Seasonal distribution of multiclass pesticide residues in the surface waters of northwest Croatia

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As part of our OPENTOX project, we evaluated the incidence and mass concentrations of multiclass pesticide residues in 23 river/stream water samples collected in urban and agricultural areas of northwest Croatia at various points of the pesticide application season in 2015. The study included 16 compounds of five herbicide classes and seven compounds of three insecticide classes. Pesticide residues were accumulated from water by solid-phase extraction and analysed using high performance liquid chromatography with UV-diode array detection and/or gas chromatography-mass spectrometry. Herbicide residues were more common than the insecticide ones, and, as expected, they peaked in the middle of the application season. Metolachlor showed the highest concentrations and was found in 91% of all samples, followed by terbuthylazine, found in 70% of the samples. The highest total mass concentration of detected pesticides was measured in the water samples of the Krapina (3992 ng/L) and Sutla (3455 ng/L) collected in rural areas with intensive agriculture. Our findings strongly speak in favour of continued monitoring of surface waters and possibly extending the list of priority water pollutants.

KEY WORDS: degradation products; herbicides; insecticides; pesticide residues; river water; seasonal variations

According to European Directive 2013/39/EU (1), nearly a half of the 45 compounds classified as priority water pollutants are legacy or currently used pesticides. In the environment, especially in watercourses flowing through agricultural areas, these pesticides are present in complex mixtures (2, 3), whose toxic effects are still insufficiently explored (4, 5). Some, such as atrazine, acetochlor, trifluraline, and chlorfenvinphos, have gradually been phased out and eventually banned in many European countries, but their residues and degradation products in water resources have remained a serious issue in different parts of the world (6–12). New pesticide classes that have replaced them have also been contributing to water pollution (7, 8).

The aim of this study was to evaluate and compare the burden of selected legacy and current-use pesticides on river/stream waters in urban and rural areas of northwest Croatia as part of the OPENTOX project (2014–2018) investigating pesticide pollution and impact on the environment and human health in a densely populated area of the most developed northwest part of Croatia. Furthermore, we wanted to compare our findings with earlier reports from this area to get a better insight into any trend that may have taken place over the years (9, 13).

MATERIALS AND METHODS

River/stream water samples were collected in 2015 with a telescopic pole for grab sampling from the bank at a depth of about 0.5 m as described earlier (9). Figure 1 shows the sampling locations: two at the Sava River a few kilometres upstream and downstream of the Zagreb city centre, two at the mouths of its tributaries Krapina (in Jablanovec) and Sutla (in Harmica), one at the Drava River in the city of Varaždin, two at its tributaries Bednja (in Stažnjevec) and Plitvica (in Greda), and one at the Bednja tributary stream Bistrica (in Ivanec). Of the two major rivers, the Sava springs in Slovenia and flows through rural and urban areas for about 200 km before it reaches the Croatian capital Zagreb, and the Drava springs in Italy to flow through rural and urban regions in Italy, Austria, and Slovenia for about 420 km before it reaches Varaždin. The minor rivers Krapina, Sutla, Bednja, Plitvica, and the Bistrica stream flow through semirural/semiurban areas of northwest Croatia dominated by corn fields, orchards, and vineyards.

Sampling was organised around seasonal pesticide application to coincide with its beginning (March), midseason (June), and end (August). The only exception was the Sava 2 location, where we did not collect the August sample.

The samples were stored in 2.5-L tinted glass bottles at 4 °C until analysis. Water pH ranged from 6.7 to 7.3. Samples were analysed for 23 pesticides (16 herbicides and
Methods

Table 2 details five methods used in this study to meet diverse analytical requirements for each compound. For each method we used appropriate single-use solid-phase extraction (SPE) cartridges: 200 mg Oasis HLB (Method 1) and 360 mg Sep-Pak C₁₈ (Methods 2 and 4) were obtained from Waters Associates (Milford, MA, USA) and 200 mg Bakerbond spe™ SDB-1 (Method 3) and 100 mg C₁₈ Polar plus/SDB-1 (Method 5) from JT Baker (Deventer, the Netherlands). The extracts were analysed using high-performance liquid chromatography with UV diode array detection [HPLC-UV(DAD)] and/or by gas chromatography – mass spectrometry using ion trap detection [GC-MS(ITD)].

Water extracts were evaporated to dryness under a gentle stream of nitrogen. For HPLC-UV(DAD) analysis, the dry residue was redissolved in 0.5 mL or 1.0 mL of deionised water or in a mixture of acetonitrile and deionised water (pH 3) in the 1:9 ratio. For GC-MS(ITD) analysis, the dry residue was redissolved in 0.5 mL or 1.0 mL of ethyl acetate. Prior to HPLC-UV(DAD) or GC-MS(ITD) analysis, the extracts were filtered through 0.2 µm pore size syringe filters.

HPLC-UV(DAD) analysis was performed on a Varian liquid chromatograph equipped with a Varian ProStar 230 SDM pump, Varian ProStar 410 autosampler employing a 100-µL sample loop, and a Varian ProStar 330 photodiode-array detector (Varian, Walnut Creek, CA, USA). The chromatographic column was Gemini C₁₈, 250x4.6 mm i.d., of 5-µm particle size with a 4.0x3.0 mm i.d. guard column of 5-µm particle size (Phenomenex, Torrence, CA, USA).
Table 1 Pesticides and pesticide degradation products analysed in this study

| Class | Pesticide                        | Chemical name                                                                 | $S^a$ (mg/L) | log $K_{ow}^a$ | $pK_{a}^b$ |
|-------|----------------------------------|-------------------------------------------------------------------------------|---------------|----------------|------------|
|       | Dinitroaniline herbicide         | Trifluralin 2,6-dinitro-N,N-dipropyl-4-(trifluoromethyl)aniline               | 0.221         | 5.27           | ND         |
|       | s-Triazines and metabolites      | Atrazine 6-chloro-N\(^2\)-ethyl-N\(^4\)-(1-isopropyl)-1,3,5-triazine-2,4-diamine | 35            | 2.7            | 1.7        |
|       |                                  | Deethylatrazine (DEA) 6-chloro-N\(^4\)-isopropyl-1,3,5-triazine-2,4-diamine   | 2700          | 1.51           | 1.3\(^a\)  |
|       |                                  | Deisopropylatrazine (DEA) 6-chloro-N\(^2\)-ethyl-1,3,5-triazine-2,4-diamine    | 980           | 1.15           | 1.2\(^b\)  |
|       |                                  | Terbuthylazine 6-chloro-N\(^2\)-tert-buthyl-N\(^3\)-ethyl-1,3,5-triazine-2,4-diamine | 6.6           | 3.4            | 1.9        |
|       |                                  | Deethylterbuthylazine (DET) 6-chloro-N\(^2\)-tert-buthyl-1,3,5-triazine-2,4-diamine | 327.1         | 2.3            | 1.35\(^b\) |
|       | Phenylurea herbicides            | Diuron 3-(3,4-dichlorophenyl)-1,1-dimethyleura                                 | 3.56          | 2.87           | ND         |
|       |                                  | Linuron 3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea                           | 63.8          | 3.0            | ND         |
|       |                                  | Chlortoluuron 3-(3-chloro-4-methylphenyl)-1,1-dimethyleura                    | 76            | 2.5            | ND         |
|       |                                  | Isoproturon 3-(4-isopropylphenyl)-1,1-dimethyleura                             | 70.2          | 2.5            | ND         |
|       | Chloroacetanilide herbicides     | Acetochlor 2-chloro-N-(ethoxymethyl)-N-(2-ethyl-6-methylphenyl) acetamide      | 282           | 4.14           | ND         |
|       |                                  | Alachlor 2-chloro-N-(2,6-diethylphenyl)-N-(methoxymethyl) acetamide             | 240           | 3.09           | 0.62       |
|       |                                  | Metolachlor (RS)-2-chloro-N-(2-ethyl-6-methyl-phenyl)-N-(1-methoxypropan-2-y)acetamide | 530           | 3.4            | ND         |
|       | Triketone herbicides and metabolite AMBA | Mesotrione 2-[4-(methylsulfonyl)]-2-nitrobenzoyl)cyclohexane-1,3-dione | 1500         | 0.11           | 3.12       |
|       |                                  | 2-Amino-4-(methylsulfonyl) benzoic acid (AMBA) 2-amino-4-(methylsulfonyl)benzoic acid | NA           | 0.38\(^e\)    | 4.24\(^d\) |
|       |                                  | Tembotrione 2-[2-chloro-4-methylsulfonyl-3-(2,2,2-trifluoroethoxyethyl)benzoyl)cyclohexane-1,3-dione | 71000        | -1.09         | 3.18       |
|       | Organophosphorous insecticides and oxo-metabolite | Chlorypyrifos-methyl O.O-dimethyl O,3,5,6-trichloro-2-pyridyl phosphorothioate | 2.74         | 4.00           | ND         |
|       |                                  | Chlorypyrifos-ethyl O.O-diethyl O,3,5,6-trichloropyridin-2-yl phosphorothioate | 1.05         | 4.7            | ND         |
|       |                                  | Chlorypyrifos-methyl-oxon Dimethyl (3,5,6-trichloropyridin-2-yl) phosphate      | NA           | 1.91\(^c\)     | NA         |
|       |                                  | Malathion Diethyl 2-[(dimethoxyphosphorothioyl)sulfanyl]butanedioate            | 148          | 2.75           | ND         |
|       |                                  | Chlorfenvinphos [(E)Z]-2-chloro-1-(2,4-dichlorophenyl)ethenyl diethyl phosphate | 145          | 3.8            | ND         |
|       | Pyrethroid insecticide           | α-Cypermethrin Raceme comprising (R) and (S) α-cyano-3-phenoxybenzyl-(1R,3R)-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropane-carboxylate | 0.004        | 5.8            | ND         |
|       | Neonicotinoid insecticide        | Imidacloprid N-[6-(6-chloro-3-pyridyl)methyl]-4,5-dihydroimidazol-2-yl nitramide | 610          | 0.57           | ND         |

\(^a\) $K_{ow}$ – $n$-octanol-water partition coefficient; \(^b\) $pK_a$ – dissociation constant; \(^c\) NA – not available; \(^d\) ND – no dissociation; \(^e\) $S$ – solubility in water (14); \(^{1}(8), {1}(15), {1}(16), {1}(17)$
The mobile phase for the analysis of triketone herbicides and their metabolites (Method 1) as well as for the analysis of terbutylazine, DET, malathion, chlorfenvinphos, imidacloprid, and chlorpyrifos-methyl-oxon (Method 2) consisted of acetonitrile and deionised water acidified with H₃PO₄ to pH 2.2. The compounds were eluted using linear gradient elution mode from 10 % to 80 % acetonitrile over 17 min (Method 1) and from 20 % to 75 % acetonitrile over 27 min (Method 2). The mobile phase solvents for the analysis of s-triazines and their metabolites and phenylurea herbicides were acetonitrile and deionised water (Method 3). Herbicides were eluted with a linear gradient from 30 % to 40 % acetonitrile over 22 min and then from 40 % to 90 % acetonitrile over 8 min as described elsewhere (9). The mobile phase flow-rate for all methods was 1 mL/min. The sample volume injected was 100 µL. The UV-spectra of all analytes were recorded at 200 nm to 400 nm (Table 2).

GC-MS(ITD) analysis was performed on a Varian Saturn 2200 GC/MS/MS system consisting of a CP-3800 gas chromatograph with 1079 on-column injector, CP-8410 autoinjector, and ion trap detector. The GC column was an HP-5MS fused silica column, 30 m x 0.25 mm i.d., film thickness 0.25 µm (Agilent Technologies, Santa Clara, CA, USA). Pesticide compounds were separated and detected under GC-MS(ITD) operating conditions described earlier (9). Their mass spectra were recorded in the full scan acquisition mode (mass range 50–550 m/z) and scan rate of three scans per second. Table 2 lists the most intensive fragment ions (m/z) selected for the quantitation of specific analytes (Methods 4 and 5).

Standard solutions for HPLC-UV(DAD) analysis were prepared in deionised water and for GC-MS(ITD) analysis in ethyl acetate. Mass concentrations of single pesticides in final HPLC standards ranged from 19 to 536 ng/mL and in standards for GC analysis from 13 ng/mL to 929 ng/mL.

For recovery experiments, river water samples were spiked with pesticide standards in aqueous or acetone solutions. Mass concentrations in spiked water samples ranged from 19 to 1429 ng/L for HPLC-UV(DAD) and from 3 to 1034 ng/L for GC-MS(ITD). The precision of the methods was determined by calculating the relative standard deviations (RSD) of recoveries obtained by repeated analysis of spiked water samples. In the investigated concentration ranges, pesticide recoveries were almost quantitative for most compounds and ranged from 90 to

Table 2 Methods for determination of pesticides and their degradation products in natural waters by SPE and HPLC-UV(DAD) or GC-MS(ITD) analysis

| Pesticide | Method of analysis | HPLC-UV(DAD) | GC-MS(ITD) |
|-----------|--------------------|--------------|------------|
|           | Method 1 – λ (nm)  | Method 2 – λ (nm) | Method 3 – λ (nm) | Method 4 – m/z | Method 5 – m/z |
| Mesotrione | 220                | Terbutylazine – 222 | Atrazine – 222 | Trifluralin – 264 | Terbutylazine – 214 |
| AMBA – 220 | DET – 214          | DEA – 214      | Atrazine – 200 | Chlorpyrifos-methyl – 286 |
| Tembotrione – 205 | Malathion – 205 | DIA – 214 | Terbutylazine – 214 | Chlorpyrifos-ethyl – 314 |
| Chlorfenvinphos – 205 | Terbutylazine – 222 | Acetochlor – 223 | Malathion – 173 |
| Chlorpyrifos-methyl-oxon – 205 | DET – 214 | Alachlor – 188 | Chlorfenvinphos – 267 |
| Imidacloprid – 270 | Diuron – 210, 245 | Metolachlor – 162 | α-Cypermethrin – 163 |
| Linuron – 210, 245 | Chlorotoluuron – 210, 245 | Isoproturon – 202, 245 |

| SPE | OASIS HLB | C₁₈ | SDB-1 | C₁₈ | C18 Polar plus/ SDB-1 |
|-----|-----------|-----|-------|-----|---------------------|
| Activation | MeOH+H₂O | ACN+H₂O | MeOH+H₂O | MeOH+H₂O | MeOH+H₂O |
| Solvent volume (mL) | 2+2 | 5+5 | 2+5 | 2+5 | 2+5 |
| Sample volume (mL) | 500 | 500 | 1000 | 500 | 500 |
| Eluent | MeOH | ACN+Et.ac | Ac | Et.ac | Et.ac |
| Eluent volume (mL) | 10 | 10+5 | 2 | 2 | 10 |

Ac-acetone; ACN – acetonitrile; Et.ac – ethyl acetate; MeOH – methanol; m/z – significant MS fragment ion selected for quantitation; *as described in (9)
107%. The only exceptions were the slightly lower but still satisfactory recoveries of chlorfenvinphos (78%) and imidacloprid (87%) analysed by Method 2 and of atrazine (82%), terbuthylazine (87%), linuron (84%), and isoproturon (88%) analysed by Method 3. Low relative standard deviations of recoveries (<1–13%) confirmed good precision of all methods.

Pesticides in river/stream water samples were quantified by external calibration with multipoint calibration lines generated daily for each compound by linear regression of its standard concentrations and the corresponding peak areas. Solvent and reagent blanks were prepared with each set of five water samples and analysed in the same manner as water extracts.

All analyses were run in duplicate. The target analytes were identified by comparing their chromatographic retention times and the corresponding UV or MS spectra with those of the known standards.

The limit of detection (LOD), defined as the average blank value plus three standard deviations (average + 3σ), was also used as the limit of quantitation (LOQ). The LOD of the GC-MS(ITD) method ranged from 5 to 30 ng/L, while the LOD of HPLC ranged from 10 to 15 ng/L.

RESULTS AND DISCUSSION

Of the 23 analysed pesticide pollutants, eight were not detected in any water samples, namely trifluralin, alachlor, malathion, chlortoluron, linuron, chlorpyrifos-ethyl, chlorfenvinphos, and α-cypermethrin. Negative findings for the first three pesticides are in line with their ban in Croatia since 2009, but the other five were still legal to use back in 2015 (18).

Among the 15 pesticide compounds detected in our river/stream water samples, 12 were herbicides and their degradation products and only three were insecticides. The number of positive water samples in all three sampling rounds and mass concentrations of detected pesticide residues are shown in Table 3. Six pesticide compounds were detected in more than half of the analysed samples: metolachlor in 91%, DEA and terbuthylazine in 70%, atrazine in 65%, DIA in 57%, and chlorpyrifos-methyl-oxon in 52%.

Atrazine and acetochlor were also found, although their use has been banned in Croatia since 2009 and 2014, respectively. While the possibility of illegal leftover use cannot be completely ruled out, as may be the case with acetochlor found in only one sample in June (see Table 3), a more likely explanation for the relatively high incidence of atrazine and its degradation products DEA and DIA is their persistence in treated agricultural soils resulting in prolonged water pollution in agricultural catchments (8, 19, 20).

Most pesticides were identified in the height of the application season (14 in June as opposed to nine in March and eight in August) (Table 3).

Of the priority water pollutants, we found only atrazine, isoproturon, and diuron, and their peak mass concentrations were one to two orders of magnitude lower than the maximum allowable concentrations defined by the Directive

### Table 3 Mass concentrations of pesticide pollutants in river/stream water samples collected in the northwest part of Croatia across application season

| Pesticide compound          | March 2015 (N=8) | June 2015 (N=8) | August 2015 (N=7) |
|-----------------------------|------------------|-----------------|-------------------|
|                             | γ (ng/L)         |                  |                   |
|                             | n     | Rangea | Medianb | n     | Rangea | Medianb | n     | Rangea | Medianb |
| Mesotrione                  | 0     | 3      | 36–107  | 0     | 0      | 0       |
| Tembotrione                 | 0     | 7      | 51–216  | 0     | 0      | 0       |
| AMBA                        | 0     | 6      | 54–444  | 74    | 1      | 61      | <LOD |
| Terbuthylazine              | 3     | 9–13   | <LOD    | 8     | 20–419 | 42      | 5     | 10–26  | 13      | <LOD |
| DET                         | 1     | 9      | <LOD    | 4     | 38–200 | 19      | 2     | 14–45  | <LOD    |
| Atrazine                    | 5     | 10–16  | 11      | 5     | 12–34  | 13      | 5     | 9–24   | 14      |
| DIA                         | 5     | 5–32   | 6       | 6     | 17–123 | 28      | 2     | 19–24  | <LOD    |
| DEA                         | 4     | 8–11   | 4       | 7     | 7–24   | 11      | 5     | 6–32   | 10      |
| Isoproturon                 | 1     | 146    | <LOD    | 0     | 0      | 0       |
| Diuron                      | 0     | 2      | 22–30   | <LOD  | 0      | 0       |
| Acetochlor                  | 0     | 1      | 28      | <LOD  | 0      | 0       |
| Metolachlor                 | 7     | 9–11   | 9       | 8     | 11–3015| 147     | 6     | 10–63  | 11      |
| Chlorpyrifos-methyl         | 0     | 1      | 26      | <LOD  | 0      | 0       |
| Chlorpyrifos-methyl-oxon    | 1     | 21     | <LOD    | 8     | 23–145 | 64      | 3     | 34–198 | <LOD    |
| Imidacloprid                | 1     | 73     | <LOD    | 8     | 12–34  | 26      | 0     | 0      |

N - number of samples; n - number of positive samples; LOD – limit of detection; Range applies to positive samples, Median applies to all samples.
as Environmental Quality Standards for surface waters (1). As there are no limits for pesticide compounds not considered priority pollutants, their mass concentrations in surface waters are often considered in terms of maximum permissible mass concentrations in water intended for human consumption of 100 ng/L for single pesticides and 500 ng/L for total pesticides (21). In this regard, Figure 2 shows that the 100 ng/L limit was mostly exceeded in the middle of the application season.

Table 4 also clearly illustrates seasonal variations in pesticide load by sampling locations. The sum of mass concentrations of detected pesticides was the lowest at the beginning (March) and the highest in the peak of the pesticide application season (June). As expected, the lowest sums of pesticide mass concentrations were measured in the Drava River sampled in the urban area and the highest in the Krapina and Sutla rivers sampled in rural areas with intensive agricultural production. In the peak of the pesticide season, it exceeded the 500 ng/L limit for drinking water (21) in the samples taken from the Sutla, Krapina, Sava, and Bednja and the Bistrica stream. Metolachlor and terbuthylazine accounted for the largest shares in total mass concentrations in the Krapina and Sutla, metolachlor with 76 % and 74 % and terbuthylazine with 10 % and 12 %, respectively (see Figure 2, June). In the Sava, the highest shares were those of metolachlor and AMBA, ranging

Figure 2 Mass concentrations of individual pesticides determined in river/stream water samples collected at the beginning (March), peak (June), and end (August) of the 2015 pesticide application season. AMBA – 2-amino-4-(methylsulfonyl)benzoic acid; DEA – deethylatrazine; DET – deethylterbuthylazine; DIA – desisopropylatrazine.
between the two sampling locations with 26–30 % and 20–24 %, respectively. The same pollutants were also dominant in the Bednja, where AMBA and metolachlor accounted for 51 % and 17 %, respectively. The high shares of AMBA point to recent application and subsequent degradation of a triketone herbicide mesotrione, which is less stable in soil and water than its degradation product (8, 22). As for the Bistrica stream, the highest shares in the sum of pesticide mass concentrations were those of tembotrione and mesotrione with 37 % and 15 %, respectively. All these findings point to the prevalence of herbicides metolachlor, terbuthylazine, tembotrione, and mesotrione in pesticide application in northwest Croatia.

The prevalence of metolachlor and terbuthylazine and their degradation products has already been noted in our earlier study of the Sava samples taken the year before (9) and earlier studies across Europe (2, 23–25).

As for insecticides analysed herein, all water samples collected in the height of the pesticide application season (June) contained trace concentrations of imidacloprid and chlorpyrifos-methyl-oxon (Table 3 and Figure 2). The finding of the latter points to a recent use of its parent compound chloropyrifos-methyl. Not only is it more persistent than the parent pesticide [over four weeks, according to Lacorte and Barceló (26)] but it is also more toxic to aquatic organisms and the environment (4) and should be regarded as pollutant of concern. As for the low imidacloprid concentrations, they are likely the consequence of restricted use in Croatia since 2013.

**CONCLUSION**

The limitation of our study is that our current data are limited to the measurements taken in 2015, while further data from the OPENTOX project (concluded with 2018) are still pending. Despite this limitation, the study has confirmed the persistence of atrazine in water environment and the domination of herbicide over insecticide use in urban and agricultural areas of northwest Croatia. Our findings further emphasise the need to extend regular monitoring of pesticides in surface waters to herbicide and insecticide compounds that are not considered priority water pollutants at the moment but are frequently used in larger amounts in regions with intensive agriculture. A systematic and regular monitoring of frequently used pesticides in surface waters can inform pesticide users and authorities and help to prevent or at least reduce their adverse effects on aquatic organisms and environment in a timely manner.

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**Conflicts of interest**

None to declare.

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Sezonska raspodjela različitih klasa pesticida u površinskim vodama sjeverozapadne Hrvatske

U sklopu našega projekta OPENTOX odredili smo masene koncentracije ostataka pesticida i njihovu učestalost u 23 uzorka vode rijeka/potoka u gradskim i ruralnim dijelovima sjeverozapadne Hrvatske, prikupljenih 2015. tijekom sezone njihove primjene. Istraživanje je obuhvatilo 16 spojeva iz pet različitih klasa herbicida i sedam spojeva iz triju klasa insekticida. Ostaci pesticida akumulirani su iz vode postupkom ekstrakcije na čvrstoj fazi i analizirani tekućinskom kromatografijom visoke djelotvornosti uz UV-detektor s nizom dioda ili vezanim sustavom plinske kromatografije i spektrometrije masa. Češće su detektirani ostaci herbicida nego insekticida, a najviše su koncentracije bile sredinom sezone njihove primjene. Metolaklor je određen u najvišoj koncentraciji i u najvećem broju uzoraka (91 %), a slijedio ga je terbutilazin, koji je nađen u 70 % uzoraka. Najviša ukupna razina određivanih pesticida bila je u uzorcima rijeka Krapine (3992 ng/L) i Sutle (3455 ng/L), koji su bili prikupljeni u ruralnom području s intenzivnom poljoprivredom. Rezultati našega istraživanja govore u prilog potrebi ne samo za kontinuiranim monitoringom pesticida u površinskim vodama nego i za proširenjem liste prioritetnih zagađivača.

KLJUČNE RIJEČI: herbicidi; insekticidi; ostaci pesticida; razgradni produkcni; riječna voda; sezonske varijacije