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UTICAJ SEZONSKIH VARIJACIJA NA SADRŽAJ ORGANSKIH MATERIJA TOKOM KOMBINOVANOG PROCESA OZONIZACIJE I GAU FILTRACIJE NA POSTROJENJU ZA PRIPREMU VODE ZA PIĆE U NOVOM SADU

EFFECT OF SEASONAL VARIATION ON THE ORGANIC MATTER CONTENT OF WATER DURING THE COMBINED PROCESS OF OZONATION AND GAC FILTRATION AT THE DRINKING WATER TREATMENT PLANT IN NOVI SAD

APSTRAKT

U radu su prikazani rezultati praćenja promene sadržaja organskih materija, nakon različitih faza obrade vode (peščane filtracije, ozonizacije i filtracije na granulovanom aktivnom uglju - GAU) u zavisnosti od perioda ispitivanja. U toku pripreme vode za piće praćen je sadržaj ukupnog organskog ugljenika (TOC), rastvorenog organskog ugljenika (DOC), UV apsorbancije na 254 i 278 nm, kao i odabranih aldehida i karboksilnih kiselina. Nakon ozonizacije i GAU filtracije postiže se smanjenje sadržaja UV_{254} apsorbujućih organskih materija u vodi u proseku oko 85%. Sadržaj aldehida i karboksilnih kiselina u vodi nakon ozonizacije raste u odnosu na sadržaj u vodi pre oksidacionog tretmana. Sezonske varijacije, odnosno promene temperature i količine padavina utiču na sadržaj organskih materija u sirovoj vodi što se dalje odražava i na njihov sadržaj u tretiranoj vodi. Tako je u zimskom periodu detektovan veći sadržaj organskih materija, dok je sadržaj aldehida i karboksilnih kiselina, kao dominantnih oksidacionih nusprodukata bio veći tokom ispitivanja u letnjem periodu.

Ključne reči: voda za piće, ozonizacija, GAU filtracija, organske materije, sezonske promene

ABSTRACT

This paper presents the results of the monitoring of changes in the organic compounds content of water after various treatment phases (sand filtration, ozonation and granular activated carbon filtration - GAC). During the drinking water preparation, the following were monitored: the contents of total organic carbon (TOC), dissolved organic carbon (DOC), biodegradable dissolved organic carbon (BDOC), UV absorbance at 254 and 278 nm, and aldehydes and carboxylic acid contents. After ozonation and GAC filtration, the content of UV_{254} absorbing organic matter was reduced on average by about 85%. Aldehyde and carboxylic acid contents in the water after ozonation increased in comparison to the water before oxidation treatment. Seasonal variations in temperature and the amount of precipitation affected the concentrations of organic compounds in the raw water and subsequently also in the treated water. The highest amounts of organic matter were thus detected in the winter, wheras the contents of aldehydes and carboxylic acids, the dominant oxidation by-products, were higher during the summer.

Key words: drinking water, ozonation, GAC filtration, organic matter, seasonal variations

1. UVOD

Priobalje Dunava predstavlja značajan resurs vode za piće usled dobrih filtracionih karakteristika, tako da se grad Novi Sad snabdeva vodom za piće upravo iz izdani ovog tipa. Međutim, izvorišta podzemnih voda locirana pored Dunava izložena su snažnom uticaju kvaliteta voda ove međunarodne reke. Pored prirodno prisutnih organskih materija (POM) u vodi Dunava, registrovana je i pojava novih polutanata kao što su lekovi, hormoni, perfluorna jedinjenja i dr. (*ICPDR,2015*). Ozonizacija je jedan od tretmana koji može doprineti uklanjanju većeg broja štetnih organskih polutanata i zato se često primenjuje u tretmanu vode za piće. U reakcijama između ozona i organskih materija nastaju različiti organski nusproizvodi, a od kojih su aldehidi (formaldehid,

1. INTRODUCTION

The bank of the Danube river has good filtration characteristics, and the city of Novi Sad extracts all the water used for water supply from this aquifer. However, the groundwater sources near the Danube are strongly affected by the water quality of this international river. In addition to natural organic matter (NOM) in the Danube, new pollutants such as drugs, hormones, perfluoric compounds, etc. have also been detected (*ICPDR, 2015*). Ozonation is one technique which can contribute to the removal of more harmful organic pollutants and is therefore often applied in drinking water treatment. In the reactions between ozone and organic matter, various organic by-products are formed, of which aldehydes (formaldehyde, acetaldehyde, glyoxal,

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acetaldehid, glioksal i metilglioksal), kao i karboksilne kiseline dominantno zastupljeni *(Papageorgiou i sar., 2014)*. Pored toga, s obzirom da su POM kao prekursori ovih karbonilnih jedinjenja, veoma promenljive kako u kvantitativnom tako i u kvalitativnom pogledu, neophodno je pratiti sudbinu nastalih organskih nusproizvoda tokom procesa ozonizacije. Bitno je napomenuti da ovako nastala karbonilna jedinjenja mogu ispoljiti štetno delovanje na zdravlje ljudi *(Moudgal i sar., 2000)*.

Tako Richardson *(2003)* ukazuje da karbonilna jedinjenja čine oko 30% nastalih dezinfekcionih nusproizvoda, među kojima su najznačajniji aldehidi i karboksilne kiseline. Richardson i sar. *(2000)* su ispitivali efekat dezinfekcije ozonom i hlor-dioksidom na formiranje karboksilnih kiselina i uočili da su formirane 33 alifatične i 10 aromatičnih karboksilnih kiselina. Dodatno, istraživanja Krasner i sar. *(2006)* koji su ispitivali sadržaj karboksilnih kiselina tokom ozonizacije i peščane filtracije vode, ukazuju na značajnije formiranje alifatičnih karboksilnih kiselina, pri čemu je najveći porast koncentracije dobijen za metansku i etansku kiselinu i to nakon faze ozonizacije. Takođe, u navedenim istraživanjima pokazano je da su sezonske varijacije u smislu promene ambijentalne temperature i količine padavina značajne za formiranje karbonilnih jedinjenja tokom tretmana vode. Maksimalne koncentracije svih ispitivanih oksidacionih nusproizvoda dobijene su u mesecima tokom hladnijih godišnjih doba (jeseni i zime), pri čemu su aromatične karboksilne kiseline detektovane samo u ovom vremenskom periodu. Autori Papageorgiou i sar. *(2014)* su ispitivali prisustvo i sudbinu karbonilnih jedinjenja kao nusproizvoda ozonizacije u toku pripreme vode za piće tokom jedne godine. Pokazali su da nakon ozonizacije nastaje do oko 14 karbonilnih jedinjenja u ukupnim koncentracijama od 32,8-111 µg/l, pri čemu je procenat uklanjanja tretmanom vode bio 64-80%. Dodatno, s obzirom da je brzina degradacije karboksilnih kiselina obično manja od brzine njihovog formiranja dolazi do porasta njihovog sadržaja u vodi, sa konsekventnom mikrobiološkom proliferacijom i formiranjem biofilma u distribucionom sistemu *(Chu i Lu, 2004; Meilan i sar., 2007; Moudgal i sar., 2000; Richardson i sar., 2000)*. Serrano i sar. *(2015)* su analizirali koncentraciju 11 aldehida u vodi uzorkovanoj nakon različitih faza u toku pripreme vode za piće. U sirovoj vodi detektovani su aldehidi, pri čemu su njihove koncentracije bile znatno veće u toku toplijih godišnjih doba (proleće i leto). Međutim, u literaturi i dalje postoji nedostatak informacija o sudbini i ponašanju ovih karbonilnih jedinjenja koja nastaju u toku pripreme vode za piće (*Zhong i sar., 2017*).

Stoga je cilj rada bio praćenje uticaja sezonskih varijacija (promene ambijantalne temperature vazduha i količine padavina), na sadržaj organskih materija, sa fokusom na karbonilna jedinjenja (aldehide i karboksilne kiseline), u vodi tokom pripreme vode za piće.

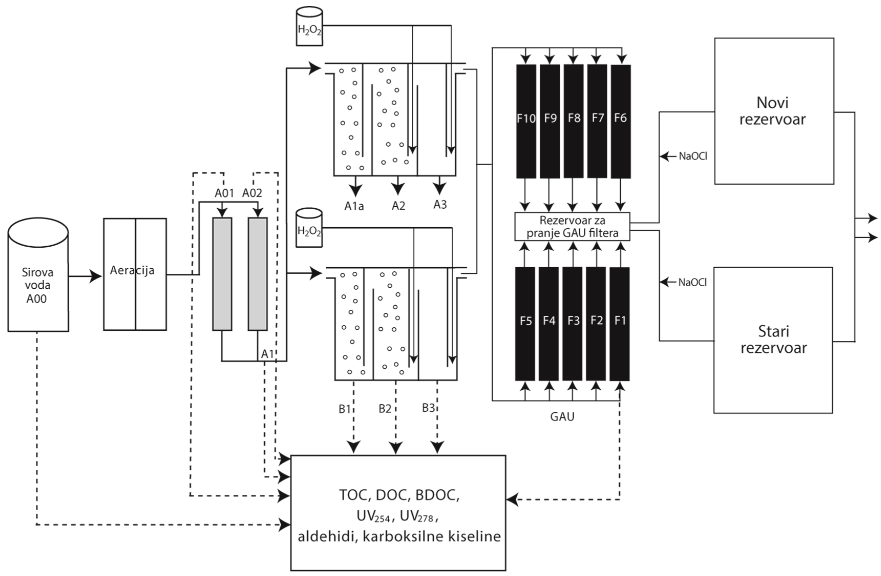
and methylglyoxal), as well as carboxylic acids are predominantly present. Considering that NOM, as a precursor of carbonyl compounds formed during the ozonation process, is highly variable both in quantitative and qualitative terms, it is necessary to monitor the fate of the organic by-products resulting from the ozonation process during drinking water treatment. Due to their potentially harmful effects on human health, it is necessary to monitor the content of these carbonyl compounds *(Moudgal et al., 2000)*.

Richardson (*2003*) indicates that carbonyl compounds account for about 30% of disinfection by-products produced, among which the most important are aldehydes and carboxylic acids. Richardson et al. (*2000*) examined the effect of disinfection with ozone and chlorine dioxide on the formation of carboxylic acids and noted that 33 aliphatic and 10 aromatic carboxylic acids were formed. In addition, research conducted by Krasner et al. (*2006*) examined the content of carboxylic acids during ozonation and sand filtration, indicate a significant formation of aliphatic carboxylic acids, with the highest increase in concentration obtained for methanoic and ethanoic acid after the ozonation phase (up to about 48 times). Furthermore, in these studies, it has been shown that seasonal variations in terms of fluctuations in ambient temperature and precipitation are significant for the formation of carbonyl compounds. The maximum concentrations of all investigated oxidation by-products were obtained during the colder seasons (autumn and winter), with aromatic carboxylic acids being detected only during this time period. Papageorgiou et al. (*2014*) examined the presence and fate of carbonyl compounds as ozonation by-products during drinking water preparation for one year. These authors showed that after ozonation, 14 carbonyl compounds were present with total concentrations of 32.8-111 µg/l, with the percentage of removal in the treated water being in the range of 64-80%. In addition, given that the degradation rate of carboxylic acids is usually lower than the rate of their formation, they accumulate which further leads to microbiological proliferation and the formation of biofilms in the distribution system (*Chu and Lu, 2004; Meulan et al., 2007; Moudgal et al., 2000; Richardson et al., 2000*). Serrano et al. (*2015*) analysed the concentration of 11 aldehydes in water sampled at different phases during drinking water preparation. In the raw water, 5 aldehydes were detected, with their concentrations being higher during warmer seasons (spring and summer). However, there is still a lack of information in the literature on the fate and behaviour of carbonyl compounds that occur during drinking water treatment (*Zhong et al., 2017*).

Therefore, the aim of the study was to monitor the influence of seasonal variations (changes in ambient air temperature and precipitation) on the content of organic matter, with the focus on carbonyl compounds (aldehydes and carboxylic acids) in water during drinking water preparation.

2. MATERIJAL I METODE

Postrojenje za pripremu vode za piće grada Novog Sada sastoji se iz sledećih tehnoloških faza prerade: aeracija, filtracija na brzim peščanim filterima, ozonizacija, uklanjanje reziduala ozona vodonik peroksidom, GAU filtracija i dezinfekcija. Blok shema tehnološke linije obrade vode data je na slici 1.



Slika 1. Blok shema tehnološke linije obrade vode i odgovarajuća mesta uzorkovanja
Figure 1. Diagram of the technological line and sampling points during the drinking water treatment in Novi Sad

Protok vode i koncentracija ozona u ulaznom gasu po liniji ozonizacije u periodu ispitivanja bili su ~2025 m^3/h i ~2252 g O_3/h, redom. Pri navedenim uslovima, ukupna produkcija ozona bila je ~1,20 g O_3/m^3, pri čemu je prosečna transferovana doza ozona u vodu iznosila 0,73 g O_3/m^3. Pri datim uslovima 0,48 g O_3/m^3 zaostaje u vodi koja dalje ide na obradu na GAU filterima. Uvođenjem doziranja vodonik-peroksida na izlazu iz-komore B3, ovaj rezidual ozona u vodi podleže destrukciji tako da se obezbeđuje da svega 0,10 g O_3/m^3 zaostaje u vodi pre GAU filtracije, što je zadovoljavajuće sa aspekta favorizovanja biološke filtracije na GAU filterima.

Uzorkovanje vode je shodno tehnološkoj liniji obrade i cilju rada, izvršeno na sledećim mestima: na ulazu u peščani filter (A01 i A02), na ulazu u sistem za ozonizaciju (A1), na izlazu iz I komore (B1), na izlazu iz II komore (B2), na izlazu iz III komore (B3) nakon doziranja vodonik-peroksida i na izlazu iz GAU (F1) (slika 1).

Program uzorkovanja definisan je u skladu sa SRPS EN ISO 5667-1. Uzorkovanje je izvršeno u toku toplijeg (letnji period maj-jul 2017. god.) i hladnijeg (zimski period novembar i decembar 2017. god. i januar 2018. god.) perioda. Dobijene vrednosti sadržaja analiziranih parametara su predstavljene kao srednje vrednosti za određeni ispitivani period. Postupci uzimanja uzoraka su definisani u skladu sa SRPS EN

2. MATERIAL AND METHODS

The drinking water treatment plant in the city of Novi Sad consists of the following water treatment phases: aeration, filtration on fast sand filters, ozonation, removal of residuals of ozone using hydrogen-peroxide, GAC filtration and disinfection. A diagram of the technological line and sampling points during the drinking water treatment in Novi Sad is given in Figure 1.

Water flow and ozone concentration in the inlet gas along the ozone line were ~ 2025 m3/h and ~ 2252 g O_3/h, respectively. Under the given conditions, the total production of ozone was ~ 1.20 g O_3/m^3, with a transferred dose of ozone in water of about 0.73 g O_3/m^3. Under these conditions, 0.48 g O_3/m^3 was retained in the water, which is further processed on GAC filters. By introducing doses of hydrogen peroxide at the exit from ozonation chamber B3, the residual ozone in the water is subject to destruction, ensuring that no more than 0.10 g O_3/m^3 in water continues to the GAC filters, which is satisfactory to maintain favourable biological filtration on GAC filters.

Water sampling was in accordance with the technological processing line and the aim of this study, and was carried out at the following locations: at the entrance to the sand filter (A01, A02), at the entrance to the ozone system (A1), at the exit of the first (B1), second (B2) and third (B3) ozonation chamber, and at the exit from the GAC (F1).

The sampling program was defined in accordance with standard SRPS EN ISO 5667-1. Sampling was carried out during the winter (November and December 2017 and January 2018) and the spring/summer (May-July 2017). The results obtained values for the analysed parameters are presented as the mean values for the investigated

ISO 5667-2. Zaštita uzoraka i rukovanje uzorcima vode vršena je prema smernicama za zaštitu uzoraka i rukovanju uzorcima vode na osnovu SRPS EN ISO 5667-3:2017 standarda.

2.1. Metode ispitivanja

Operativni parametri faze ozonizacije vode na postrojenju za pripremu vode za piće grada Novog Sada praćeni su primenom *Master PLC* za upravljanje postrojenjem za ozonizaciju, proizvođača Siemens, Nemačka.

Uzorci vode analizirani su na sadržaj organskih materija i to merenjem ukupnog organskog ugljenika (TOC), rastvorenog organskog ugljenika (DOC), biodegradabilnog rastvorenog organskog ugljenika (BDOC), UV apsorbancije na 254 nm (UV_{254}) i 278 nm (UV_{278}), sadržaja aldehida (acetaldehid, formaldehid, glioksal i metil-glioksal) i karboksilnih kiselina (metanska i etanska).

Sadržaj TOC i DOC u vodi određivan je na aparatu Elementar LiquiTOCII u skladu sa metodom SRPS ISO 8245:2007. Granica detekcije metode iznosi 0,2 mg C/l, a granica kvantitacije 0,5 mg C/l. Sadržaj biodegradabilnog rastvorenog organskog ugljenika (BDOC) određivan je tehnikom pričvršćenih bakterija na biološkom pesku *(Escobar i Randall, 1999; Ugarčina Perović, 2012).* BDOC je izračunat prema formuli $BDOC = DOC_{startni} - DOC_{minimalni}$.

UV apsorbancija na 254 i 278 nm merena je na spektrofotometru UV-1800 Shimadzu u skladu sa standarnom metodom (APHA, 2012). Granica detekcije metode iznosi 0,0001 cm^{-1}. Specifična UV apsorbancija na 254 nm ($SUVA_{254}$, l mg^{-1} m^{-1}) dobijena je računskim putem primenom formule: $SUVA_{254} = (UV_{254} \cdot 100)/DOC$.

Sadržaj karboksilnih kiselina (metanske i etanske kiseline) određivan je na jonskom hromatografu Dionex ICS-3000 u skladu sa procedurom proizvođača opreme DIONEX Application Note 154. Granice kvantitacije metode iznose po 5 µg/l za svako jedinjenje.

Sadržaj aldehida u vodi određivan je gasnom hromatografijom sa masenom spektrometrijom (GC/MS, Agilent 7890A/5975C) nakon derivatizacije u vodenoj sredini sa PFBHA (O-(2,3,4,5,6- pentafluorobenzil) hidroksilamin hidrohlorid) *(Glaze i sar., 1989)*. Granica kvantitacije metode za formaldehid iznosi 0,4 µg C/l, za acetaldehid 0,16 µg C/l, za glioksal 0,4 µg C/l i za metilglioksal 0,34 µg C/l.

3. REZULTATI I DISKUSIJA

3.1. Ukupan sadržaj organskih materija u vodi

Kvalitet vode u pogledu sadržaja organskih materija, izraženih preko ukupnog (TOC), rastvorenog organskog ugljenika (DOC) i biodegradabilnog

periods of sampling. Sampling procedures were defined in accordance with SRPS EN ISO 5667-2. Preservation and handling of water samples were conducted according to the guidelines given in SRPS EN ISO 5667-3:2017.

2.1. Methods of investigation

The water ozonation plant during the preparation of drinking water for the city of Novi Sad is monitored by a *PLC* device, Siemens, Germany.

The organic contents of the water samples were analysed by total organic carbon (TOC), dissolved organic carbon (DOC), biodegradable dissolved organic carbon (BDOC), UV absorbance at 254 nm (UV_{254}) and 278 nm (UV_{278}), aldehyde content (acetaldehyde, formaldehyde, glyoxal and methyl-glyoxal) and carboxylic acids (methanoic acid and ethanoic acid).

TOC and DOC contents were determined by TOC analyzer (Elementar LiquiTOCII) in accordance with SRPS ISO 8245:2007.The method detection limit is 0.2 mg C/l, and the quantitation limit is 0.5 mg C/l. The content of bio-degradable soluble organic carbon (BDOC) was determined by the technique of attached bacteria on biological sand (*Escobar and Randall, 1999; Ugarčina Perović, 2012*). BDOC was calculated according to the equation $BDOC = DOC_{start} - DOC_{minimum}$.

UV absorbance at 254 and 278 nm was measured by UV-1800 Shimadzu spectrophotometer according to the standard method (*APHA, 2012*). The detection limit of the method is 0.0001 cm^{-1}. The value of specific UV absorbance at 254 nm ($SUVA_{254}$, l mg^{-1} m^{-1}) was obtained by calculating: $SUVA_{254} = (UV_{254} \times 100)/DOC$.

The content of carboxylic acids was determined byy ion chromatograph Dionex ICS-3000 in accordance with the procedure of the DIONEX equipment manufacturer, Application Note 154. The method quantitation limit for each carboxylic acid was 5 µg/l.

Aldehyde contents were determined by gas chromatography with mass spectrometry (GC/MS, Agilent 7890A/5975C) after derivatization in an aqueous environment with PFBHA (O-(2,3,4,5,6-pentafluorobenzyl) hydroxylamine hydrochloride) (*Glaze et al., 1989*). Method quantitation limits for formaldehyde, acetaldehyde, glyoxal and methylglyoxal were 0.4 µg/l, 0.16 µg/l, 0.4 µg/l and 0.34 µg/l, respectively.

3. RESULTS AND DISCUSSION

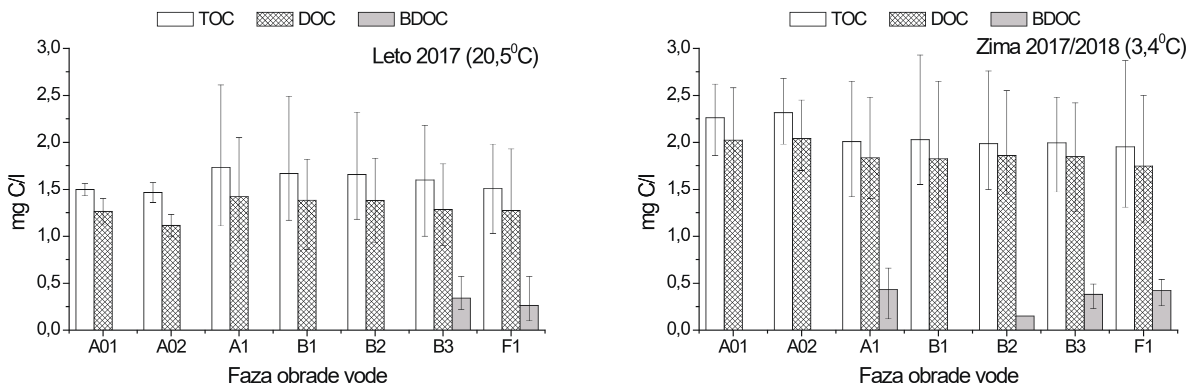
3.1. The total content of organic matter in the water

The water quality, in terms of the total (TOC) and dissolved organic carbon (DOC) and biodegradable organic carbon (BDOC) contents after different organskog ugljenika (BDOC) nakon različitih faza obrade predstavljen je na slici 2. Analizirani parametri predstavljeni su kao srednje vrednosti za ispitivani letnji i zimski period, kao i dobijene maksimalne i minimalne vrednosti.

Ispitivanim tretmanima (ozonizacija i GAU filtracija) se generalno sadržaj TOC i DOC u vodi smanjuje do ispod 2,0 mg C/l, uz manje fluktuacije u zavisnosti od primenjene faze obrade vode. Dodatno, u letnjem periodu ispitivanja prosečni sadržaj TOC iznosio je 1,47-1,74 mg C/l, dok se za zimski period kretao u opsegu 1,95-2,32 mg C/l, za sve faze obrade vode.

treatment phases, is presented in Figure 2. The results are presented as the mean values for the investigated summer and winter seasons as well as the maximum and minimum values observed.

The treatments (ozonation and GAC filtration) reduced the TOC and DOC contents to below 2.0 mg C/l, with minor variation depending on the applied water treatment phase. In addition, in the summer period, the average TOC content was in the range of 1.47-1.74 mg C/l, while the average TOC value for the winter period was in the range of 1.95-2.32mg C/l for all phases of water treatment.



Slika 2. *Srednja vrednost, maksimalni i minimalni sadržaj organskih materija u zavisnosti od različitih faza obrade vode za zimski i letnji period ispitivanja*

Figure 2. *Mean, maximum and minimum values of organic matter contents in the different water treatment phases during the winter and spring/summer periods*

Prosečna DOC vrednost za sve faze obrade vode, u toku letnjeg perioda bila je u opsegu 1,12-1,42 mg C/l, dok je sadržaj DOC u zimskom periodu bio u opsegu 1,75-2,04 mg C/l. U ispitivanim periodima (leto/zima) sadržaj biodegradabilnih organskih materija u vodi nije značajnije varirao (0,15 do 0,43 mg C/l) (slika 2).

Sadržaj organskih materija u vodi, izražen preko ukupnog i rastvorenog organskog ugljenika, za sve faze obrade vode veći je tokom zimskog u odnosu na letnji period ispitivanja. Naime, tokom zimskog perioda ispitivanja niža prosečna ambijentalna temperatura vazduha (3,4°C), kao i manja prosečna količina padavina (oko 33,1 mm) u odnosu na letnji period ispitivanja (20,5°C i prosek padavina od oko 98,9 mm) (*RHMZ, 2017, 2018*) značajno utiče na sadržaj organskih materija, pa time i na kvalitet sirove i tretirane vode.

Na slici 3 predstavljene su srednje, maksimalne i minimalne vrednosti promene koncentracije komponenti koje apsorbuju UV zračenje na talasnim dužinama 254 i 278 nm. U skladu sa relativno niskim TOC i DOC vrednostima u vodi nakon različitih faza obrade, sadržaj UV_{254} apsorbujućih organskih materija takođe nije visok i kretao se u granicama od 0,0175 do 0,1124cm^{-1} u letnjem periodu, odnosno od 0,0149 do 0,1107 cm^{-1} u zimskom periodu. Sadržaj

The mean DOC value for all water treatment phases during the winter period was in the range of 1.75-2.04 mg C/l, while the DOC content in the spring/summer period was in the range of 1.12-1.42 mg C/l. The content of biodegradable organic matter in the water did not vary significantly over the course of the year (0.15 to 0.43 mg C/l) (Figure 2).

The content of organic matter expressed as total, dissolved and biodegradable organic carbon for all phases of water treatment is higher during the winter compared to the spring/summer. In winter, the average ambient air temperature (3.4°C) and average precipitation (about 33.1 mm) are lower than during the spring/summer (20.5°C and about 98.9 mm) (*RHMZ, 2017, 2018*). This has a significant influences on the content of organic matter and thus the quality of the raw and treated water.

Figure 3 presented the mean, maximum and minimum values of the concentrations of material which absorbs UV radiation at wavelengths of 254 and 278 nm. In accordance with relatively low TOC and DOC values in the water after different treatment phases, UV_{254} absorbing organic matter contents are also not high, ranging from 0.0175 to 0.1124 cm^{-1} in the summer and from 0.0149 to 0.1107 cm^{-1} in the winter. UV_{278} absorbing organic matter in the summer was in the

UV_{278} apsorbujućih organskih materija za letnji period bio je u opsegu 0,0108-0,1088 cm^{-1}, a za zimski period od 0,0105 do 0,1000 cm^{-1} nezavisno od faze obrade vode. Merenjem vrednosti UV_{278} apsorbancije u vodi nakon različitih faza obrade (slika 2) utvrđeno je postepeno uklanjanje jedinjenja koja su potencijalni prekursori dezinfekcionih nusprodukata *(Edzwald i Tobiason, 1999).*

Sumarno posmatrano, promene sadržaja UV apsorbujućih materija u vodi nakon različitih faza obrade u odnosu na topliji i hladniji period ispitivanja nisu uočene, što implicira da tokom godine ne dolazi do značajnijih promena u strukturnim karakteristikama u vodi prisutnih organskih materija.

Tokom obrade vode dolazi do smanjenja UV_{254} apsorbujućeg organskog sadržaja u proseku za oko 66% (prosek za A01 i A02) nakon peščane filtracije tokom oba ispitivana perioda. Daljim procesom ozonizacije, ove vrednosti dodatno opadaju (u proseku za oko 45%). Kompletnom obradom vode (uključujući i GAU filtraciju), postiže se efikasnost uklanjaja UV_{254} apsorbujućih materija u proseku za oko 85%, u oba ispitivana perioda. Smanjenje sadržaja UV_{254} apsorbujućih materija nakon različitih faza obrade vode je očekivano, s obzirom da pri oksidaciji ozonom dolazi prvenstveno do raskidanja nezasićenih, dvostukih veza u molekulima organske materije, a koji su upravo i odgovorni za apsorpciju UV zračenja na datoj talasnoj dužini *(Roccaro i sar., 2009).* Dodatno, $SUVA_{254}$ vrednost u vodi opada tokom ozonizacije i GAU filtracije na vrednosti <2 l mg^{-1} m^{-1}, ukazujući na predominantno hidrofilni karakter u vodi zaostalih organskih materija *(Edzwald i Tobiason, 1999).*

3.2. Sadržaj karbonilnih jedinjenja u vodi

Srednja vrednost, maksimalan i minimalan sadržaj aldehida i karboksilnih kiselina (metanske i etanske kiseline) u vodi nakon različitih faza obrade

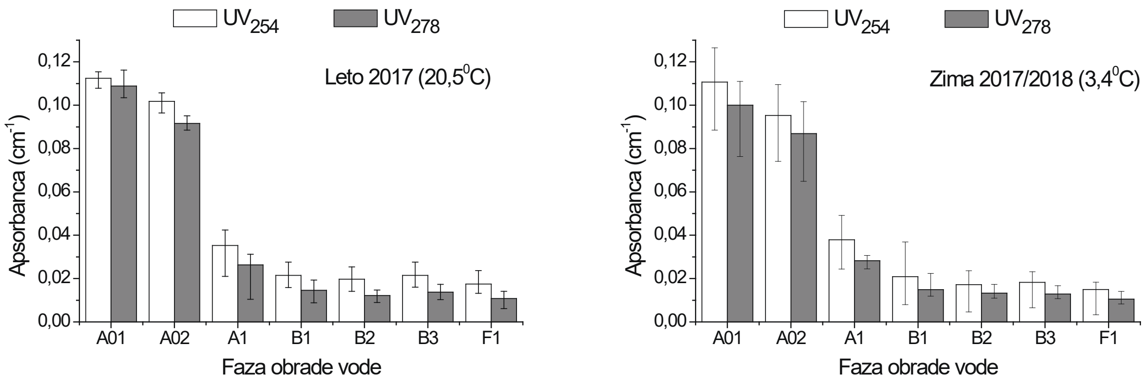
range 0.0108-0.1088 cm^{-1}, and in the winter period from 0.0105 to 0.1000 cm^{-1} for all phases of water treatment. The gradual reduction in the contents of . UV_{278} absorbing organic matter as the treatment progresses, corresponds to a gradual reduction in the amounts of potential disinfection by-products precursors *(Edzwald and Tobiason, 1999).*

At no stage in the treatment process was there a significant difference observed in the contents of UV absorbing organic matter between the summer and winter months, which implies that the structural characteristics of the organic matter present in the water is stable over the course of the year.

During water treatment, the UV_{254} absorbing organic matter decreases by an average of about 66% (averaged over A01 and A02) after sand filtration in both investigated periods. The ozonation process achieves an additional reduction of about 45% on average. The complete water treatment (after GAC filtration) achieves around 85% removal of UV_{254} absorbing organic matter for both investigated periods. The continued reduction of UV_{254} adsorbing organic matter after each treatment phase is to be expected, since oxidation occurs primarily with ozone, breaking the unsaturated bonds in the organic matter which are responsible for the absorption of UV radiation at a given wavelength *(Roccaro et al., 2009).* The $SUVA_{254}$ values in the water decreased during ozonation and GAC filtration to <2 l mg^{-1} m^{-1}, indicating the predominantly hydrophilic character of the residual organic matter *(Edzwald and Tobiason, 1999).*

3.2. The content of carbonyl compounds in water

The mean, maximum and minimum contents of aldehydes and carboxylic acids in water after various treatment phases is presented in Figure 4. In general,



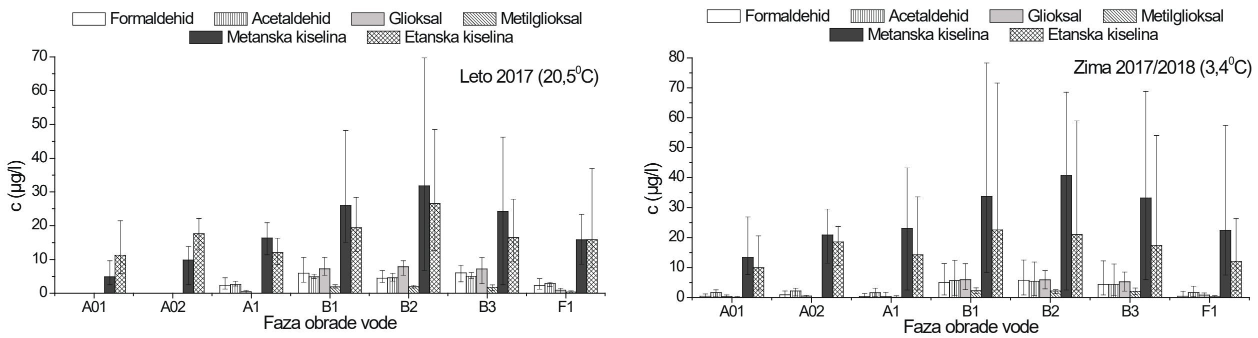
Slika 3. *Srednja vrednost, maksimalni i minimalni sadržaj UV asporbujućih organskih materija u zavisnosti od različitih faza obrade vode za zimski i letnji period ispitivanja*

Figure 3. *Mean, maximum and minimum value of content UV absorbing organic matter after the different water treatment phases during the winter and summer periods*

predstavljen je na slici 4. Generalno, sadržaj aldehida i karboksilnih kiselina u vodi nakon ozonizacije raste u odnosu na sadržaj u vodi pre oksidacionog tretmana za oko 50%. Ipak, povećan sadržaj formiranih jedinjenja se dalje reguliše obradom vode GAU filtracijom.

aldehyde and carboxylic acids contents increase by about 50% compared to their concentrations before the oxidation treatment. However, the increased concentrations of the compounds formed is further regulated by the GAC filtration treatment.

In the summer, the concentration of total aldehydes



Slika 4. *Srednja vrednost, maksimalan i minimalan sadržaj aldehida i karboksilnih kiselina u zavisnosti od različitih faza obrade vode za letnji i zimski period ispitivanja*

Figure 4. *The mean, maximum and minimum amounts of aldehydes and carboxylic acids after each water treatment phase in the winter and summer periods*

Srednja vrednost koncentracije ukupnih aldehida, u zavisnosti od faze obrade vode, za letnji period je iznosila 5,42-20 µg/l, dok se ukupna koncentracija aldehida u toku zimskog perioda ispitivanja kretala u opsegu 2,44-19,3 µg/l. Prosečna vrednost sadržaja metanske kiseline u vodi nakon različitih faza obrade kretala se u opsegu 4,87-31,8 µg/l (leto), odnosno 13,4-40,7 µg/l (zima). Slično, prosečna koncentracija etanske kiseline za letnji i zimski period kretala se u opsegu 11,8-26,6 µg/l i 9,94-22,6 µg/l, redom.

U slučaju karbonilnih jedinjenja utvrđeno je da je srednji sadržaj aldehida, kao i etanske kiseline veći tokom letnjeg perioda, dok je u zimskom periodu ispitivanja detektovan nešto veći sadržaj samo metanske kiseline, nezavisno od faze obrade vode. Generalno, veći sadržaj karbonilnih jedinjenja u toku letnjeg perioda verovatno je posledica (1) povećane mikrobiološke aktivnosti (favorizovane ambijentalnom temperaturom), koja rezultuje većim stepenom biodegradacije u vodi (ali i u sloju izvorišta) prisutnih organskih komponenti, odnosno (2) povišenog sadržaja prekursora koji favorizuju formiranje karbonilnih jedinjenja *(Papageorgiou i sar., 2014)*. Pored toga, promena strukturnih karakteristika organske materije tokom godine, kao rezultanta biotičkih i abiotičkih transformacija, kojima ove materije podležu u životnoj sredini (konkretno zoni obalske filtracije), može uticati na povećanje sadržaja karbonilnih jedinjenja u toplijem periodu godine. Potrebno je istaći i da je veća koncentracija karbonilnih jedinjenja detektovana upravo u periodu koji karakteriše povećana količina padavina (za prolećno/letnji period srednja vrednost padavina iznosila je 98,8 mm). Prema, Zhong i sar. *(2017)* upravo je količina padavina jedan od ključnih faktora koji utiču na formiranje karbonilnih jedinjenja.

in the water samples ranged from 5.42-20 µg/l, while the total aldehyde concentration during the winter was in the range 2.44-19.3 µg/l depending on the water treatment phase. The average methanoic acid concentration in water after the various treatment phases was in the range 4.87-31.8 µg/l (summer) and 13.4-40.6 µg/l (winter). The average concentration of ethanoic acid for the summer and winter period was 11.8-26.6 µg/l and 9.94-22.6 µg/l, respectively.

In the case of carbonyl compounds, the mean contents of aldehyde and ethanoic acid were found to be higher during the summer period, while in the winter slightly higher contents of methanoic acid were detected. Generally, the higher content of carbonyl compounds during the summer period can be due to (1) increased microbiological activity (more favourable ambient temperature), resulting in a higher degree of biodegradation in the water (and also in the source layer) of the organic components present or (2) increased contents of precursors favouring the formation of carbonyl compounds *(Papageorgiou et al., 2014)*. Over the year, the structural characteristics of the organic matter change as a result of biotic and abiotic transformations, especially in the environment in the bank filtration zone. This can increase the content of carbonyl compounds during the warmer period of the year. It should be noted that the highest concentration of carbonyl compounds was detected in the summer period with high precipitation (mean rainfall for spring/summer period was 98.8 mm). According to, Zhong et al. *(2017)*, the amount of precipitation is also a key factor that influences the formation of carbonyl compounds.

4. ZAKLJUČAK

Sadržaj organskih materija u vodi nakon oksidacije ozonom i GAU filtracije može se okarakterisati kao rastvoreni organski ugljenik, koji čini u proseku više od 85% ukupnog organskog ugljenika, a oko 10% čini biodegradabilni rastvoreni organski ugljenik. Dodatno, nakon ozonizacije i GAU filtracije, smanjuje se sadržaj UV_{254} apsorbujućih organskih materija za oko 85%. Sadržaj aldehida i karboksilnih kiselina u vodi nakon ozonizacije raste u odnosu na sadržaj u vodi pre oksidacionog tretmana. Međutim, daljom obradom vode GAU filtracijom, generalno dolazi do smanjenja sadržaja ispitivanih karbonilnih jedinjenja, rezultujući dobijanjem vode za piće koja omogućava mikrobiološku stabilnost tokom njene dalje distribucije. Sezonske varijacije u smislu promene ambijentalne temperature vazduha i količina padavina utiču na sadržaj i strukturu u vodi prisutnih organskih materija, a time i na efikasnost njihovog uklanjanja tokom tretmana vode.

4. CONCLUSION

More than 85% of the residual organic matter in the water after oxidation by ozone and GAC filtration can be characterized as dissolved organic carbon, and about 10% is biodegradable dissolved organic carbon. In addition, after ozonation and GAC filtration, about 85% of the UV_{254} absorbing organic matter is removed. The aldehyde and carboxylic acid concentrations increase after ozonation in comparison with the water before the oxidation treatment. However, further treatment of the water by GAC filtration generally results in a decrease in the content of those compounds, resulting in the production of microbiologically stable drinking water ready for further distribution. Seasonal variations the ambient air temperature and the amount of precipitation affect both the content and structure of the organic matter present in the water, and therefore also affect the efficiency of their removal during water treatment.

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