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QUALITY OF SURFACE WATER IN THE AGRICULTURAL DISTRICT LONJA FIELD (CROATIA)

SUMMARY

The objective of this study was to estimate the impact of land use on the surface water quality. Water samples were collected in the main drainage channel, in the agricultural area of Lonja field, Croatia. Lonja field is the largest protected wetland in both Croatia and the entire Danube basin. It extends along the river Sava and the lower course of the river Lonja. Sampling was performed during the spring months in 2015, 2016 and 2017. Investigation was done through the measurements of physicochemical indicators: pH value, biochemical oxygen demand (BOD), concentration of oxygen, nitrate, phosphate, trace metals (Zn, Pb and Cd), dissolved organic carbon (DOC), and surface active fraction of DOC. The obtained results were compared with those of the Lonja and Sava rivers. The significant higher concentrations of DOC (up to about 13 mg C dm^{-3}) have been observed in the water from main drainage channel. It is known that, high DOC concentrations in surface waters have negative effects on the water quality and water habitats.

Keywords: surface water quality, agricultural area, physicochemical indicators, dissolved organic matter.

INTRODUCTION

Water quality for a particular purpose is determined on the basis of indicators of the composition, properties and concentration of individual substances in water (Šimunić, 2016).

In various soil-plant systems, pollutants may constitute a potential risk to the environment through their uptake by plants and subsequent input the food chain and, and the danger ensuing from their tendency to accumulate in vital organs of human, animals and plants, or because of possible contamination of drinking water.

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Excessive nitrate and phosphorus concentration in water may lead to eutrophication of watercourses or stock watering places. If such water is used for human consumption, it may cause methemoglobinemia in infants and animals (Pratt and Jury, 1984; Matson et al., 1997). Potencial cancer risk from nitrate and nitrite in water and food has been reported Rademacher et al. (1992). Leaching of nitrates from soil depends on many factors, such as amount, frequency and intensitety of precipitation, soil properties, crop type and it's development, evaporation, soil tillage and nitrogen fertilization (Vidaček et al., 1999; Nemeth, 2006; Josipović et al., 2006; Nemčić et al., 2007; Šimunić at al., 2011). The problem of nitrate (and other pollutants) leaching is even pronounced in agrecosystems of hydroameliorated fields, especially in drained soils because of changed infiltration and filtration capabilities of these soils.

One of the parameters in evaluation criteria of the natural waters ecological status is trace metals concentrations (Water Framework Directive, 2000). Metals may include non-essential ones, such as Cd and Pb that can be toxic even at trace levels, and biologically essential elements, such as Cu, Fe, Mn and Zn, which might cause toxic effects at elevated concentrations (Wong et al., 2006; Jakovčić at al., 2003). The essential heavy metals exert biochemical and physiological functions in plants and animals. Metals are non-biodegradable and accumulative in nature (Tchounwou et al., 2012). Although the speciation of metals is important because has a profound effect on their biological availability, the total/dissolved concentration gives a general overview of the particular water body (Cukrov et al., 2008).

Dissolved organic matter (DOM), one of the most complex naturally occurring mixtures, plays a central role in the biogeochemistry and the photochemistry of natural waters. Dissolved organic carbon (DOC) is the measurable elemental organic carbon content of DOM

(Filella, 2009) and is generally defined as compounds that can pass through a 0.45 μm or 0.7 μm filter. DOC provides a nutritional and energy base for life i.e. micro-and macro-organisms, and is a source for nutrient regeneration, ion exchange capacity, light and heat absorption, having major impact on the speciation of many trace elements. However, high DOC concentrations in surface waters have negative effects on the water quality and water habitats. Further, in the biogeochemical processes in aquatic environment, the physicochemical properties of organic matter are often more important than the amount present. The fraction of DOC which possesses surface active properties may be very important for natural freshwater. The molecules of surface active substances (SAS) have their hydrophilic parts oriented towards the water phase while the hydrophobic ends are located on the air, which is a thermodynamically favourable configuration. Organic SAS are concentrated by adsorption processes on natural phase boundaries: water–atmosphere, water-sediment, water–suspended particles, where they greatly affect transfer of mass and energy (Ćosović and Vojvodić, 1998). Research on the DOC and SAS provides an important tool for better understanding of the content, distribution, physico-

chemical characteristics as well as dynamics of the complex mixture of DOM in the natural waters (Orlović-Leko et al., 2016).

The objective of this study was to estimate the impact of the use of hydromeliorated agricultural land for cultivation of agricultural crops on the surface water quality.

MATERIAL AND METHODS

Hydroameliorated agricultural land is located in the central part of the river Sava valley and partially borders the Lonja field Nature Park, which is the largest protected wetland both in Croatia and the entire Danube basin. It extends along the river Sava and the lower course of the river Lonja. Total area of the hydroameliorated land is about 4.000 ha.

Water samples were collected in the main drainage channel and rivers Sava and Lonja. Sampling was performed during the spring months in 2015, 2016 and 2017. Investigation was done through the measurements of physicochemical and chemical indicators: pH value, biochemical oxygen demand (BOD), concentration of oxygen, nitrate, phosphate, trace metals (Zn, Pb and Cd), dissolved organic carbon (DOC), and surface active fraction of DOC.

- pH value was measured by pH meter-HRN ISO 10523:2012.
- Electrical conductivity is determined by norm HRN EN 27888:2008.
- Biochemical oxygen demand by norm HRN ISO 5815:1998 en.
- Concentration of oxygen by HRN EN 25813:1998 en.
- Nitrate was determined by spectrophotometrically method-HRN ISO 13395:1996.
- Phosphorus was determined by method continous flow analysis-HRN ISO 15681-2:2008.
- Trace elements were determined by AAS- HRN ISO 8288:1998 (ISO 8288:1986).
- Dissolved organic carbon (DOC) concentrations were determined by using a high-temperature
- Catalytic oxidation analyzer (TOC-5000 Model, Shimadzu, Japan).
- Surface active substances (SAS) were measured by the electrochemical method (AC voltammetry, out of phase). For the quantification of the SAS content in samples a calibration plot of the nonionic surfactant Triton-X-100 was used (Ćosović and Vojvodić, 1998; Orlović-Leko et al., 2016).
- The quality of the surface waters is determined on the basis of the Water Classification Decree (National Gazette, 137/08).

RESULTS

Water quality is determined by a number of indicators that can be divided into pyisicochemical, oxygen regime indicators, nutrients and biological indicators.

Results of investigation are presented in Tables 1 - 5. Pysicochemical indicators are presented through pH value, electrical conductivity (EC) (Table 1).

Oxygen regime indicators are presented through concentration of oxygen and biochemical oxygen demand (Table 2). Nutrients through nitrates, ammonia and phosphorus (Table 3). Trace metals (Zn, Pb and Cd) are listed in Table 4. Additionally, organic matter is investigated through the study of surface activity (SA) of dissolved organic carbon (DOC), Table 5 and the ratio SAS/DOC values (Table 6).

DISCUSSION
Pysicochemical indicators

Value of pH is an important indicator of water quality. If the pH values of water are in the range between pH = 6.5 and pH = 8.5, it means that water can be used for all purposes. If the pH value falls between pH= 6.0 and pH= 6.5 than water have to be purifed before for any purpose of use and outside these pH values, water is a undesirable environment for plants and animal world and is not recommended for use in technological purposes. In Table 1 are presented the pH values of the investigated water samples.

According to the pH values, the water were in first class and were rated as a high state. Electrical conductivity (EC) is an indicator of salt concentration in water, i.e. water salinity. Informations about salt concentration in water indicates its usability in irrigation, since a higher salt concentration can cause soil salinity, that is, higher concentration of salt in soil solutions has an adverse effect on water uptake through plant roots, which in turn causes a drop in turgor pressure. Reduced turgor leads to plant limpness, drying and falling of leaves, as well as lower yields. As most plants are sensitive to the presence of salts, it is recommended that salt concentration in irrigation water should not surpass limit value of 3 dS/m (Ayers and Westcot, 1985), or more precisely salt concentration to 0.7 dS/m there are no limitations.

Table 1: Pysicochemical indicators

Water system	pH			Electrical conductivity – EC (dS/m)		
	2015	2016	2017	2015	2016	2017
Main drainage channel	7.6	7.7	7.5	0.380	0.356	0.370
Rating for each indicator	I	I	I	I	I	I
River Lonja	7.7	7.8	7.8	0.440	0.439	0.453
Rating for each indicator	I	I	I	I	I	I
River Sava	7.7	7.7	7.7	0.420	0.442	0.438
Rating for each indicator	I	I	I	I	I	I

From the Table 1, it is evident that the EC in all surface water were less than 0.5 dS/m and puts water in the first class and was rated as a high state.

Based on physico-chemical indicators, surface water of all water bodies are classified into the first class and their condition is marked as high.

Oxygen regime indicators

Organic matter in water refers to all substances that are in natural water in dissolved and suspended form. Total organic matter is divided into biologically degradable and nondegradable substances. According to its origin, organic matter in water can be a product of biochemical processes or a product of human activities. Occurrence of water pollution is a consequence of soil leaching by precipitation water as well as of components of urban and industrial westwaters. Indicator of organic matter degradability in water by microorganisms is called the biochemical oxygen demand (BOD). Total biochemical oxygen consumption is the amount of oxygen required for complete organic matter degradation (Šimunić, 2016).

As evident from Table 2, the oxygen concentration in the water channel was in the category of the third class and the water status was rated as moderately, while according to biochemical oxygen demand water channel was in the category of the second class and the water status was rated as good.

According to the indicator group, the channel water corresponds to the third category and the water status is rated as moderate.

In all years of research the oxygen concentrations in the rivers of Lonja and Sava were in the category of the first class and the water status was rated as high, while according to biochemical oxygen demand water were in the category of the third class and the water status was rated as moderate. According to the indicator group, the water of rivers Lonja and Sava are classified in the third category and the water status is rated as moderate.

Table 2: Oxygen regime indicators

Water system	Oxygen (mg O_2/L)			Biochemical oxygen demand– BOD_5 (mg O_2/L)			Rating by indicator group
	2015	2016	2017	2015	2016	2017	
Main drainage channel	5.54	4.69	5.90	3.09	3.16	3.87	
Rating for each indicator	III	III	III	II	II	II	III
River Lonja	8.01	9.61	9.49	4.76	5.53	4.33	
Rating for each indicator	I	I	I	III	III	III	III
River Sava	8.17	8.32	8.06	4.82	5.12	4.12	
Rating for each indicator	I	I	I	III	III	III	III

Nutrients

Nutrients in water mostly refer to dissolved nitrogen and phosphorus compounds. Nutrients can get into water by leaching from agricultural soils where they are used as mineral fertilizers and from household and industrial wastewater. Increased concentration of nutrients in water causes intensified production of primary organic matter, namely, eutrophication, These compounds

are found in water in different forms and are subject to changes, in dependence on the amount of oxygen in water.

In the investigated period, concentration of nitrates in main water channel was in the category of the third class and the water status was rated as moderately, while according to concentration of ammonia, it was in the category of the fifth class and the water status was rated as bad. According to the concentration of phosphorus it was in the second class and was rated as good. (Table 3). According to the indicator group, the water channel is classified into the fifth category and the water status is rated as bad.

Table 3: Nutrients

Water system	Nitrates NO3-N (mg/L)			Ammonia NH4-N (mg/L)			Phosphorus PO4–P (mg/L)			Rating by indicator group
	2015	2016	2017	2015	2016	2017	2015	2016	2017	
Main drainage channel	2.52	3.17	3.43	3.62	1.55	2.27	0.15	0.13	0.16	
Rating for each indicator	III	III	III	V	V	V	II	II	II	V
River Lonja	1.69	1.72	1.57	1.47	1.20	1.30	0.08	0.11	0.14	
Rating for each indicator	III	III	III	IV	IV	IV	I	II	II	IV
River Sava	1.45	1.69	1.70	1.37	1.24	1.22	0.10	0.11	0.13	
Rating for each indicator	II	III	III	IV	IV	IV	II	II	II	IV

Concentrations of nitrates in the rivers of Lonja and Sava were in the category of the third class and the water status was rated as moderate, while according to concentration of ammonia water were in the fourth category and the water status was rated as poor and according to the concentration of phosphorous in water, they are classified into second category. According to the indicator group, the water of rivers Lonja and Sava are classified in the fourth category and the water status is rated as poor. It is evident that the concentration of nitrates and ammonia in the water channels was higher in all years than in the Lonja and Sava river waters, which could have caused a lower oxygen concentration in the water channel, or a weaker nitrification process. The concentration of nitrates and ammonia in the rivers was similar to that of phosphorus concentrations, while the phosphorus concentration in the water channel was somewhat higher. Another reason for increased nutrient concentration in water channel is fertilization and cultivation of agricultural crops on hydromeliorated areas. Nutrient concentrations and their leaching depend on several factors, such as the amount

of mineral fertilizer input, hydrological conditions, soil type, cultured crops and so on (Vidaček et al., 1999; Mesić et al., 2007; Šimunić et al., 2011).

Trace metals

Concentrations of trace metals (Zn, Pb and Cd) in all water samples did not indicate water pollution (Table 4), which is in agreement with the results obtained by Moore (1981), Đumija et al. (1989), Čoga (1998) and Šimunić et al. (2002). Different mean concentrations of Zn and Cd were recorded both between years and between different aquatic bodies. The same may be assumed for Pb due to detection limit (< 1.0 μg/L).

Based on concentrations of Zn, the investigated surface water are classified into the first class and their state is marked as high. According to the concentrations Pb and Cd, water are classified into the second class and their state is marked as good.

Table 4: Trace metals

Water system	Zn (μg/L)			Pb (μg/L)			Cd (μg/L)		
	2015	2016	2017	2015	2016	2017	2015	2016	2017
Main drainage channel	15.2	12.7	11.6	<1.0	<1.0	<1.0	0.25	0.18	0.21
Rating for each indicator	I	I	I	I or II	I or II	I or II	II	II	II
River Lonja	22.1	10.5	10.8	<1.0	<1.0	<1.0	0.23	0.20	0.35
Rating for each indicator	I	I	I	I or II	I or II	I or II	II	II	II
River Sava	22.9	18.4	14.2	<1.0	<1.0	<1.0	0.19	0.23	0.27
Rating for each indicator	I	I	I	I or II	I or II	I or II	II	II	II

Organic matter

Data on the dissolved organic carbon, DOC and surface active substances, SAS are presented in Table 5.

Table 5: Concentrations of DOC and SAS

Water system	DOC mg C dm^{-3}	SAS mg dm^{-3} eq. Triton-X-100
Main drainage channel	9.48 - 13.35	0.195– 0.197
River Lonja	4.62 - 7.75	0.209–0.211
River Sava	1.60 1.57 - 3.30*	0.200 0.017–0.620*

*Orlović-Leko et al., 2004.

Concentration of DOC in the main water channel were in the range of 9.48 to 13.35 mg C dm^{-3} (Table 5). These DOC concentrations are significant higher (2 to 8 times) than those measured in the surface freshwater systems of the rivers Lonja and Sava. In comparison, concentrations of DOC in the drainage water of hydroameliorated agricultural areas in the central Sava river valley, Croatia, were in the range from 1.07 do 9.93 mg C dm^{-3} (Orlović-Leko et al., 2016). Concentrations of DOC in natural fresh waters range from ~1 to 60 mg C dm^{-3}, but are commonly from 1-5 mg C dm^{-3} (McDonald et al., 2004).

Table 6: The ratio SAS/DOC values obtained in investigated water samples and in different model substances (Ćosović et al., 2007; Orlović et al, 2016)

SAS	SAS eq T-X-100/ DOC	Dominant SAS in the water samples
Triton-X-100	1.54	
Lignosulphonate	6,8 x 10^{-4}	
Monocarboxylic acids		
Caprylic acid (pH=4)	0.016	
Capric acid (pH=4)	0.17	
Capric acid (pH=6.5)	0.015	
Oleic acid	2.7	
3-Hydroxybutanoic acid	0.05	
3-Hydroxybenzoic acid	8.2x10^{-4}	
cis-Pinonic acid	0.001	
Polycarboxylic acids		
Humic acid	0.04	
Fulvic acid	0.17	
Protein		
Albumine	0,20	
Polysaccharide		
Xanhtan	0.04	
Water samples in this work		
Main drainage channel	0.017	Monocarboxylic acids
River Lonja	0.03	Xanhtan, Humic acid
River Sava	0.16	Fulvic acid

A quantification of adsorbable organic substances was performed by using a calibration plot of Triton-X-100 (Ćosović and Vojvodić, 1998; Orlović-Leko et al., 2016). The relative concentrations of surface active substances (SAS) for all investigated water samples were relatively low (Table 5). The relative concentrations of SAS values obtained in the drainage water samples were between 0.11 and 0.45 mg dm^{-3} eq. Triton-X-100, with the average value of 0.36

± 0.10 mg dm^{-3} (Orlović-Leko et al., 2016). However, the concentration of SAS also depends on the nature of the organic molecules in the samples.

The rapid and rough SAS characterization in the studied samples was done by comparisson of its SAS/DOC ratio values with SAS/DOC ratios of different model substances, possible constituents and/or pollutants in aquatic system (Table 6). Triton X-100, here presented as a model of strongly adsorbable surfactant, it is reasonable to expect that very small amounts of some strongly adsorbable substances, for example pollutants, could markedly increase surfactant activity of water samples (Orlović-Leko, 2004).

As can be seen from Table 6, SAS in the main drainage channel water were with similar adsorption behaviour like monocarboxylic acids, while in the river Lonja, SAS/DOC = 0.03 and are very close to the ones determined for xanhtan and humic acid. Further, from the result for Sava river (SAS/DOC = 0.16) can be concluded that fulvic acid represent a predominant class of surface active material. Generaly, in the freshwater samples humic and fulvic acid main class of surface active material, mainly from terrestrial input (Orlović-Leko et al., 2016). The presence of the monocarboxylic acids in the main drainage channel can be probable consequence proceses of the decomposition of complex organic material.

CONCLUSION

On the basis of the indicators for determining water quality in the main drainage channel and rivers of Lonja and Sava, the following can be concluded that the impact of the use of hydromeliorated agricultural land for cultivation of agricultural crops on the surface water quality has been established for nutrient which is obviously a consequence of mineral fertilization and organic matter.

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