LEACHATE QUALITY ASSESSMENT OF PROTECTED WATER BODIES IN SERBIA AND CROATIA

Tijana Adamov[1], Mladenka Novaković[1], Nevena Živančev[1], Ivan Špánik[2], Ivana Mihajlović[1], Maja Petrović[1]

[1]University of Novi Sad, Faculty of Technical Sciences, Department of Environmental Engineering and Occupational Safety and Health, Trg Dositeja Obradovića 6, 21000 Novi Sad, Serbia
[2]Institute of Analytical Chemistry, Faculty of Chemical and Food Technology, STU, Radlinského 9, 812 37 Bratislava, Slovakia
e-mail: majadjogo@uns.ac.rs

Abstract
Modern agricultural production can not be imagined without the use of pesticides and, if their use is improper, it could lead to continuous introduction of pesticide residues to different environmental media. Water pollution which originates from agricultural activities is a common problem in both observed countries, Serbia and Croatia. The paper provides evaluation of leachate water quality of protected water bodies, Tompojevački ritovi, Croatia, and Lake Zobnatica, Serbia, with the results of detected pesticide residues and other relevant organic micropollutants.

Introduction

Nowadays, the use of pesticides on crops is a necessity, conditioned by the need to preserve yields. Until 2020, over 400 pesticide active ingredients were registered for use in Serbia in the form of 1076 plant protection products, for use on seeds, soil, aboveground parts of plants, fruits or in any other way.

Glyphosate is a versatile herbicide that has been used for more than 40 years to easily, safely and effectively control problematic weeds. Since its introduction in 1974, glyphosate-based products have become the most widely used herbicides in the world due to their ability to control a wide range of weeds, great economic and environmental benefits and a strong safety profile. During the 1990s, the combination of glyphosate with glyphosate-resistant crops led to the transformation of agriculture in many parts of the world and the beginning of the era of modern agricultural biotechnology [1,2,3]. Glyphosate is currently approved for use in over 130 countries, and the current world amount is estimated at about 600 kilotons per year. Glyphosate is especially used in the production of soybeans, corn, potatoes and cotton that are genetically modified to tolerate glyphosate [4].

Glyphosate-based herbicides pollute drinking water sources through rainwater, surface runoff, and infiltration into groundwater, thereby adding drinking water, bathing water, and washing water as possible everyday routes of exposure for humans [1,2,3].

Poor water quality of protected water bodies in Serbia and Croatia is not the only cause of biodiversity loss in wetlands, but often makes surface waters inadequate for irrigation. The main objectives of the study were to provide information about water quality through determination of main physicochemical parameters and pesticides distribution and other relevant organic micropollutants identified in leachates from the wetland area Tompojevački ritovi and Lake Zobnatica.

Experimental

The selected leachate samples were collected near agricultural fields from Lake Zobnatica surrounding area (Republic of Serbia) and wetlands of Tompojevački ritovi (Croatia).

Leachate samples for physicochemical parameters analysis were collected in 1 L bottles, plastic and glass. On site, collected water samples were stabilized by the addition of concentrated nitric acid until pH value was adjusted to 2.

In order to conduct field analysis such as measurement of pH value and dissolved oxygen, Multi 340i multimeter (WTW) was used. The other target parameters were measured under standard laboratory procedures using UV-VIS DR5000 (HACH) spectrophotometer for determination of inorganic ions (orthophosphates, PO_4^{3-} and nitrites, NO_2^-) and chemical oxygen demand (COD). The total organic carbon (TOC) and total nitrogen (TN) were measured on Vario TOC Select (Elementar).

Samples for screening analysis were collected in amber glass 2 L bottles, without stabilization. All samples represent 2-hour composite sample, which is consisted of 8 random samples collected in 2 hours, in 15 minutes intervals, from 1 m depth from the surface. Samples were transported and kept at 4°C until analysis. Samples were prepared by liquid-liquid extraction and analyzed by GC-MS (Shimadzu QP2010Ultra) in SCAN and SIM mode.
The capillary column HP-5MS was used for the analysis. Oven temperature gradient program was set to hold time of 10 minutes on 40 °C, and then increase of 2 °C per minute was adjusted to 300 °C. MSD was used during the analysis in scan mode (m/z 45-600). Helium was used as carrier gas.

Results and discussion

In order to define the origin of leachate pollution, concentration levels of relevant physicochemical parameters at the sampling locations are shown in Table 1.

Table 1. Values of relevant physicochemical parameters at the sampling locations – Lake Zobnatica and Tompojevački ritovi

	pH value	Dissolved O_2 (mg L^{-1})	Orthophosphates PO_4^{3-} (mg L^{-1})	Total N (mg L^{-1})	Other relevant parameters (mg L^{-1})
Lake Zobnatica	> 8,5	< 4	1,7 – 4,5	12,59 – 73,26	0,436 (NO_2^-)
Wetland Tompojevački ritovi	9,5	< 1	7,7 – 10	275,68	79,9 (TOC) 180 (COD)

As presented in Table 1, measured concentration levels of total nitrogen were in range of 12,59 – 73,26 mg L^{-1} while concentration of orthophosphates ranged from 1,7 – 4,5 mg L^{-1}. The influence of the green belt on the reduction of concentration levels of total nitrogen and nitrite was observed [5]. The pH value (higher than 8,5) and concentration of dissolved oxygen (lower than 4 mg L^{-1}) point out anthropogenic activities as possible pollution source. The high level of nitrites concentration (0,436 mg L^{-1}) was detected in one representative sampling point.

The elevated concentration levels of orthophosphate (7,7 – 10 mg L^{-1}) and total nitrogen (275,68 mg L^{-1}), indicate that major pollution sources are implemented agricultural activities resulting

in agricultural runoff. Nitrogen compounds in water are products of organic matter degradation [5]. pH value was greater than 9,5 while measured values of dissolved oxygen were lower than 1 mg L^{-1}. The increased concentration levels for TOC and COD were 79,90 and 180 mg L^{-1}, respectively.

Screening analysis of agricultural runoff water indicated the presence of the following substances shown in Table 2.

Table 2. Comparison of leachate analysis results in Serbia and Croatia

Study (Location)	***Serbia, 2019***	***Croatia, 2019***
Substance		
3-(n-Propylamino)-2,1-benzisothiazole		x
Aminomethyl phosphonic acid (AMPA)	x	
N-Butylbenzenesulfonamide		x
Benzyl butyl phthalate		x
Cholesteryl formate (26-Nor-5-cholesten-3.beta.-ol-25-one)		x
Dibutyl phthalate	x	x
Diisobutyl phthalate	x	x
Diphenyl sulfide	x	
Eicosane	x	
Phenanthrene-D10 (IS)	x	x
Glyphosate (*N*(phosphonomethyl)glycine)		x
2,4-bis(1,1-dimethylethyl)- phenol	x	
Triphenylphosphine oxide		x

Table 2. shows comparison of the obtained results at Lake Zobnatica, Serbia, and Tompojevački ritovi, Croatia. There is a lack of knowledge about distribution of wide range of organic micropollutants in protected water areas. It is much more common to examine the presence of glyphosate and/or AMPA in the leachate of agricultural land, or land treated with agrotechnical measures, than a complete screening analysis. Glyphosate was detected in samples collected from wetlands located in Tompojevački ritovi, Croatia, while it was not detected in samples from Lake Zobnatica, Serbia. However, the glyphosate metabolite aminomethyl phosphonic acid (AMPA) was detected in samples from Lake Zobnatica, and not detected in samples from Tompojevački ritovi. The phthalic acid esters (Dibutyl phthalate (DBP) and Diisobutyl phthalate) were detected in both studied protected areas. DBP is defined as priority pollutant with endocrine disruptor properties. The natural antimicrobial compound, 2,4-bis(1,1-dimethylethyl)-phenol, was detected in study conducted in Serbia.

Due to the presence of the above-mentioned organic substances in leachates, as well as glyphosate and aminomethylphosphonic acid (AMPA), it can be concluded that the contamination of leachates with these substances and herbicide, as well as its metabolite, is due to anthropogenic activity through the usage of agrotechnical measures on the land.

Results of reported research of pesticide residues in protected areas are oriented at their presence in the air and soil or sediment [6, 7], and therefore, the results presented in this paper from the study of water quality in Serbia and Croatia protected areas are valuable and rare.

Conclusion

The results of the study presented in this paper prove that due to the use of glyphosate and glyphosate-based herbicides, its identification in water samples of protected areas is possible, and therefore there is potential for its occurrence in drinking water sources due to incomplete degradation or inadequate usage. Further research should be aimed at establishing a detailed monitoring programs to assess the quality of leachate water media at protected water areas with desirable inclusion of detected organic micropollutants.

Acknowledgements

This research has been supported by the Ministry of Education, Science and Technological Development through the project no. 451-03-68/2020-14/200156: "Innovative scientific and artistic research from the FTS (activity) domain" and the Bilateral project funded by the Ministry of Education, Science and Technological Development (contract no. 337-00-107/2019-09/16).

References

[1] W.A. Battaglin, M.T. Meyer, K.M. Kuivila, J.E. Dietze, J. Am. Water Resour. As. 50 (2014), pp. 275–90.
[2] M.S. Majewski, R.H. Coupe, W.T. Foreman, P.D. Capel, Environ. Toxicol. Chem 33(2014), pp. 1283–93.
[3] R.H. Coupe, S.J. Kalkhoff, P.D. Capel, C. Grégoire, Pest Manag. Sci. 68(2016), pp. 16–30.
[4] M.G. Dill, D.R. Sammons, C.C.P. Feng, F. Kohn, K. Kretzmer, A. Mehrsheikh, M. Bleeke, L.J. Honegger, D. Farmer, D. Wright, A.E. Haupfear, in John Wiley & Sons Inc, Glyphosate: Discovery, development, applications and properties, Hoboken, New Jersey, 2010.
[5] Active Sensor Monitoring Network and Environmental Evaluation for Protection and Wise use of Wetlands and Other Surface Waters. http://senswetlands.ferit.hr/rezultati
[6] S. Wang, T. Steiniche, K.A. Romanak, E. Johnson, R. Quiros, R. Mutegeki, M.D. Wasserman, M. Venier, Environ Sci Technol 53 (2019), pp. 6171-6181.
[7] Y. Sanchez-Palencia, J.E. Ortiz, T. Torres, J. Llamas, J Iber Geol 43 (2017), pp: 539-557.