost.

#### *Determination of physical-chemical indicators*

The wastewater samples were taken at the input and output pipeline of the central wastewater treatment plant in Koprivnica for the analysis of physical-chemical indicators of water quality every month for 3 years period (2014-2016).

#### *Determination of total nitrogen*

Total nitrogen (TN) was determined using the TOC Shimadzu/TOC-V<sub>CPN</sub> instrument. After pre-treatment, the sample was injected into the cuvette which was heated up to 720 °C. In the cuvette, the sample was converted to nitrogen monoxide, which, after dehumidification and cooling, was transferred by a stream of purified air (130 mL/min) to a chemiluminescent detector. The obtained signal was compared with the standard sample signal and the concentration of total nitrogen in the sample was determined according to norms (Water quality-Determination of ammonium - Part 1: Manual spectrometric method, HRN ISO 7150-1:1998) and American Public Health Association - APHA (1999).

#### *Determination of total phosphorus*

The determination of phosphate ( $\text{PO}_4^{3-}$ ) was carried out using a HACH DR 5000 UV/VIS spectrophotometer. According to standard norm (Water quality - Determination of phosphorus -

Ammonium molybdate spectrometric method, EN ISO 6878:2004), 10 ml water sample was placed in a glass cuvette and PhosVer 3 Phosphate Reagent was added. Orthophosphates react with molybdate in an acid medium to form a mixed phosphate/molybdate complex, and ascorbic acid reduces the complex to an intense molybdenum blue colour. The measurement wavelength was 880 nm.

#### *Determination of biological oxygen demand (BOD<sub>5</sub>)*

BOD<sub>5</sub> (biological oxygen demand after five days) was determined on an OxiTop device. The sample temperature was adjusted to 20 °C and the pH to 6 - 8. Depending on the expected oxygen concentration in mg/L after 5 days a certain volume of homogenized sample was measured and transferred to a dark glass vial. A few drops of nitrification inhibitor (1 drop per 50 ml sample) and two NaOH granules were added (Water quality, 1998).

Measurement using OxiTop is based on pressure measurement in a closed system. Microorganisms in the sample consume the oxygen and produce CO<sub>2</sub> which is then absorbed by NaOH, creating a vacuum which can be read directly as a measured value in mg/l BOD. The used sample volume regulates the amount of oxygen available for a complete BOD.

#### *Determination of Chemical Oxygen Demand (COD)*

The process for the determination of COD is based on the oxidation of organic constituents in water using KMnO<sub>4</sub> solution. A sodium oxalate solution was prepared by dissolving 0.1675 g sodium oxalate in 250 ml distilled water with addition of few drops of concentrated sulfuric acid and heated until oxalate dissolved. After that, 100 ml of water sample was filtered and transferred to an Erlenmeyer flask and 15 ml of sulfuric acid (1:3) was added. The mixture was heated to boiling point and heated for another 5 min. A solution of potassium permanganate (0.002 M) was added to the hot solution and heated for another 10 min. After that, sodium oxalate solution was added and heated until the solution discoloured. The hot

solution was titrated with KMnO<sub>4</sub>. The consumption of KMnO<sub>4</sub> during titration is a relevant indicator of the amount of organic matter in water.

#### *Determination of suspended matter*

The filter paper was dried and cooled in the desiccator, and then weighed. The filter paper types were black tape, Ø = 55 mm - for the inlet water sample, with glass phase, Ø = 55 mm - for the sludge and cellulose nitrate sample, Ø = 50 mm - for the outlet water sample. Filter paper was placed on the vacuum pump and washed with a small amount of distilled water. A certain volume of the mixed sample (depending on the amount of suspended substance expected) was filtered through filter paper, washed with a small amount of distilled water and placed in an oven at 105 °C for about 60 minutes. The dried filter paper was placed in a desiccator for cooling for at least 30-60 minutes, then weighed again.

## **Results and discussion**

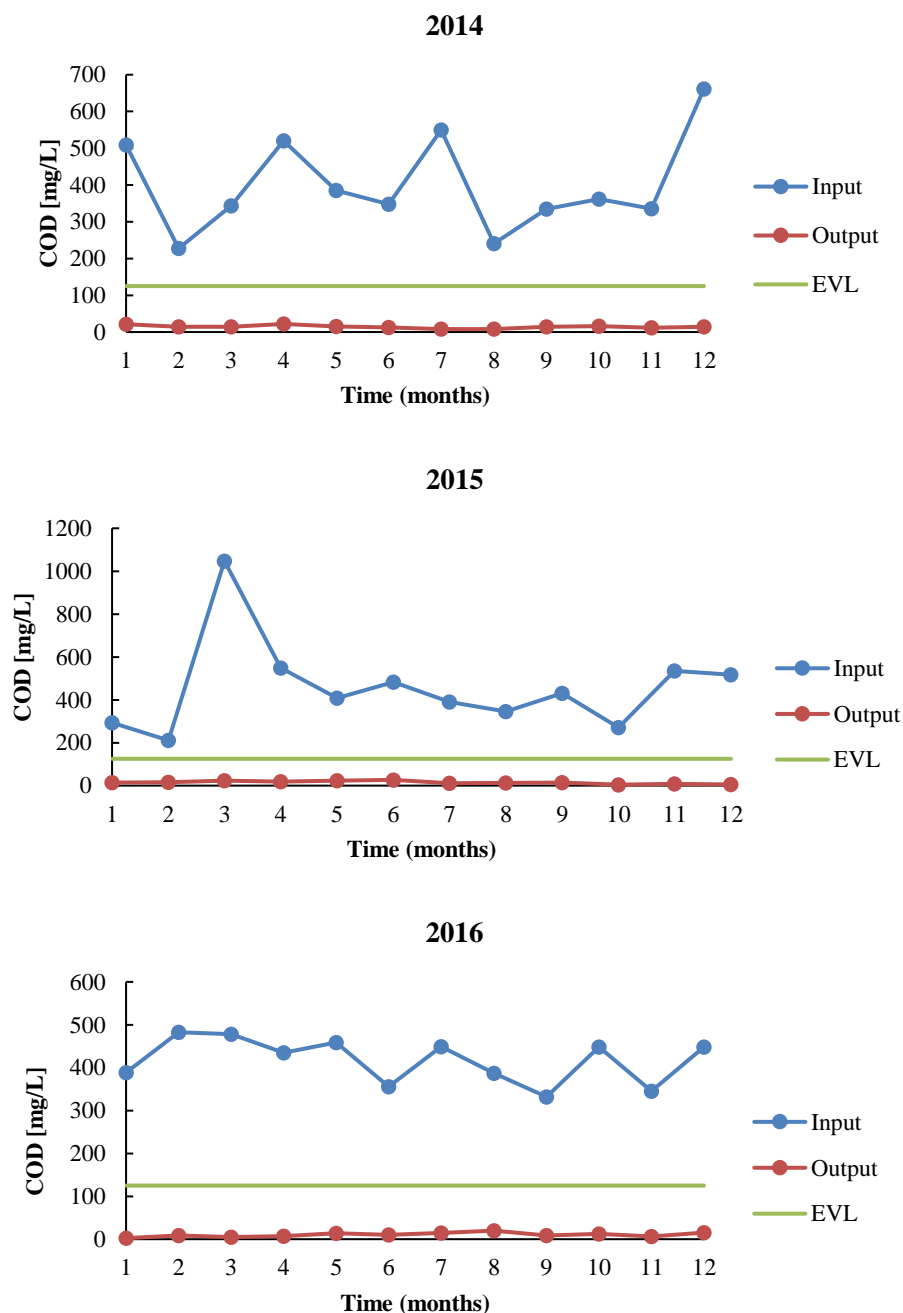
The wastewater treatment plant in Koprivnica carries out the third-stage wastewater treatment for which, according to the Regulation on the Emissions Values Limit of Wastewater (OG 80/13, 43/14, 27/15, 3/16) total nitrogen, total nitrates, COD, BOD<sub>5</sub> and suspended solids. Wastewater treatment plant is supplied with domestic wastewaters, rainfall waters and industrial wastewaters. Industrial plants, by discharging wastewater, significantly contribute to the elevated concentrations of physical-chemical indicators of water quality. Wastewater from the food industry causes the increase in BOD<sub>5</sub>, solids and fats. The pharmaceutical industry causes the increase in the COD values, acids and alkalis, while wastewater from the brewing industry affects the increase in COD, BOD<sub>5</sub>, oils and fats. According to the Regulation on the Emissions Values Limit of Wastewater (OG 80/2013), the emission values limit (EVL) of physical-chemical indicators in wastewater are shown in Table 1.

**Table 1.** Emission limit values for pollutants in wastewater

Physical-chemical indicators	Measurement unit	Emission values limit (EVL)
COD	(mg/L) O <sub>2</sub>	125
BOD <sub>5</sub>	(mg/L) O <sub>2</sub>	25
Total N	(mg/L) N	15
Total P	(mg/L) P	2
Suspended matter	mg/L	35

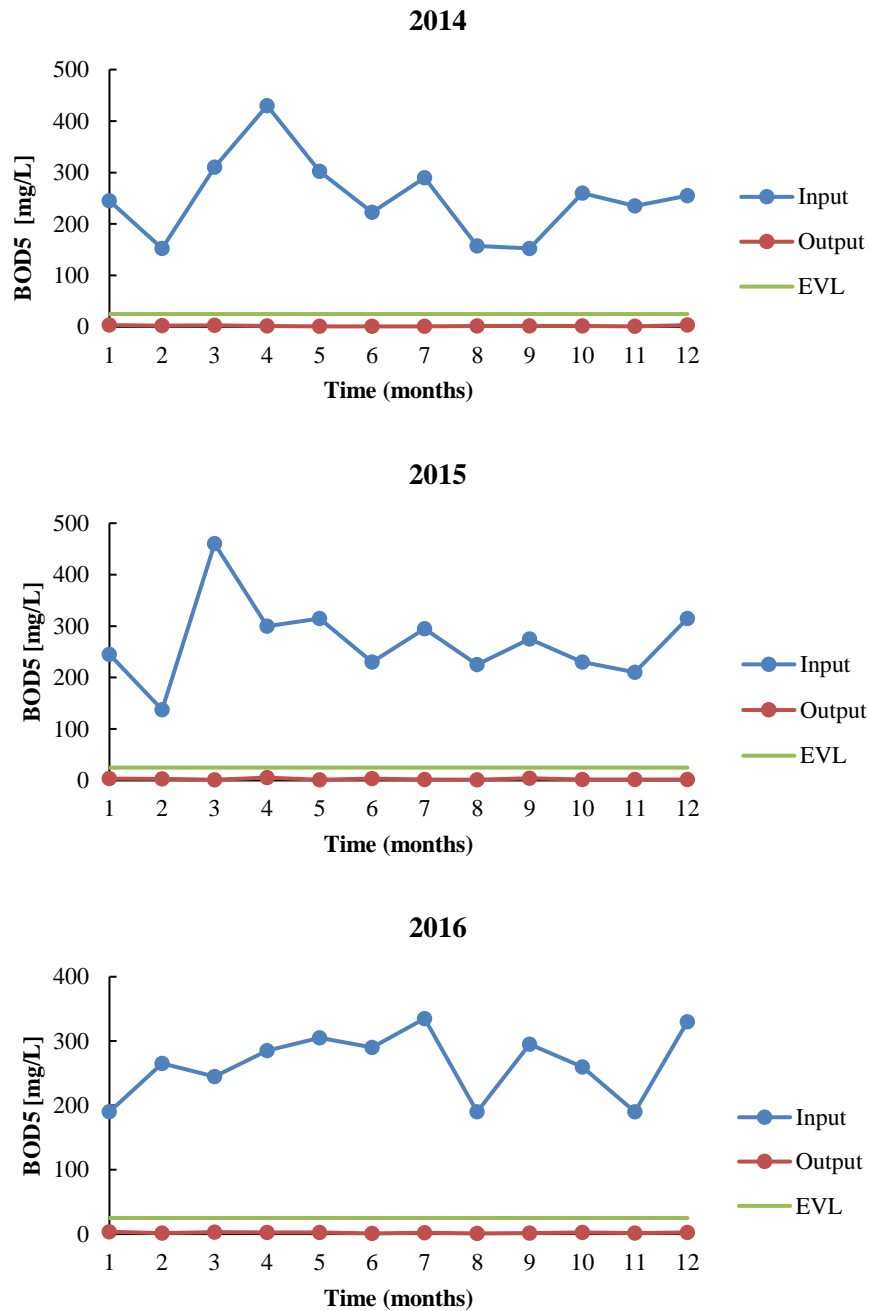
Figs. 3 and 4 show the measured values of COD and BOD<sub>5</sub> concentrations for the period 2014-2016. The input values of the indicators show large alternating oscillations (COD of 200 - 1200 mg/L O<sub>2</sub>, BOD<sub>5</sub> of 140 - 460 mg/L O<sub>2</sub>) as a result of retention of the inlet wastewater in the retention basin, which means that the solid particles settle to the bottom which causes lower concentrations of organic and inorganic pollution on the surface and higher concentrations of

pollution are present at the bottom of the basin (Devi et al., 2008; Lu et al., 2015; Cossu et al., 2017). The pump first draws water from the surface, so the input values of COD, BOD<sub>5</sub> and suspended solids are lower. By lowering the water level, a denser mass was drawn, and for this reason the values of the indicators were much higher. As it can be seen from the results, the output values were below the EVL which indicates the efficient operation of the device.



**Fig. 3.** Values of chemical oxygen demand (COD) concentrations measured monthly during 2014, 2015 and 2016 on samples taken from WWTP input, output and their EVL values

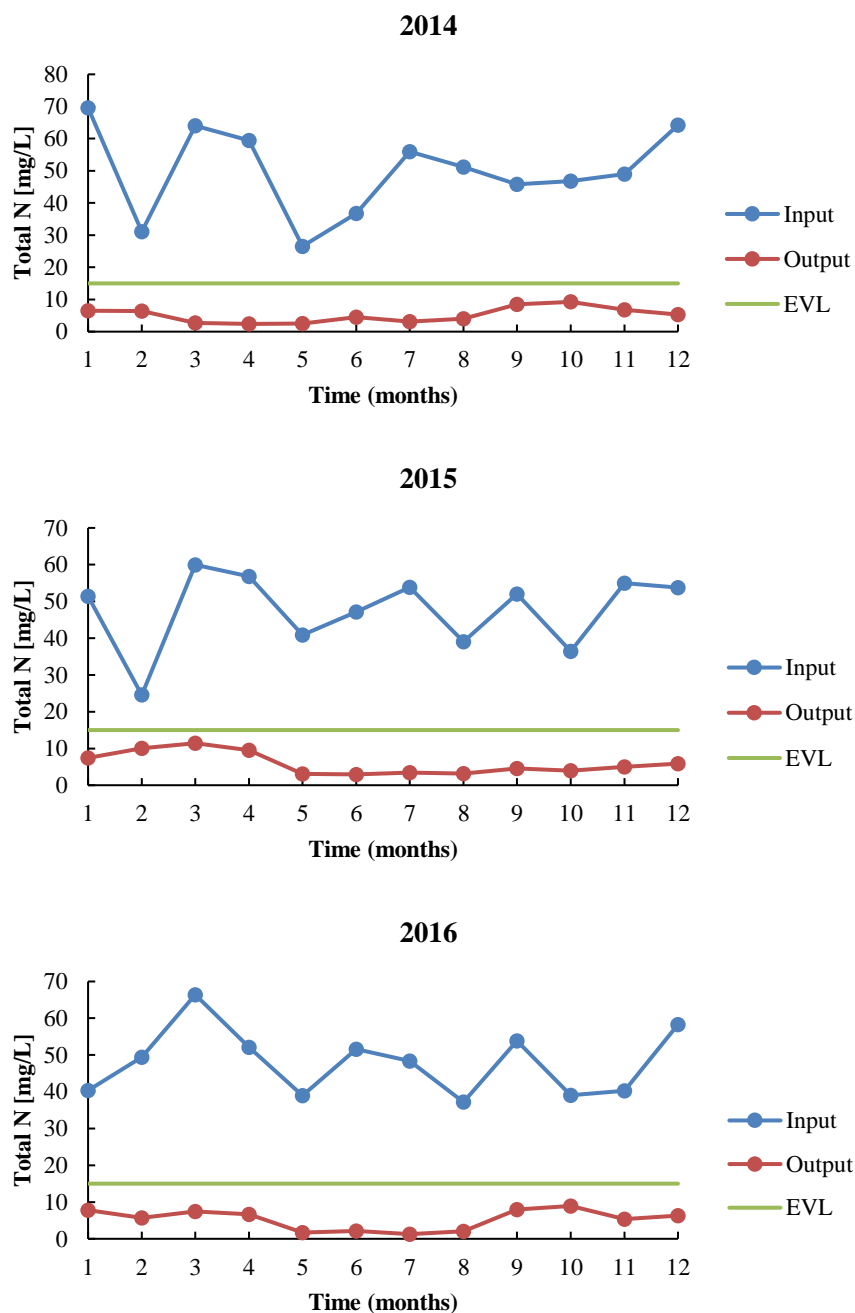




**Fig. 4.** Values of biological oxygen demand ( $BOD_5$ ) concentrations measured monthly during 2014, 2015 and 2016 on samples taken from WWTP input, output and their EVL values

Figure 5 shows fluctuations in the input values of the total nitrogen concentration during the year (24 - 70 mg/L), which can be attributed to the increased use of mineral fertilizers on agricultural land, but the output values are below the permitted values. Nitrogen, as a gas, is found in the atmosphere, and under special conditions it is oxidized to nitrogen (IV) oxide and, when “flushed out” of the atmosphere, enters the water systems. Certain types of algae, bacteria and plants can take nitrogen from the atmosphere, but most of the

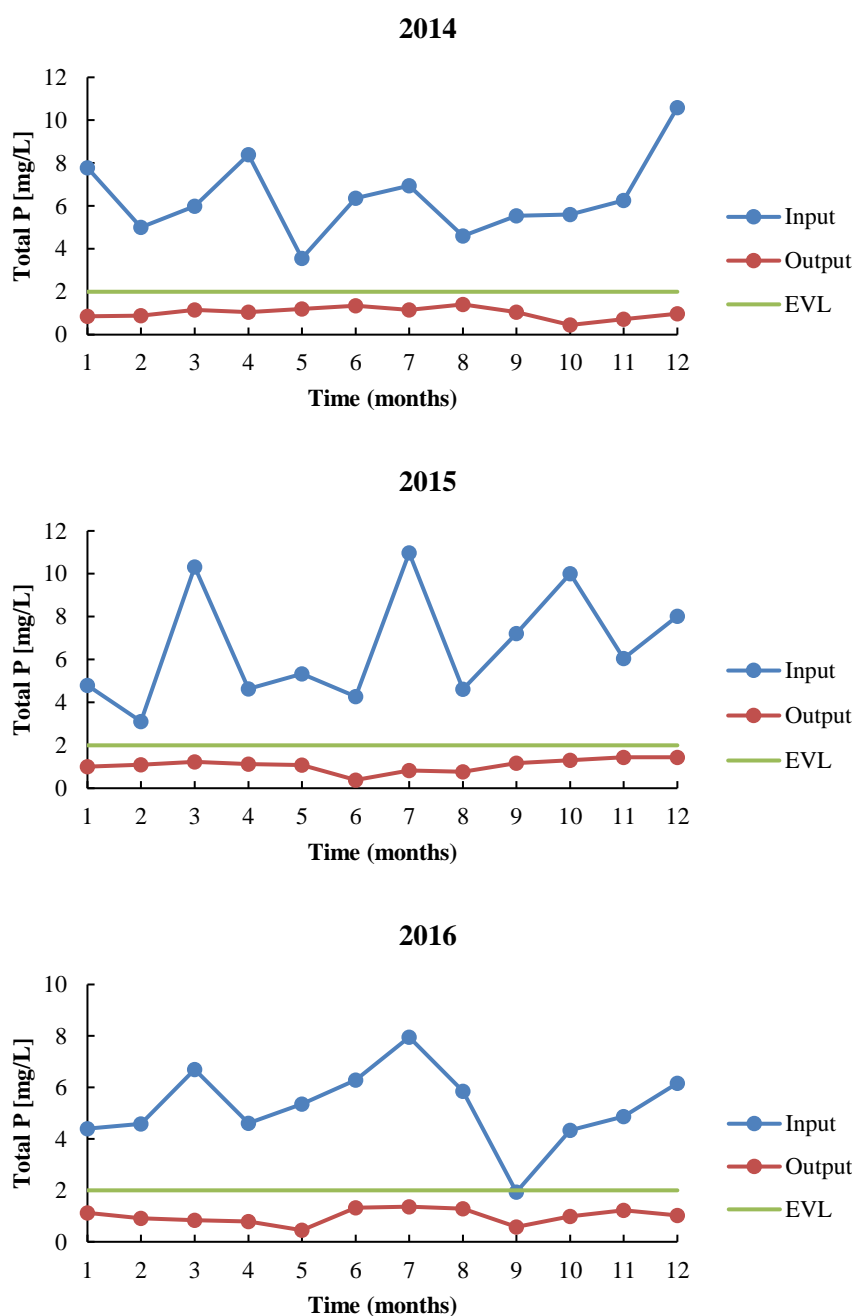
nitrogen compounds in the water are due to the decomposition of organic matter. Extra quantities are also brought in by flushing agricultural land. If sufficient amounts of dissolved oxygen are present in aqueous systems, processes of organic matter breakdown occur thereby reducing the oxygen concentration in the water. The high concentration of nitrate in wastewater is an indicator of the final degree of stabilization of bio-waste or heavily fertilized fields (Van Puijenbroek et al., 2019; Hendrickx et al., 2012).



**Fig. 5.** Values of total nitrogen concentrations measured monthly during 2014, 2015 and 2016 on samples taken from WWTP input, output and their EVL values

Fig. 6 shows the phosphorus concentration values over three years. Input values of phosphorus concentrations range from 2 - 11 mg/L and significant oscillations, most likely due to human activities and anthropogenic activities, are evident. The phosphorus in the waters can be of natural and anthropogenic origin (soil and rocks, industrial and domestic wastewater, drains of fertilized surfaces, etc.). Phosphorus is found in water in the form of orthophosphates, polyphosphates and organically bound phosphorus, it is non-toxic but

increases the production of primary organic matter and thus increases the eutrophication of water systems (Gooddy et al., 2018). It enters the water by decomposing organic matter and leaching soil, especially agricultural. Natural waters contain phosphorus at very low concentrations, and an increase in phosphorus concentration can cause several adverse events (algal blooms, decrease in dissolved oxygen concentrations, dying of some fish species) (Berg et al., 2005; Bian et al., 2011).

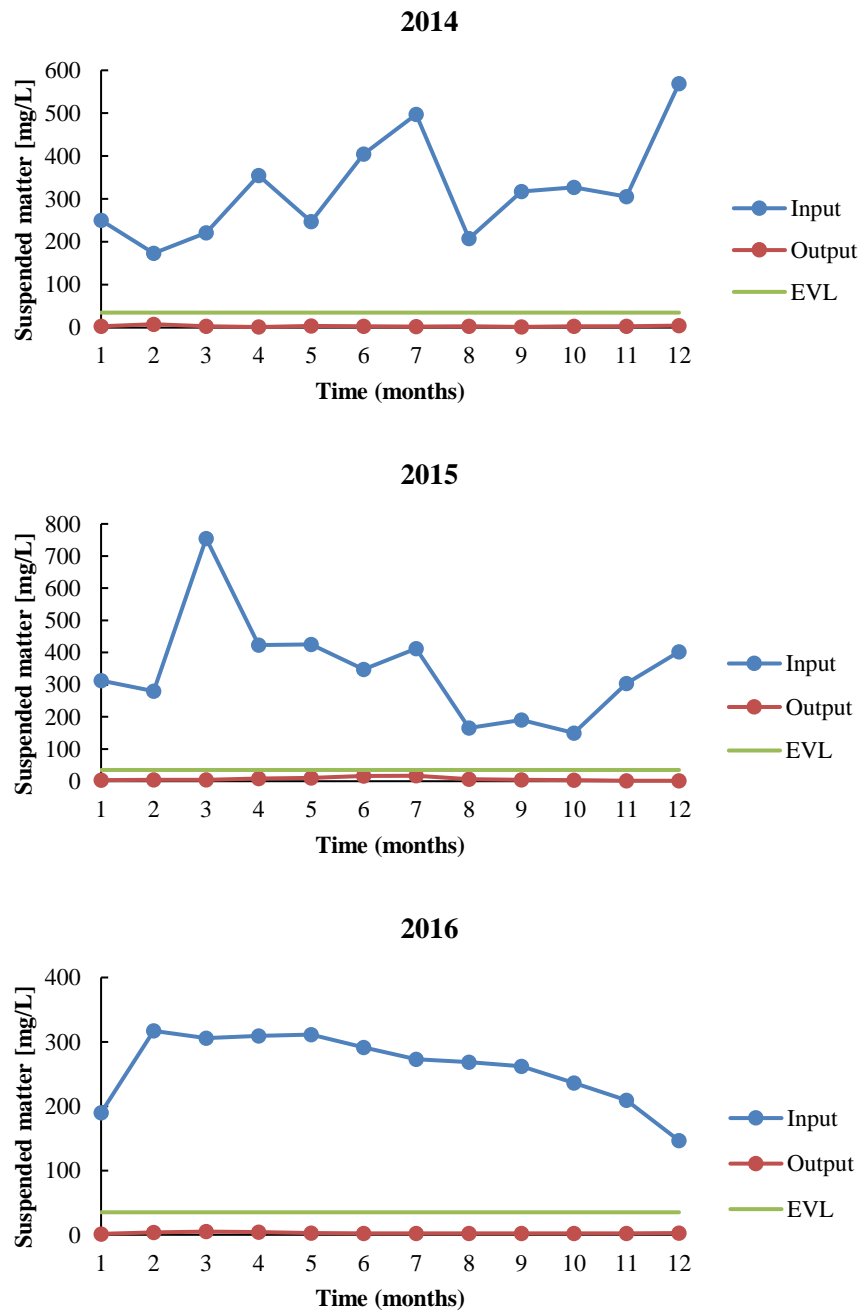


**Fig. 6.** Values of total phosphorus concentrations measured monthly during 2014, 2015 and 2016 on samples taken from WWTP input, output and their EVL values

Fig. 7 shows a wide range of suspended solids inputs (150-750 mg/L) during 2014 and 2015, which can be largely attributed to the effects of precipitation and stormwater. Rainwaters, which flush the atmosphere as well as the surfaces of cities, differ significantly from each other, but they have a common feature that during initial surface flushing, suspended matter concentrations are sometimes higher than their concentrations in domestic wastewater. After prolonged rinsing of surfaces, the concentration of suspended solids in

precipitation water decreases. Suspended substances cause turbidity of water, i.e. cause aesthetic pollution of water, prevent the penetration of light into water, which limit the processes of photosynthesis and the development of algae and the antibacterial effect of light on pathogenic organisms (Bilotta and Brazier, 2008). After purification, it is evident that the values of the suspended solids concentrations are within the EVL and almost constant, which confirms the effective purification process at the WWTP.



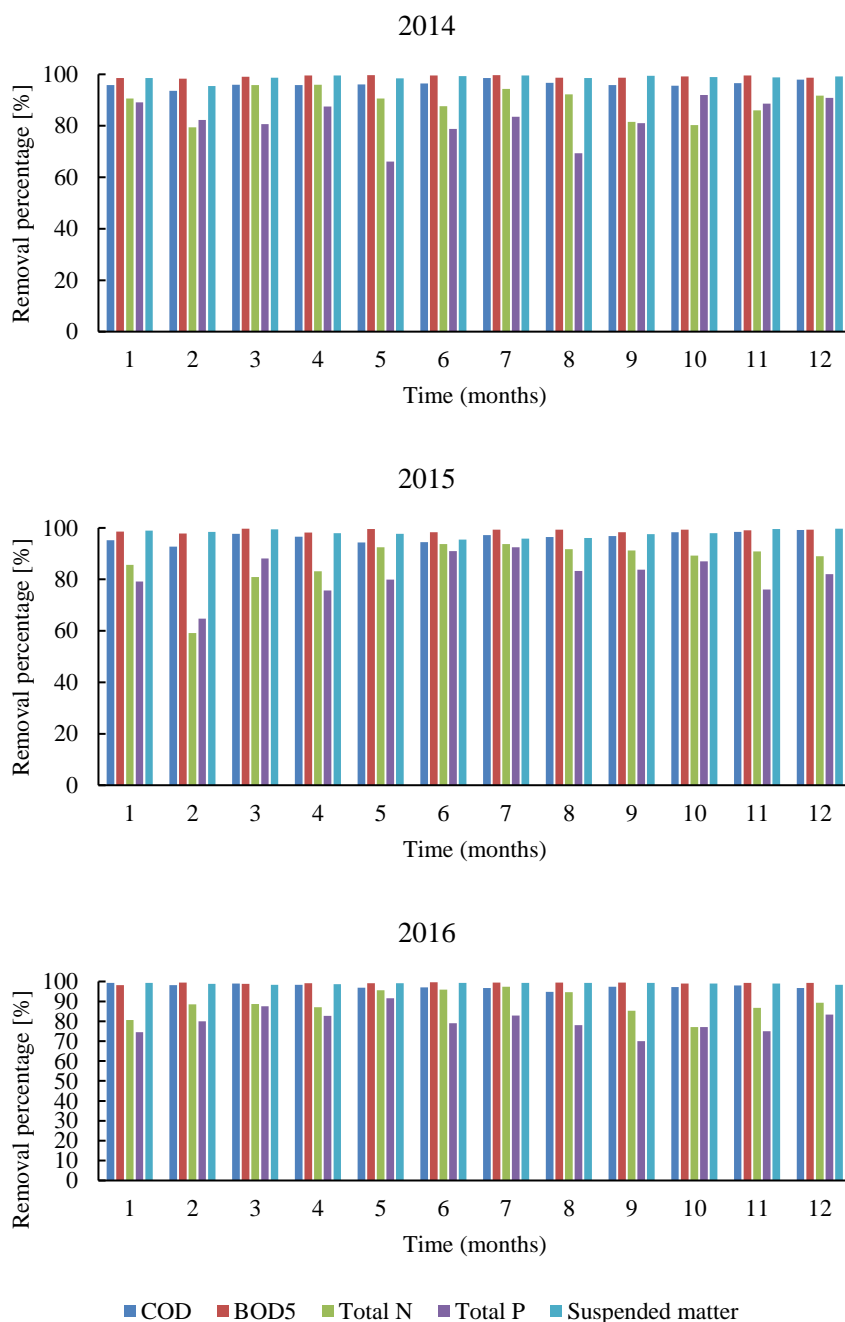


**Fig. 7.** Values of suspended matter concentrations measured monthly during 2014, 2015 and 2016 on samples taken from WWTP input, output and their EVL values

Fig. 8 shows the removal of pollutants in percentages or physical-chemical indicators of wastewater quality calculated according to the equation:

$$\begin{aligned} \% \text{ removal efficiency} &= \frac{\text{input (mg/L)} - \text{output (mg/L)}}{\text{input (mg/L)}} \\ &\cdot 100\% \end{aligned}$$

A continuous and very high percentage of removal is visible, i.e. 80-100 % of the pollutants have been removed over a three-year period, which indicates a good wastewater treatment process. Comparing the physical-chemical parameters of wastewater and purified water it can be concluded that the water has a good quality and that the observed physical-chemical parameters are within the EVL.



**Fig. 8.** Removal efficiency of monitored physicochemical indicators during the period 2014 - 2016

## Conclusion

Monitoring the quantity and quality of water is a legally defined process and an integral part of water management procedures. Monitoring of physicochemical parameters of waste water carried out in WWTP Koprivnica according to the standard methods at monthly intervals in a three-year period (2014-2016). Results showed that during the observed period, the input values of the examined parameters (COD, BOD<sub>5</sub>, total

nitrogen, total phosphorus, suspended matter) increased in summer months, but all output values are within the emission value limits. High removal efficiency (80-100 %) indicates that the wastewater treatment plant is efficient. Wastewater treatment affects the conservation of the overall biological diversity and the sustainable use of natural resources, but the benefit of present and future generations depends not only on the treatment methods but also on the preservation of these precious natural resources.

## References

- American Public Health Association (APHA), American Water Works Association, Water Environment Federation. Standard Methods for the Examination of Water and Wastewater. 1999.
- Berg U., Donnert D., Ehbrecht A., Bumiller W., Kusche I., Weidler P.G., Nuesch R. (2005): "Active filtration" for the elimination and recovery of phosphorus from wastewater. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 265, 141–148. <https://doi.org/10.1016/j.colsurfa.2004.10.135>
- Bian D., Shengshu A., Jing L., Yan Z., Xi T. (2011): Treatment of phosphorus wastewater using crystallization method. *Journal of Environmental Sciences* 23, 106–109. [https://doi.org/10.1016/S1001-0742\(11\)61088-7](https://doi.org/10.1016/S1001-0742(11)61088-7)
- Bilotta G.S., Brazier R.E. (2008): Understanding the influence of suspended solids on water quality and aquatic biota. *Water Research* 42 (12), 2849–2861. <https://doi.org/10.1016/j.watres.2008.03.018>.
- Biondić, B., Biondić, R. (2014.): Hydrogeology of the Dinaric Karst in Croatia. Faculty of Geotechnical Engineering, Varaždin, Croatia, 341 pp.
- Cossu R., Fantinato G., Pivato A., Sandon A. (2017.): Further steps in the standardization of BOD<sub>5</sub>/COD ratio as a biological stability index for MSW. *Waste Management* 68, 16–23. <https://doi.org/10.1016/j.wasman.2017.06.035>
- Crini, G., Lichtfouse, E. (2019.): Advantages and disadvantages of techniques used for wastewater treatment. *Environ Chem Lett* 17, 145–155. <https://doi.org/10.1007/s10311-018-0785-9>
- Determination of the chemical oxygen demand index (COD) (HRN ISO 15705:2003).
- Devi R., Dahiya R.P. (2008.): COD and BOD removal from domestic wastewater generated in decentralised sectors. *Bioresource Technology* 99, 344–349. <https://doi.org/10.1016/j.biortech.2006.12.017>
- Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy.
- EU Special Report (2014.) EU-funding of urban waste water treatment plants in the Danube river basin: further efforts needed in helping Member States to achieve EU waste water policy objectives. [https://www.eca.europa.eu/Lists/ECADocuments/SR15\\_02/SR\\_DANUBE\\_RIVER\\_EN.pdf](https://www.eca.europa.eu/Lists/ECADocuments/SR15_02/SR_DANUBE_RIVER_EN.pdf). Accessed March 16, 2020.
- Goody D. C., Bowes M.J., Lapworth D.J., Lamb A.L., Williams P.J., Newton R.J., Davies C.L., Surridge B.W.J. (2018): Evaluating the stable isotopic composition of phosphate oxygen as a tracer of phosphorus from wastewater treatment works. *Applied Geochemistry* 95, 139–146. <https://doi.org/10.1016/j.apgeochem.2018.05.025>
- Hendrickx T.L.G., Wang Y., Kampman C., Zeeman G., Temmink H., Buisman C.J.N. (2012): Autotrophic nitrogen removal from low strength waste water at low temperature. *Water Research* 46, 2187–2193. <https://doi.org/10.1016/j.watres.2012.01.037>
- Official Gazette 66/19 – Water Law.
- Official Gazette 80/13, 43/14, 27/15, 3/16 - Regulation on the Emissions Values Limit of Wastewater.
- Ramalho R. (2012.): Introduction to Wastewater Treatment Processes.
- Samer M. (2015.): Biological and Chemical Wastewater Treatment Processes. In: Wastewater Treatment Engineering, Samer M. (ed.), IntechOpen, <https://doi.org/10.5772/61250>.
- van Puijenbroek P.J.T.M., Beusen A.H.W., Bouwman A.F. (2019): Global nitrogen and phosphorus in urban wastewater based on the Shared Socio-economic pathways. *Journal of Environmental Management* 231, 446–456. <https://doi.org/10.1016/j.jenvman.2018.10.048>
- Water quality - Determination of ammonium - Part 1: Manual spectrometric method (HRN ISO 7150-1:1998).
- Water quality - Determination of biochemical oxygen demand after n days (BOD<sub>n</sub>) - Part 1: Dilution and seeding method with allylthiourea addition (ISO 5815:1989, modified; EN 1899-1:1998).
- Water quality - Determination of biochemical oxygen demand after n days (BOD<sub>n</sub>) - Part 2: Method for undiluted samples (ISO 5815:1989, modified; EN 1899-2:1998).
- Water quality - Determination of phosphorus - Ammonium molybdate spectrometric method (EN ISO 6878:2004).
- Water quality - Determination of suspended solids - Method by filtration through glass fibre filters (EN 872:2005).