Screening analysis of pesticides in the protected area of Zobnatica Lake

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Abstract. The aim of study was to characterize pollution of water in protected area of Zobnatica Lake in the vicinity of Backa Topola, Serbia. The sampling campaigns were conducted in spring and summer 2019 in order to identify organic pollutants in water samples. Samples were prepared by liquid-liquid extraction and analyzed by GC-MS in SCAN and SIM mode. Screening analyses indicated the presence of pesticides: terbuthylazine, alphacypermethrin, aminomethyl phosphonic acid (AMPA) and urea. Terbuthylazine was detected in both sampling campaigns. Results specified the need for comprehensive water monitoring program in order to determine specific pollutants in protected area of Lake Zobnatica caused water pollution by agricultural activities.

1. Introduction
The water consumption in agricultural activities worldwide is around 70%. Pollution caused by agriculture can contaminate not only water, but also the whole environment. The basic task of modern agricultural production is to achieve high and quality yields of agricultural crops. All crops in any form of production are accompanied by characteristic harmful organisms; hence it is necessary to implement appropriate protection measures. The use of herbicides is one of the chemical measures to control weeds. Herbicides may possess selective action, i.e. to destroy only certain types of weeds or total action, to control all kinds of weeds. Herbicides used in agriculture could be transported by rain and melting snow to surface water and from soil to groundwater by leaching processes [1]. Impaired and degraded ecosystems have reduced tolerance and adaptability to environmental condition variations.

Screening analyses and identification of specific pesticides in protected areas caused water pollution by agricultural activities are of great importance in defining the comprehensive monitoring programs as the first step in recognition of water pollution and mitigation of negative impacts of agricultural activities. According to the literature research, only few studies are based on pesticides identification in water samples of protected areas [2, 3].
Main sources of water pollution in Vojvodina, Serbia, are agricultural activities. The poor water quality is not only causing the loss of biodiversity in wetlands, but often makes the surface waters inadequate for irrigation [4-6].

The objective of study was to obtain information about pollution of protected area of Zobnatica Lake by pesticides used in agricultural activities in the vicinity of Lake. Evaluation of water pollution from agricultural sources will result in better management of environmental protection in region. Two sampling campaigns were conducted in spring and summer in 2019 for the purpose of identification of pesticides in run-off water samples in protected area of Zobnatica Lake.

2. Material and methods

2.1. Sampling site
Run-off water samples were collected in the vicinity of Lake Zobnatica, Serbia, in two sampling campaigns, in spring and summer 2019. Water from collectors, with labels K-a to K-f (K-a - 45°53'8.72"N, 19°36'54.73"E; K-b - 45°53'8.78"N, 19°36'55.24"E; K-c - 45°51'21.61"N, 19°36'43.98"E; K-d - 45°51'24.87"N, 19°36'56.60"E; K-e - 45°51'23.45"N, 19°36'56.00"E; K-f - 45°51'21.95"N, 19°36'53.58"E) were used for analyses of run-off water quality. Lake Zobnatica was formed in 1976 in the valley of the river Krivaja. Zobnatica is located 5 km north of Bačka Topola. Water samples were collected in amber glass 2 L bottles and represent 2-hour composite sample, which is consisted of 8 random samples collected in 2 hours, in 15 minutes intervals. Samples were collected and analyzed in duplicate.

![Sampling site – Lake Zobnatica, Serbia](image)

2.2. Sample analysis
Water samples were prepared with liquid-liquid extraction (LLE) using dichloromethane as solvent. The extract was evaporated to 1.5 mL in Kuderna-Danish apparatus. Screening analysis was performed in SCAN and SIM mode on a gas chromatogram (GC) coupled with a mass selective
detector (MSD) (Shimadzu QP2010Ultra). GC injector was set to splitless operating mode. The capillary column HP-5MS (30m•0.25mm•0.25μm df) was used for the analysis. Oven temperature gradient program was set to hold time of 10 minutes on 40 °C, then increase of 2 °C per minute was adjusted to 300 °C. Helium was used as carrier gas. The NIST Mass Spectral Library was used to identify chemical compounds.

3. Results and discussion
Detected pesticides within the screening analysis of run-off water with their chemical structure, similarity index with NIST database and names of commercially used products in agriculture are presented in Table 1.

| Detected pesticide | Chemical structure | Similarity index (with NIST database) % | Comercial product |
|--------------------|--------------------|----------------------------------------|-------------------|
| Terbutylazine      | ![chemical structure](image1) | 98                                     | Terbis, Rezon, Radazin- herbicide |
| Alpha-cypermethrin | ![chemical structure](image2) | 99                                     | FASTAC® 10 EC - insecticide |
| Urea               | ![chemical structure](image3) | 95                                     | UREA N 46 - herbicide |
| Aminomethyl phosphonic acid (AMPA) | ![chemical structure](image4) | 98                                     | Primary degradation product of the herbicide glyphosate (GLIFOHEM, GLIFOL) |

The screening analyses indicated the presence of pesticides: terbutylazine, alpha-cypermethrin, aminomethyl phosphonic acid (AMPA) and urea. Terbutylazine was detected in both sampling campaigns, in spring and summer 2019.

Terbutylazine belongs to the Triazine group. The herbicide Terbutylazine essentially acts as an inhibitor of photosynthesis. It forms a herbicidal film that prevents weed germination, but is also adopted through weed leaves. This pesticide is a selective for potatoes, maize, fruit trees and other plant species.

Cypermethrin is synthetic compound and insecticide with contact and digestive action. It has a pronounced effect on adult insects and larvae, but it also has a significant effect on eggs with a thin membrane. In higher concentrations Cypermethrin has a repellent effect on pests. Cypermethrin is lipophilic, makes direct contact with the waxy substances of the plant cuticle and enables regulatory
function to plant growth. Cypermethrin is toxic to aquatic insects and moderately toxic to human. Toxic effects are expressed by dermal exposure.

Urea herbicides have broad spectrum of action on a large number of weeds, but do not affect perennial weeds. The maximum concentration of the Urea herbicide is maintained at the surface layer of the soil and plant absorbs it by the root. Urea herbicides act primarily through the roots. They are translocated via water to the leaves where they bind to the chloroplast and interfere with the photosynthesis process resulting in the death of sensitive weeds. Urea herbicides bind tightly to soil particles, they are poorly rinsed and persistent. They decompose within 3-6 months and express low acute toxicity [7].

AMPA is the primary degradation product of herbicide glyphosate.Glyphosate is organophosphorus compound and non-selective highly systemic pesticide used for the control of a large number of annual grass and broadleaf weeds. It is most commonly used in the form of the isopropyl amino salt and applied to weed leaves. Glyphosate binds strongly to soil colloids to such an extent that it is no longer accessible to plants. In the soil, decomposition takes place mostly with the help of microorganisms, and to a lesser extent, chemically by hydrolysis, oxidation and photodegradation. Detected herbicides and insecticide could cause surface and ground water pollution with negative impact on biota and human health.

4. Conclusions
Screening analyses indicated water pollution with pesticides and need for detailed analyses. Results specified the need for comprehensive water monitoring program in order to determine the natural and artificial impacts and to maintain the required water quality, as the first step in mitigation of negative impacts of agricultural activities and biodiversity protection. Further research should be aimed at establishing detailed monitoring programs to assess the quality of water media at protected water areas with desirable inclusion of detected organic micropollutants, such as pesticides.

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