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Article

Pesticide Residues in Water and Sediment

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Abstract: The term pesticide refers to all chemical compounds predominantly used in agriculture for the control of the pathogens, weeds and pests. In order to intensify the agricultural production the use of pesticides has increased over the years in many developing countries. Since the monitoring of the presence of pesticides is rarely conducted and fairly difficult, the potential hazardous effects towards the human health, the biodiversity and the environment are hard to anticipate. The aim of the study is to provide a preliminary assessment of the situation by looking for the presence of pesticides in the water and sediment of the lake used for the irrigation. SPE and LC-MS/MS were used to purify and analyze the samples for the presence of 150 pesticides. The nicosulfuron was detected in the unusually high concentrations in water (97.80 μg/L) and the sediment (224 μg/kg).

Keywords: pesticide residues; water; sediment; LC-MS/MS.

1. Introduction

Due to the growing concern regarding the aim to ensure the economic progress compatible with the environment, in 2015 the United Nations adopted the 2030 Agenda for Sustainable Development in order to promote the prosperity while protecting the planet. Among the 17 proposed goals, the protection of the aquatic ecosystems, as well as the reduction of the aquifer pollution were presented [1]. The term pesticide refers to all chemical compounds predominantly used in agriculture for the control of the pathogens, weeds and pests, in order to improve crop production and increase the yields. However, the pesticide residues tend to persist and accumulate in the environment, where they can affect the environment itself, as well as the human health, even at low concentrations [2]. In case of the aquatic ecosystems, the bioaccumulation rate of the pesticides depends on their solubility and the octanol-water partition coefficient (logKow). The pesticides can get into the water by: desorption from the sediments and aquatic organisms, atmospheric precipitation, the pesticides application, washing the protective clothing and the machines after the treatment, the incorrect use of sprayers, and by the pesticide packaging waste [3]. After getting into the water, the routes of pesticides transformation consist of physical, chemical and biological processes. Numerous persistent and toxic compounds can become an integral part of the sediment through bounding to the solid matter. The resuspension of the polluted sediment presents the permanent source of these pollutants, as well as the largest potential source of the water quality risks [4]. There are some directives in the European Union which regulate the presence of pesticides in water such as Directive 2006/118/EC which refers to groundwater pollution [5]. Also, Directive 98/83/EC is related to the quality of water intended for human use [6]. The Water Framework Directive 2000/60/EC

(WFD), sets the base for common action in the field of water policy [7]. WFD on water of the European Union represents a legal framework for the protection and improvement of the quality of all aquatic resources such as rivers, lakes, groundwater, coastal water and others in the European Union [3]. The Regulative set the value of 0.1 μg/L as the maximum concentration (MACs) for each pesticide detected in a water sample, and 0.5 μg/ L for the sum of all individual pesticides detected and quantified in the monitoring procedure, including their relevant metabolites, degradation, and reaction products in water for human consumption [1]. Atrazine and some of its degradation products, terbutryn and alachlor, are part of the list of the 45 priority substances to be controlled in the field of water policy and established the parameters of environmental quality standard (EQS) expressed as the MACs, updated through Directive 2013/39/EU [8]. The Regulation No. 1107/2009 lays down the maximum concentrations/contents of the approved pesticides in soils through the estimation of the Predicted Environmental Concentrations (PEC) for each of the approved active substances in the review process preceding the authorization and commercialization of the plant protection products [9].

The use of pesticides is one of the most important ways to protect plants and plant products from harmful organisms [10]. Pesticides are considered to be highly toxic substances in the environment, however, there is very little information about their distribution and use in Serbia. The results of the monitoring program for the surface and groundwater are not enough and they are mainly based on the organochlorine pesticides in the world [11-17].

Accordingly, the objectives of this study were (i) to evaluate the pesticide residues in surface water from the lake used for the irrigation, and (ii) to compare the occurrence of pesticide residues in water and those detected in the sediment of the same lake.

2. Materials and Methods

Water and sediment sample collection

The water and sediment samples from the irrigation lake were collected on 23/06, Vojvodina province, Serbia. The water sample was taken from the boat, at the central position of the lake. The water was collected in amber glass bottles (1 L) by plunging at a depth of 30 cm and closing with the lid under the water surface. The sample was transported to the laboratory in handy cool box and kept at 4 ºC until the analysis. The sediment (1 kg) was collected using Ekman sediment grabber operated manually from the bridge and placed in the aluminium foil. For the further analysis, an ice box was used to store the sample immediately and transport it to the laboratory.

Pesticide analysis

The pesticide analysis of 150 pesticides was performed with an Agilent 1200 HPLC system equipped with a G1379B degasser, a G1312B binary pump, a G1367D autosampler and a G1316B column oven (Agilent Technologies, Waldbronn, Germany). Chromatographic resolution was achieved with Zorbax XDB C18 analytical column of 50×4.6 mm and 1.8 μm particle size (Agilent Technologies) maintained at 30 °C. The analytical separation was performed using a gradient program starting with 90% mobile phase B and progressing to 5% mobile phase B at 15 min, with methanol as mobile phase A, and water as mobile phase B, both containing 0.1% formic acid. The flow rate was maintained at 0.3 mL/min. The tandem mass spectrometry analysis was carried out with an Agilent 6470B Triple Quadrupole mass spectrometer equipped with Agilent Jet Stream

Source (Agilent Technologies, Palo Alto, CA, USA). The following ionization conditions were used: positive electrospray ionization (ESI^+) in MRM mode, drying gas (nitrogen) temperature 250 °C, drying gas flow rate 13 L/min, nebulizer pressure 30 psi, sheath gas temperature 300 °C, sheath gas flow 12 L/min and capillary voltage 4000 V. The data acquisition and quantification was conducted using MassHunter Workstation software version B.10.01 (Agilent Technologies 2016-2020). The method was validated according to SANTE/11312/2021 document [18]. The limits of detection (LODs) were determined as the lowest concentration giving a response of three times the average baseline noise. The signal/noise ratio (S/N) in the obtained chromatograms for the LOD estimation was calculated by MassHunter Qualitative Software. LODs were defined as analyte peaks giving the S/N ratio of 3 extracted from the less intense (confirmation) MRM transition, calculated using an extract of Milli–Q water (250 mL) spiked at the 10 ng/L level. The linearity was checked using matrix matched standards (MMS) at concentrations from 10 to 200 ng/mL. The recovery was checked by enriching of a blank sample (250 mL of tap water) with the mixture of pesticide standards of 1 μg/mL to get the final mass concentration of 20, 100 and 200 ng/L, with the addition of the internal standards carbofuran-D3, atrazine-D5 and isoproturon-D6 (mass concentration 10 μg/mL).

The water samples (blank, spiked and real sample), preparation was performed with Bond Elut Plexa cartridges (200 mg, 3 mL) which were conditioned with 5 mL of methanol and 5 mL of HPLC - grade water. After conditioning, 250 mL volume of water (previously filtered through the 0,45 μm filter) was enriched onto the cartridge with the flow rate settled between 5 and 10 mL/min. The cartridge was flushed with 5 mL of HPLC - grade water and dried for 15 min under a gently stream of nitrogen. Pesticides were eluted from the sorbent with 5 mL of methanol and collected in the 12 mL amber glass vial. The solvent was evaporated under a gentle stream of nitrogen in a Techne-Dry block and the residue was dissolved in 0.25 mL of initial mobile phase composition. An extract volume of 10 μL was injected into the LC/MS-MS for the detection.

The sediment samples (blank, spiked and real sample), were extracted using QuEChERS method. Namely, into a 50 mL centrifuge tube 5 ± 0.1 g of sediment plus 10 mL water and 10 mL of ACN were added and shaken vigorously. Next, the extraction salts were added, shaken vigorously for 10 min on 2500 rpm by vortex. After that, the samples were centrifuged for 5 min/4000 rpm. An aliquot of supernatant extract (6 mL) was cleaned using PSA and C18, shaken for 1 min, centrifuged for 5 min/4000 rpm and after that the extract was filtered through 0.45 μm Chromafil® PET filters and analysed by LC-MS/MS.

3. Results and Discussion

The previously validated LC-MS/MS methods for both matrices according to Mezei et al. [19] and Mačkić et al. [20], exhibited an excellent linearity (R^2>0.99) in the concentration range from 10 to 200 ng/mL, with the precision expressed as relative standard deviation (RSD<20%), for all 150 pesticides (in water and sediment). The recovery of all investigated analytes in both matrices was in the range from 60-120%. The achieved LOQs for water were 0.01 μg/L (for sediment 10 μg/kg) for all of the tested pesticides. These values are suitable for monitoring pesticides in surface water according to the Directive 2008/105/EC, Commission Implementing Decision 495/2015/EC and 1107/2009/EC [21, 22, 9].

As the LC-MS/MS chromatographic results of the analysis of the blank water sample, spiked sample (from lake) and water samples were presented on the Figure 1, as they are listed.

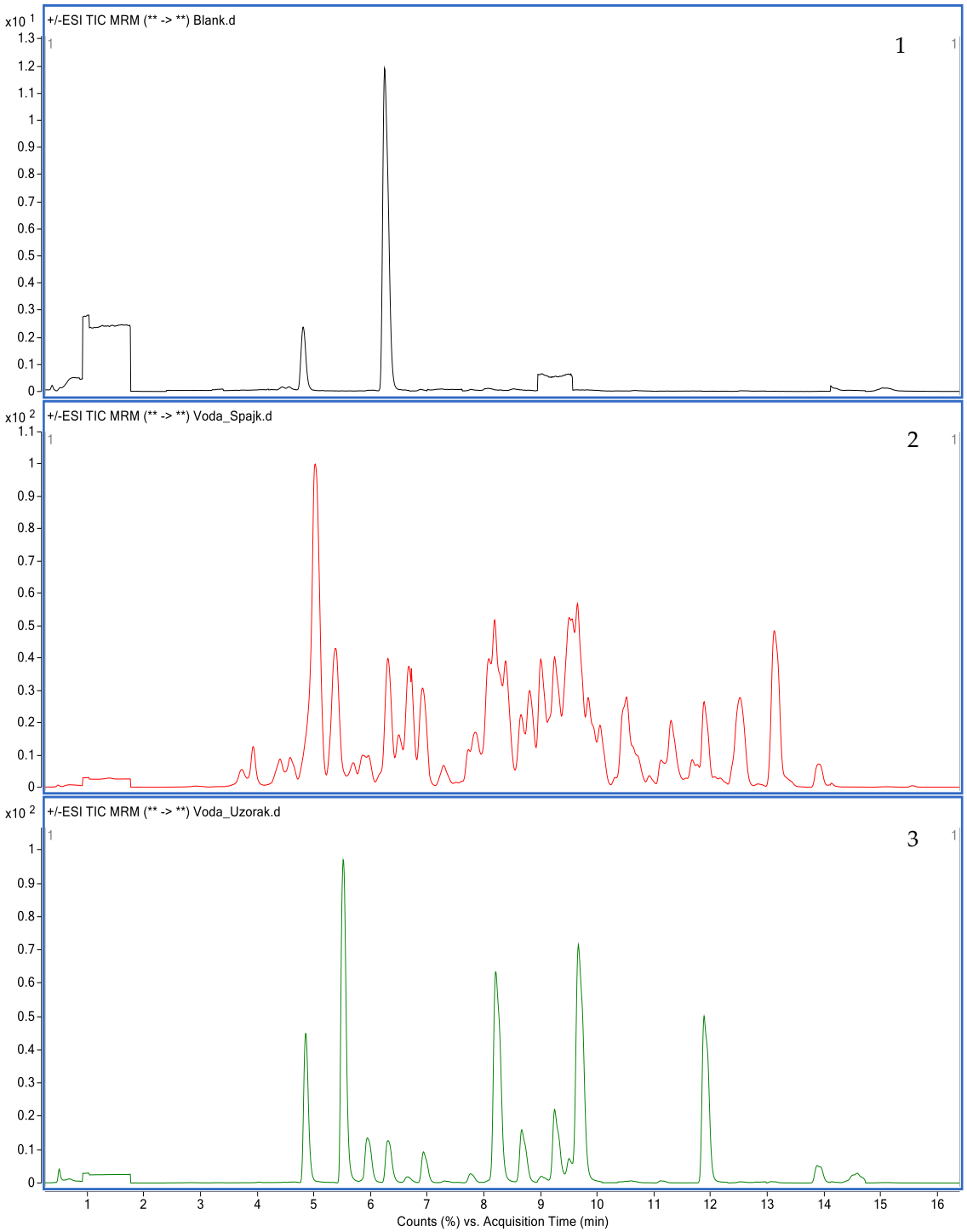

Figure 1. Total Ion Chromatograms (TIC) of the blank (1), spiked water sample (2) and lake water sample (3).

Taking into account the previously stated MAC in water (MAC of 0.1 μg/L as the maximum concentration for each pesticide detected in a water sample) and based on the tabulated results (Table 1), it can be concluded that the nicosulfuron is detected in the abnormally high concentration of 97.8 μg/L. In addition to this herbicide, twelve more pesticides (acetamiprid, metolachlor, trifloxystrobin, terbuthylazin, tribenuron methyl, tebuconazol, rimsulfuron, metolachlor, pyridaben, fenpropidin, thifensulfuron-methyl and fluopiram) were detected in the concentrations above the MAC, while one pesticide (imidacloprid) was at the very limit and three pesticides were below MAC (fluopicolide, pyraklostrobin and azoxystrobin).

Concerning the pesticide residues in sediment, the detected pesticides were the same as the ones detected in the water. Namely, seven pesticides were detected (nicosulfuron, acetamiprid, trifloxystrobin, tebuconazol, metolachlor, fluopiram and fluopicolide) in the concentrations from minimum of 16 to maximum of 224 μg/kg.

Table 1. Detected pesticides in water and sediment

Pesticides	**Water (μg/L)**	**Sediment (μg/kg)**
Nicosulfuron	97.80	224
Acetamiprid	2.24	16
Metolachlor	1.40	*
Trifloxystrobin	0.75	32
Terbuthylazin	0.53	*
Tribenuron methyl	0.47	*
Tebuconazol	0.39	38
Rimsulfuron	0.32	*
Metolachlor	0.32	84
Pyridaben	0.12	*
Fenpropidin	0.11	*
Thifensulfuron-methyl	0.11	*
Fluopiram	0.11	60
Imidacloprid	0.10	*
Fluopicolide	0.04	58
Pyraklostrobin	0.03	*
Azoxystrobin	0.02	*

In the Republic of Serbia there is a Regulation on the limit values of the pollutants in surface, groundwater and the sediment, as well as the deadlines for achieving them [23], in which MACs for the organochlorine pesticides in sediment were placed. As there are no official established standards, we can only discuss the detected concentrations of the pesticides in this matrix. Musa et al. [24], stated that, according to the Indonesian standards, the MAC of pesticide residues in sediment is 0.2 mg/kg. If we refer to this concentration, then nicosulfuron would still be present in an illegal amount in the sediment.

The LC-MS/MS chromatographic analysis of the spiked sediment sample and sediment from the lake sample gives the TIC chromatograms presented on the Figure 2, as they are listed.

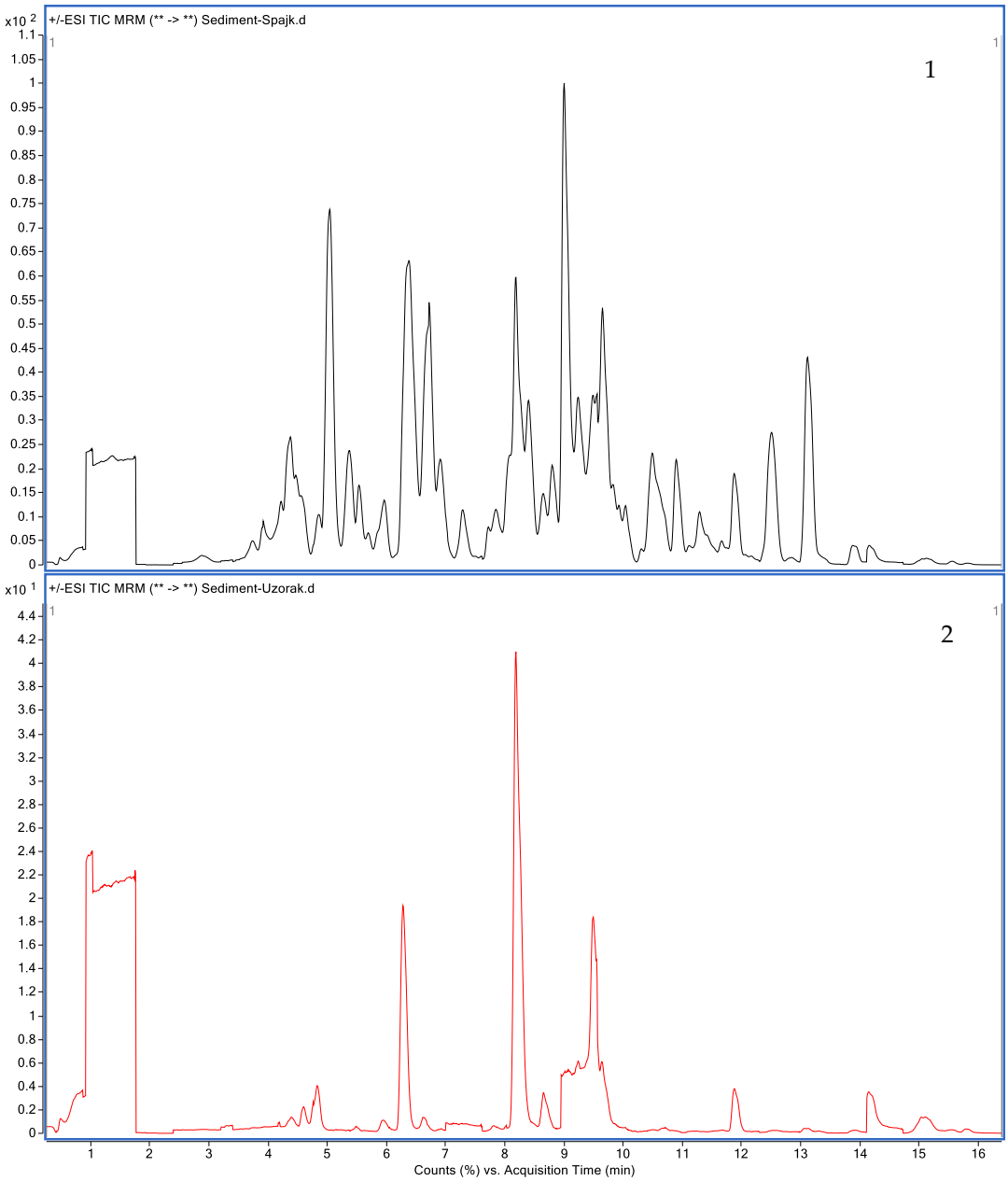

Figure 2. TIC chromatograms of the spiked sediment sample (1) and lake sediment sample (2).

Hence, it is essential to establish monitoring systems adapted to the needs of the water body at hand, specially having in mind that the lake water quality monitoring is equally important [25]. The lake water in the agricultural area is used for the irrigation of different kinds of crops (such as food crops, feed crops, fiber crops, oil crops, ornamental crops and industrial crops). The use of the contaminated water leads to the arrival of various hazard substances on agricultural products, which can harm the health of people and animals.

4. Conclusion

The study assessed the occurrence of 150 pesticide residues in sediment and water samples from irrigation lake. From all the investigated pesticides in the LC-MS/MS analysis 17 of them were detected in water sample (nicosulfuron, acetamiprid, metolachlor, trifloxystrobin, terbuthylazin, tribenuron methyl, tebuconazol, rimsulfuron, metolachlor, pyridaben, fenpropidin, thifensulfuron-methyl, fluopiram, imidacloprid, fluopicolide, pyraklostrobin and azoxystrobin), in the concentration rage from 0.02 to 97.8 μg/L; while the nicosulfuron, acetamiprid, trifloxystrobin,

tebuconazol, fluopiram and fluopicolide were detected in sediment (16-224 μg/kg). The results indicate the need for constant monitoring of pesticide residues in irrigation systems.

Conflicts of interest: The authors declare no conflict of interest.

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