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Spatiotemporal analysis of multi-pesticide residues in the largest Central European shallow lake, Lake Balaton, and its sub-catchment area

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Abstract

Background: The present study aimed to gain a comprehensive knowledge of the presence and environmental risks of pesticide and repellent residues in Lake Balaton and its sub-catchment area (Hungary). A unique analysis of 439 active substances and 17 metabolites was carried out on surface waters and one effluent wastewater as the only direct discharge into Lake Balaton from June 2017 until August 2020. Altogether 203 water- and 85 sediment samples were collected and analysed during the 3-year monitoring period. To determine the environmental risks of the detected pesticides to aquatic ecosystems, environmental risk assessment (ERA) was carried out using two approaches (worst- and general-case scenarios).

Results: Fifty-two pesticides and one insect repellent were detected, of which 26 belonged to herbicides (24 active substances and two metabolites), 15 to fungicides (15 active substances), and 11 to insecticides (eight active substances and three metabolites), of which only nine of the total analysed compounds are listed to be monitored in surface waters with threshold limit values (TLVs). The most frequently detected compounds were terbuthylazine, diethyltoluamide (DEET), desethyl-atrazine, and metolachlor. Glyphosate, aminomethylphosphonic acid (AMPA), and DEET were found with the highest concentrations of 3.0, 2.0, and 1.57 µg/L, respectively. The pesticide exposures were higher during the summer periods indicating a stable seasonal pattern. According to the performed ERA, the calculated Risk Quotients (RQs) indicated 18 compounds with a high level of risk including nine that had been banned for at least a decade.

Discussion: This study expands knowledge on the spatiotemporal occurrence of pesticides in inland surface waters and highlights the need to consider widening the number of analysed pesticides beyond the European Water Framework Directive (EWFD). According to our results, additional authority and legislation procedures should come into force for pesticides not indexed in the priority European Union Watch List.

Keywords: Lake Balaton, Pesticides, Terbuthylazine, Glyphosate, DEET, Atrazine, Seasonal effects, Environmental risk assessment

Background

Pesticides are mainly used for agricultural, horticultural, and home gardening/household purposes. The major sources of pesticide pollution are civil or agricultural/industrial activities and environmental phenomena such as water runoff or atmospheric deposition [1]. As a result of the surface drainage, runoff, and spray drift,

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pesticides pollute the soil and freshwater ecosystems and are expected to leach into the deeper layers of subsurface and ground waters. The quantity of the transported pesticides to surface waters depends on many factors such as seasonal microclimate changes (temperature, extreme rainfall events, atmospheric humidity, winds), geographical constraints, soil composition/properties, or vegetated buffer strips [2]. Surface waters can be exposed to pesticides along with their metabolites and breakdown products either directly through effluents of municipal wastewater treatment plants or (bio) degradation processes [3–5]. These xenobiotics are not only detectable in industrially and agriculturally developed areas but in distant locations as well [6, 7]. Many of them can disperse and circulate afterwards, infiltrating environmental compartments and persist for several years (or maybe decades) due to their physical–chemical properties and resistance to degradation processes [8].

Many studies have focused on the influence of pesticides on the surface-, subsurface-, and groundwater systems surrounding agricultural catchment areas in EU-wide surveys, and according to the results, the number of detected pesticide residues and their concentrations have increased over the years [8–16]. In most cases, these residues were found in surface waters at relatively high concentrations, which were three orders of magnitude higher than the maximum values for individual pesticides (0.1 µg/L) and total pesticides (0.5 µg/L) established by the Drinking Water European Directive 98/83/EC [10, 16, 17]. From 2017 to 2019, almost 800,000 tons of pesticides were sold in the European Union (over 18,000 tons in Hungary alone) [18, 19]. Incidentally, pesticides currently applied in the highest quantities are the same that occur most often in surface waters [4].

Regarding the European Water Framework Directive (EWFD), every EU member state must achieve good ecological and chemical status for all water bodies to protect the surface- and ground waters based on the Directive 2000/60/EC [20]. The Environmental Quality Standards (EQS) for priority substances and certain other pollutants listed for chemical monitoring are centrally and compulsorily defined by the EU in the Annexes I. and II. of the Directive 2013/39/EU [21]. In Hungary, these directives were transposed by Decree No. 10 of 2010. (VIII. 18.) of the Ministry of Rural Development providing limit values for water pollutants in surface waters and rules of application. Hazardous or priority substances pose a significant risk to the biota and ultimately to humans through the aquatic environment. To achieve a good chemical status the concentrations of the priority compounds must not exceed the EQS limit values [annual average (AA)-EQS and maximum allowable concentration (MAC)-EQS, respectively]. However, from the 56 specific pollutants on the list of the EQS values, only 25 pesticide compounds are indexed that member states could apply to the surface waters. Due to the limitations of the existing EQS lists, this approach can be extremely outdated and under-regulated during a complex environmental risk assessment [22]. In Hungary, based on Decree No. 6 of 2009 (IV. 14.) KvVM-EüM-FVM, guided by the Directive 2006/118/EC [23], the limit values for soil and groundwater pollutants are 0.1 mg/kg dry weight and 0.1 µg/L for each active substance of pesticides, and 0.5 mg/kg dry weight and 0.5 µg/L for total pesticides (including all metabolites, degradation, and reaction products), respectively. Above these limit values, a remediation procedure shall be initiated. For sediments, the soil limit values should be applied.

During previous research in the early 2000s in Hungary, two regions of the northern part of Lake Balaton (Balatonfűzfő and Tihany) and the lake water body were sampled and monitored to detect pesticides in surface-, ground-, and raw drinking water during May, June, and August [24, 25]. The studies focused on the effect of the main former pesticide industrial site called Nitrokémia Chemicals Industrial Plc. located on the northeast coast of the sub-catchment area in Balatonfűzfő. Atrazine and acetochlor were found at extremely high concentrations in surface (8.24–13.95 µg/L) and groundwater (7.54–10.07 µg/L) samples. Prometryn and terbutryn were also detected at lower concentrations (1.025 µg/L and 0.605 µg/L). Acetochlor has been found in surface waters in the region of Tihany, in Lake Balaton, and the main outflow stream Sió-Canal at higher concentrations (> 0.3 µg/L) [24, 25]. However, these preceding studies were limited in scope (sampling on local scales and sediments are not included), have not examined the pesticide pollution discharged by WWTPs, and targeted only ten (acetochlor, atrazine, carbofuran, diazinon, fenoxycarb, metribuzin, phorate, prometryn, terbutryn, trifluralin) for potentially water-polluting target compounds.

The purpose of our work was to gain a comprehensive knowledge of the spatiotemporal pesticide contamination (seasonal changes) in the waters and sediments of the main inflows, the sole outflow, and the lake body of Balaton, the largest freshwater lake in Europe, a water base particularly sensitive and vulnerable to contamination. The system of unique analytical screening methods (multi-pesticide residue analyses) provided by this work enabled the detection of more than 450 pesticide residues simultaneously. The individual screening- and monitoring method was applied for the first time to a variety of pesticide families to cover the majority of substances used in high quantities and the not approved ones in Hungary and the EU. Another goal of the present study is to estimate the environmental risks of the detected

pesticides in Lake Balaton and its sub-catchment area considering both the general and worst-case scenarios.

Material and methods

Area of study

Lake Balaton, the largest shallow lake in Central Europe, is located in the western part of Hungary, in the middle of Transdanubia. It has a surface of around 594.3 km^2, a length of 78 km, and an average width of 7.7 km. It has water storage of about 2 billion m^3 and an average depth of 3.2 m. The length of the coastline is around 235 km. The whole catchment area is 5757 km^2. The lake itself is divided into four basins (1: Keszthely, 2: Szigliget, 3: Szemes, and 4: Siófok basins) (Fig. 1). Its main feeding watercourse is the inflow of the Zala River on the western side, with a hold of 45% of the total catchment area. The sub-catchment area is formed by two subunits, one of them is the watershed of Lake Balaton and the other is the Zala River watershed. Excess water is drained through the Sió-Canal into the Danube River at the southeast corner of the lake. There are a total of 101 surface water bodies (90 watercourses and 11 lakes with seven surface- and 144 subsurface water bases) in the sub-catchment area. On the watershed of Lake Balaton, 42 surface watercourses can be found. The only direct wastewater discharge into Lake Balaton is the effluent (2300 m^3/d) of the Révfülöp wastewater treatment plant (Révfülöp WWTP) with an annual flow rate of 381,000 m^3 [26]. Lake Balaton basin is a mosaic of agricultural lands (43%), forests (26%), grasslands (11%), and vineyards (3%). 5% of the total agricultural lands of Hungary (approximately 3000 km^2) are located here. Arable fields (principally grain cereals) and vineyards are dominating the northern sub-catchment region, enclosed by mountains hills, and forests (Additional file 1: Fig. S1). The Balaton-felvidéki National Park, a protected ecological system spreading over 56 997 hectares and established in 1997 is located at the Balaton Uplands (northern shorelands of the Lake Balaton) (Additional file 1: Fig. S1.). The southern coast is a sandy beach. More than 200 natural and artificial ponds are located in the southern sub-catchment area surrounded by livestock farms and agricultural lands toward the south [27–29].

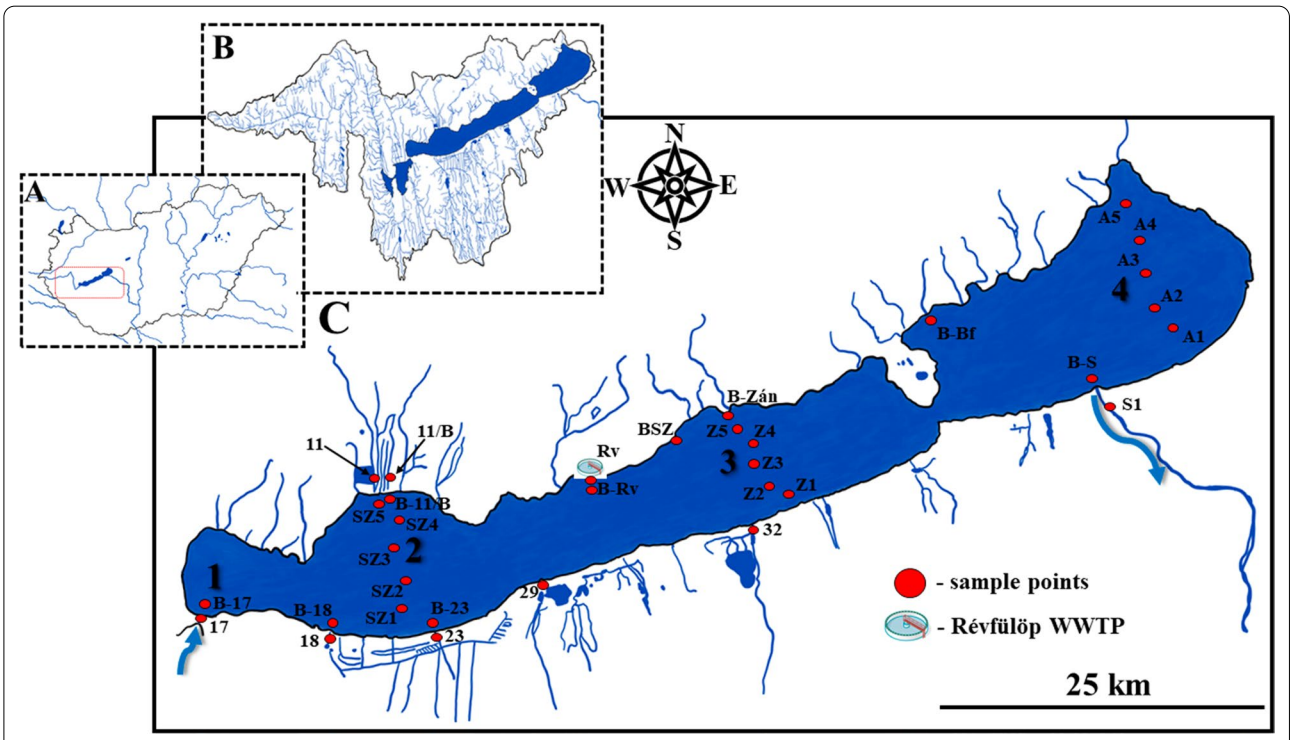

Fig. 1 The geographical location of the studied area in Hungary. Lake Balaton sub-catchment area's position and detailed representation are indicated in **A** and **B**. **C** is presenting Lake Balaton and the watersheds of the lake in the northern and southern catchment areas. Red dots and the WWTP pictogram show the sampling points. Blue arrows show the flow direction of the main feeding watercourse (River Zala) at the south-end corner and the only outflowing watercourse (Sió-Canal) on the southeast side. 1 Keszthely basin, 2 Szigliget basin, 3 Szemes basin, 4 Siófok basin. Inflow and outflow watercourses: point "Rv" wastewater discharge of Révfülöp WWTP; point "11/B" Tapolca stream; point "11" Lesence stream; point "17" Zala River mouth; point "18" Nyugati-övcsatorna; point "23" Balatonfenyvesi nyomóárok; point "29" Pogányvölgyi-víz; point "32" Irmapuszta effluent; point "S1" Sió-Canal

Sampling points and sampling methods

Our sampling strategy mainly focused on the watercourses that flow directly into and out of Lake Balaton, that are in direct association with agricultural areas and/or fishponds, and have high water yields. The distribution of sampling points in Lake Balaton was based on the international standard ISO 5667-4:2016 using three parallel transects crossing the basins from inlet to outlet designed for long-term multifunctional monitoring on the chosen shallow lake [30]. Thirty-three sampling points (Fig. 1, Additional file 1: Table S1) were chosen for regular sampling after a preliminary, comprehensive analytical survey performed in June 2017. Based on the preliminary analytical results, watersheds that represent the highest environmental risk were chosen for regular monitoring. A total of 203 surface water samples and 85 sediment samples were collected and analysed for three consecutive years from 2017 June to 2020 August. Samples were collected in June 2017, every month from April to October in 2018, from March to October (except September) in 2019, and in August 2020, considering the intensive agricultural pesticide application and spraying season. Sampling of the discharge of Révfülöp WWTP began in 2018 September and ended in August 2020.

Water samples have been collected approximately 20–30 cm below the water surface and poured into brown-coloured, borosilicate, 1 L glass bottles leaving a small headspace. For glyphosate and aminomethylphosphonic acid (AMPA), samples were collected into 50 mL polypropylene tubes. After homogenization, sediment samples were loaded into translucent, 5 L plastic buckets. The samples were stored in cooler bags and cooled with freezer packs in the field, then at 4 °C in the refrigerator until shipped to the chemical analytical laboratory (Wessling Hungary Ltd., Hungary) within 24 h.

Applied chemical-analytical methods

Using the unique multi-pesticide residues screening method of accredited Wessling Hungary Ltd., we were able to examine the presence of 435 pesticide active substances or parent compounds and 16 metabolites (451 individual compounds) in the samples. Multi-pesticide residue analysis from the surface waters and their sediments were performed by gas chromatography-mass spectrometry [WBSE-47:2010 method—GC–MS (Agilent/HP 6890 GC with 5973 MSD with a 7683 Injector) with SIM mode Quantitative Analysis for lower detection limits can be obtained] coupling with high-performance liquid chromatography-mass spectrometry [WBSE-93:2013 method—HPLC–MS/MS Agilent 1290 Infinity HPLC and Agilent 6490 QQQ)].

For the water samples, the limit of detection (LOD) for 2,4′-DDD; 4,4′-DDD and 2,4′-DDT; 4,4′-DDE; 4,4′-DDT was 0.0002 µg/L/component, while for the other chlorinated insecticides, such as aldrin, chlordane, endrin, dieldrin, it was 0.001 µg/L/component. LOD was 0.01 µg/L for all other pesticides.

For the sediments, the LODs were 0.002 mg/kg dry weight (d.w.)/component for α-HCH, β-HCH, δ-HCH, ϒ-HCH and 0.01 mg/kg d.w./component for other pesticides, except glyphosate and AMPA, for which the concentrations were measured from aqueous extracts and have been given in µg/L.

Aside from the 451 individual compounds detected by the multi-pesticide screening method, the presence of cybutryne, diethyltoluamide (DEET), and mesotrione were measured by LC–MS (WBSE-93:2013, LOD = 0.01 µg/L), while glyphosate and AMPA were detected by HPLC–MS/MS (ISO 16308:2014, LOD = 0.05 µg/L). Overall, 456 chemicals were detected by chemical analytical methods.

Environmental Risk Assessment (ERA) by ecotoxicological Risk Quotient (RQ)

The environmental risk assessment (ERA) for pesticides could be classified and categorized as locally hazardous to the ecosystem by determining and ranking the Risk Quotient (RQ). The RQ value can be calculated by the quotient of the Measured Environmental Concentration (MEC), which is the measured, realistic environmental concentration of a chemical in the investigated water body, and the Predicted No Effect Concentration (PNEC) value, which indicates the estimated concentration of the same chemical that has no adverse effect to the aquatic ecosystem [MEC/PNEC or, if the actual measured values are not known, PEC (Predicted Environmental Concentration)/PNEC]. All measured concentration data used for the calculation of RQ mean and RQ max were above the LOD. Principally, individual RQ values are divided into three risk classes: $0.01 \leq RQ \leq 0.1$, indicating low risk; $0.1 \leq RQ \leq 1$, where the level of the risk is medium; and $1 \leq RQ$, meaning high risk [31, 32]. RQs have been calculated for algae, *Daphnia magna* (invertebrates), crustaceans, and fish to estimate the environmental risk of the presence of pesticides in surface waters [33]. In our study, ERA's method was carried out using two forms of RQ equation, following the worst-case scenario and the general state case as described by EC 2003 [34] and Thomaidi et al. [35], respectively with minor modifications on the second equation.

1. Worst-case scenario, where the *maximumMEC* is the highest measured concentration in the whole investigation period for each substance.

$$RQ\ max = \frac{maximum\ MEC}{PNEC}$$

2. General state case, where the *meanMEC(regional)* is the mathematical average of the measured concentration, that describes the specific sub-region of the area (e.g., northern, southern catchment area, Lake Balaton, or WWTP) and provides the baseline risk characteristics for a particular area.

$$RQ\ mean\ (regional) = \frac{mean\ MEC\ (regional)}{PNEC}$$

If available, PNEC values were collected from the literature for the pesticides and repellent substances. When more than one PNEC value was available for aquatic organisms representing different trophic levels, the lowest PNEC value was chosen. When PNEC values could not be found in the literature, they were calculated based on the ecotoxicological results of the Pesticide Properties Database of the University of Hertfordshire [36] and the EnviroTox Database [37] by the following quotient using assessment factors (AFs).

$$\mathrm{PNEC} = \frac{EC50,\ LC50\ or\ NOEC}{AF}$$

AF = 1000 was used whenever only EC_{50} or LC_{50} toxicological data were available from three trophic levels; AF = 100 and AF = 50 were applied when NOEC (No Observed Effect Concentration) was available from one or two various trophic levels, respectively. If NOEC was known at least three different trophic levels, AF = 10 was used [34]. Due to the absence of toxicity data for disulfoton sulfoxide metabolite, PNEC was expressed for the parent compound (disulfoton insecticide) [37].

Raw data transformation, descriptive statistics, and graphical presentation

The GPS coordinates of the sampling points were recorded on Google® Maps, converted to geographic coordinates (Additional file 1: Table S2), and visualized in Fig. 1. Additional file 1: Fig. S1 represent the land cover of Lake Balaton, and its sub-catchment area was generated by open access QGIS 3.10 A Coruna as geographical informatics software and based on OTAB (Official Hungarian Maps Database) and CORINE Land Cover 2018 layers. Summarized data of the detected compounds are presented in Fig. 2, while the spatiotemporal distribution and RQ values are shown in Figs. 3, 4, and 5, respectively. Data for the environmental risk assessment are presented in Table 1. The graphical presentation has been performed using GraphPad Prism 7 software (GraphPad Software Inc., San Diego, USA). Significant differences with $0.05 \geq p$ between the seasons were determined using One-way Analysis of Variance (ANOVA) followed by Tukey's multiple comparison test. Because of highly skewed values, after logarithmic transformation, Fig. 5. shows the RQs' mean values in each sampling region, while the numeric data are presented in Additional file 1: Table S4. The raw data entry and computation or descriptive statistics (mean-, minimum and maximum concentration, frequency of occurrence, RQs) have been performed in Microsoft® Office Excel® 2016.

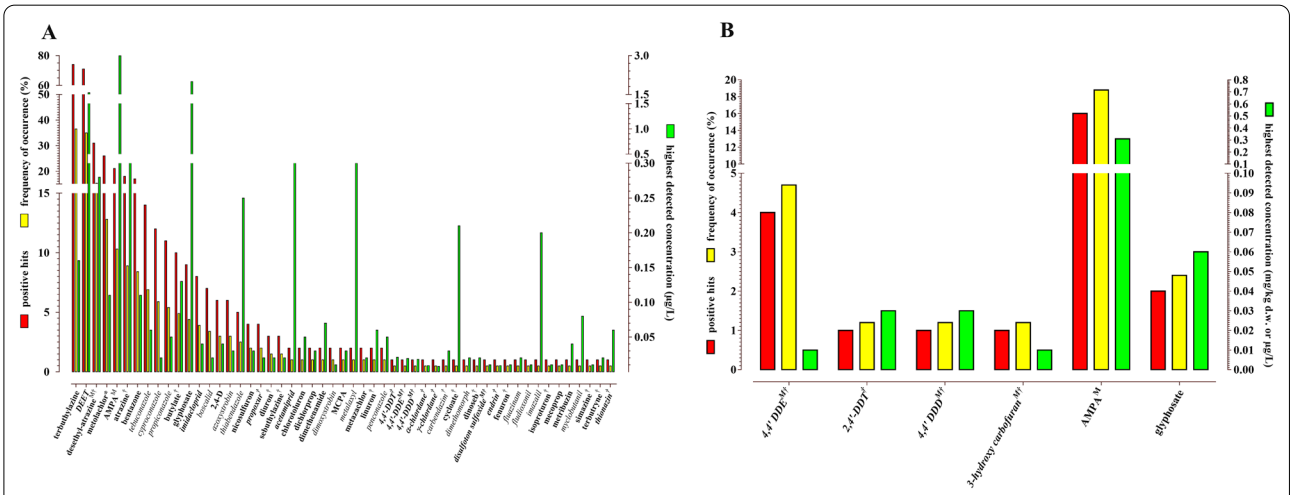

Fig. 2 Summary of the detected compounds in water (**A**) and sediment (**B**) samples. Red columns: the number of positive hits; yellow columns: frequency of occurrence; green columns: the highest detected concentration for each compound detected in Lake Balaton and its whole sub-catchment area. †banned pesticide residues in Hungary during the investigation period. *sum of the enantiomer/isomer composition of metolachlor. Mmetabolite of an active substance. Fungicides are shown in italics; herbicides are shown in bold; insecticide and repellent residues are shown in bold and italics

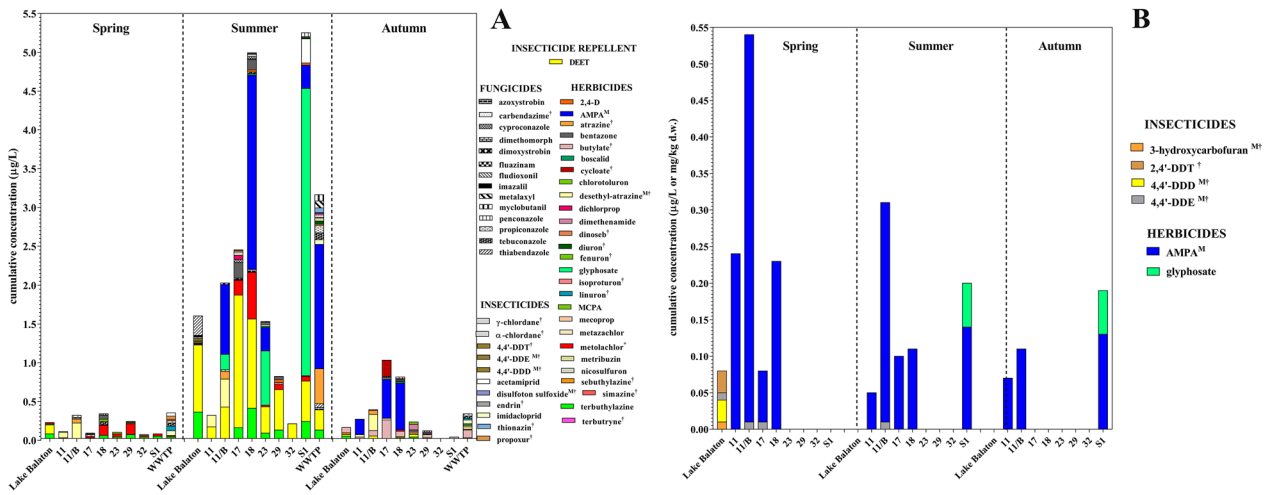

Fig. 3 Spatiotemporal distribution and cumulative concentrations of the detected compounds in waters (**A**) and sediments (**B**). †banned pesticide residues in Hungary during the investigation period. *sum of the enantiomer/isomer composition of metolachlor. Mmetabolite of an active substance. Detailed data are summarized in Additional file 1: Table S2

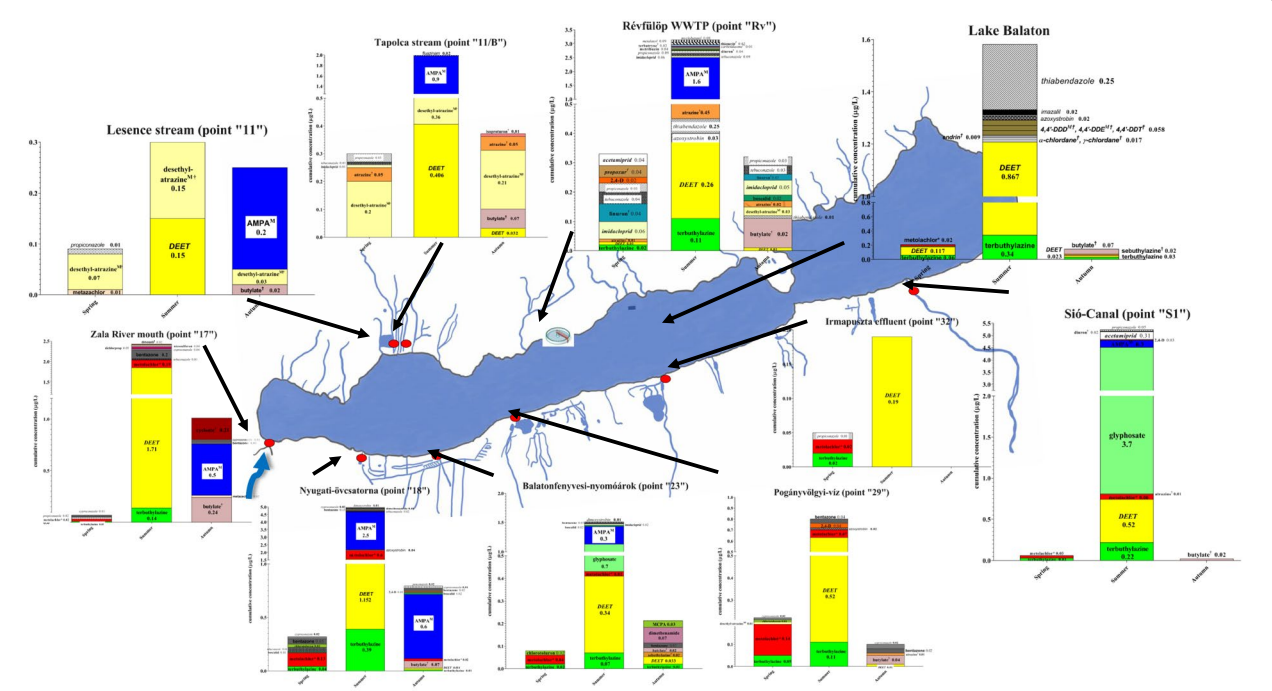

Fig. 4 Geographical- and temporal distribution of pesticide and insect repellent residues detected in waters. Legend: †banned pesticide residues in Hungary during the investigation period. *sum of the enantiomer/isomer composition of metolachlor. Mmetabolite of an active substance. Detailed data are summarized in Additional file 1 Table S2

Results

According to the 3-year monitoring data presented here, 53 out of the 456 individual compounds were detected from the 203 surface water samples representing the whole sub-catchment area (Fig. 2). Terbuthylazine and DEET were the most frequently detectable substances (number of the positive hits: 74 and 71, respectively), followed by desethyl-atrazine, metolachlor, AMPA, atrazine, and bentazone with the frequency of occurrence (FO%) 36.5%, 35%,

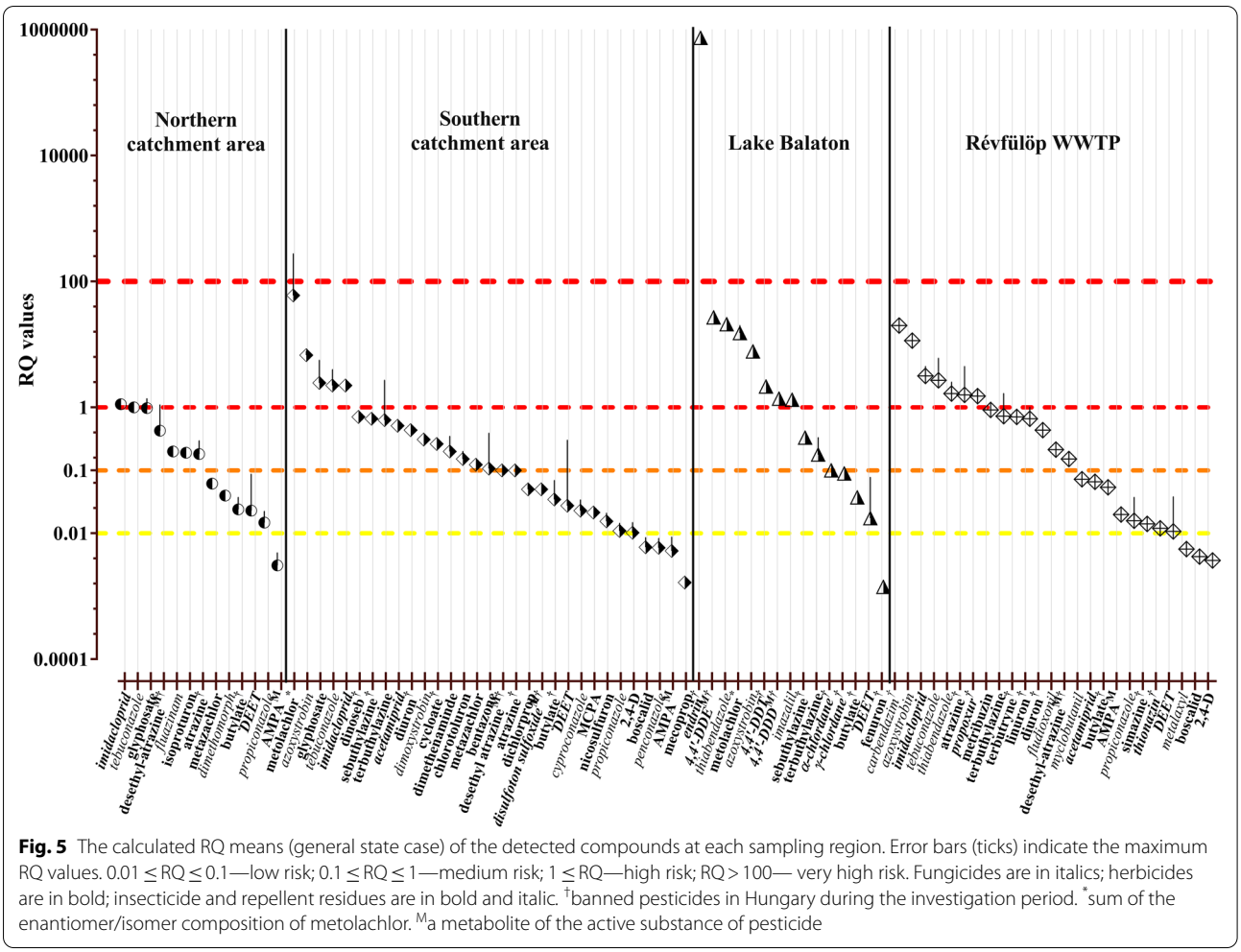

Fig. 5 The calculated RQ means (general state case) of the detected compounds at each sampling region. Error bars (ticks) indicate the maximum RQ values. 0.01 ≤ RQ ≤ 0.1—low risk; 0.1 ≤ RQ ≤ 1—medium risk; 1 ≤ RQ—high risk; RQ > 100— very high risk. Fungicides are in italics; herbicides are in bold; insecticide and repellent residues are in bold and italic. †banned pesticides in Hungary during the investigation period. *sum of the enantiomer/isomer composition of metolachlor. [M]a metabolite of the active substance of pesticide

15.3%, 12.8%, 10.3%, 8.4%, and 8.4%. AMPA (3.0 µg/L), glyphosate (2.0 µg/L), and DEET (1.57 µg/L) were detected at the highest concentrations (Table 1). Herbicides were the most frequently detectable pesticide residues representing 26 compounds, followed by the group of fungicides with 15 agents of active ingredients and insecticides or insect repellents with 12 residues including nine prohibited active substances and breakdown products (Table 1, Fig. 2). In the 85 sediment samples, only six pesticide residues were found above the LOD, namely the two metabolites and an isomer of DDT (4,4′-DDE; 4,4-DDD and 2,4′-DDT), one carbamate metabolite (3-hydroxycarbofuran) with an occasional detectability, one phosphonoglycine-type active substance (glyphosate–two positive hits, highest detected concentration: 0.06 µg/L in aqueous extract) and its primary transformation product (AMPA) with relatively high incidence (16 cases, at a maximum concentration of 0.310 µg/L in aqueous extract and FO% = 18.8) (Fig. 2).

Spatial and temporal distribution of detected compounds and their frequency of occurrence

Seasonal occurrence of pesticides

Cumulated concentration values of the pesticides and insect repellent detected in the samples during the investigation period are displayed in Figs. 3, and 4. Detailed data are summarized in Additional file 1: Table S2.

During the summer periods (from June to August), the total concentrations of the detected components were the highest in all sampling points and were larger by one order of magnitude than that of spring and autumn. DEET was present in each water sample at a concentration range of 0.15 –1.71 µg/L. The cumulative concentrations were the lowest in the Lesence stream (point "11"), the Irmapuszta effluent (point "32"), and the Balatonfenyvesi-nyomóárok (point "29") while the Nyugati-övcsatorna (point "18") and the Sió-Canal (point "S1") outflow were the most pesticide-laden watercourses. The summative pesticide concentration in Lake Balaton with the inflows and outflow was 22.16 µg/L during the summer

Table 1 Environmental risk assessment of the detected pesticides following the worst-case scenario

Detected compound	Number of positive hits	Frequency of occurrence (FO) [%]	AA-EQS [µg/L]	mean MEC [µg/L] / water body	MAC-EQS [µg/L]	maximum MEC [µg/L]	PNEC (present in literature) [µg/L]	Critical toxicity endpoint of aquatic organisms	RQ max	Level of risk
Endrin†	1	0.5	0.01[1]	0.0006	n. a	0.009	1.22E-08[a]	acute crustacean LC_{50}	7.38E + 05	High
Metolachlor*	26	12.8	–	–	–	0.11	0.001[b]	chronic algae 96/72 h NOEC	110	
4,4′-DDEM†	1	0.5	0.025[2]	0.0005	n. a	0.019	0.0007[c]	acute crustacean LC_{50}	27.1	
Thiabendazole	5	2.5	–	–	–	0.25	0.012[b]	chronic fish 21 d NOEC	20.8	
Carbendazim†	1	0.5	–	–	–	0.03	0.0015[b]	chronic invertebrate 96/72 h NOEC	20.0	
Imazalil	1	0.5	–	–	–	0.2	0.015[b]	chronic invertebrate 96/72 h NOEC	13.3	
Azoxystrobin	6	3.0	–	–	–	0.03	0.0026[d]	chronic invertebrate 21 d NOEL	11.5	
Tebuconazole	14	6.9	–	–	–	0.06	0.01[b]	chronic invertebrate 96/72 h NOEC	6.0	
Glyphosate	9	4.4	–[4]	–	–[4]	2.0	0.355 l	chronic algae 32 d NOEL	5.6	
Atrazine†	17	8.4	0.6	0.016, 0.057, 0.0053	2.0	0.45	0.1[b]	chronic algae 96/72 h NOEC	4.5	
Imidacloprid	8	3.9	–	–	–	0.04	0.009[f]	HC_5 from chronic SSD	4.4	
Desethyl-atrazineM†	31	15.3	–	–	–	0.28	0.1[d]	acute algae 12 d EC_{50} growth	2.8	
Terbuthylazine	74	36.5	–	–	–	0.16	0.06[d]	chronic algae 5 d NOEL	2.7	
4,4′-DDT†	1	0.5	0.01[3]	0.0004	n. a	0.021	0.0098[c]	acute crustacean LC_{50}	2.1	
Propoxur†	4	2.0	–	–	–	0.02	0.01[d]	acute invertebrate 48 h LC_{50}	2.0	
4,4′-DDDM†	1	0.5	0.025 [2]	0.0005	n. a	0.018	0.0129 g	acute crustacean LC_{50}	1.4	
Metribuzin	1	0.5	–	–	–	0.04	0.044 l	chronic algae 96 h NOEC	1.1	
Linuron†	2	1.0	–	–	–	0.06	0.06 [d]	chronic algae 72 h EC_{50}	1.0	

Table 1 (continued)

Detected compound	Number of positive hits	Frequency of occurrence (FO) [%]	AA-EQS [µg/L]	mean MEC [µg/L] / water body	MAC-EQS [µg/L]	maximum MEC [µg/L]	PNEC (present in literature) [µg/L]	Critical toxicity endpoint of aquatic organisms	RQ max	Level of risk
Dinoseb[†]	1	0.5	–	–	-	0.02	0.028 h	acute fish 96 h LC_{50}	0.7	Medium
Terbutryn[†]	1	0.5	0.065	0.0067	0.34	0.02	0.028[b]	chronic algae 96/72 h NOEC	0.7	
Sebuthylazine[†]	3	1.5	–	–	–	0.02	0.03[e]	provisional	0.7	
Acetamiprid	2	1.0	–	–	–	0.31	0.6[d]	acute insect 48 h NOEL mortality	0.5	
Chlorotoluron	2	1.0	–	–	–	0.05	0.1[d]	chronic algae 96 h NOEC	0.5	
Bentazone	17	8.4	– [4]	–	– [4]	0.11	0.285 l	chronic algae 7 d NOEC	0.4	
Diuron[†]	3	1.5	0.2	0.0083, 0.006	1.8	0.02	0.046[d]	chronic algae 96 h NOEC	0.4	
Dimethenamide	2	1.0	–	–	-–	0.07	0.2[d]	plant 14 d NOEL	0.4	
DEET	71	35	–	–	–	1.57	5.21[j]	chronic algae 96/72 h NOEC	0.4	
Dimoxystrobin	2	1	–	–	–	0.01	0.032 k	chronic fish 97 d NOEC	0.3	
Cycloate[†]	1	0.5	–	–	–	0.21	0.7899[c]	acute crustacean LC_{50}	0.3	
Fluazinam	1	0.5	–	–	–	0.02	0.1 m	acute fish 96 h LC_{50}	0.2	
Fludioxonil	1	0.5	–	–	–	0.01	0.0466[i]	chronic algae 96 h, NOEL	0.2	
Isoproturon[†]	1	0.5	0.3	0.0053	1.0	0.01	0.052[b]	chronic algae 96/72 h NOEC	0.2	
Metazachlor	2	1.0	–	–	–	0.02	0.162[d]	acute algae 72 h EC_{50}	0.1	
α-chlordane[†]	1	0.5	–	–	–	0.009	0.09[n]	acute fish 96 h LC_{50}	0.1	
ϒ-chlordane[†]	1	0.5	–	–	–	0.008				

Table 1 (continued)

Detected compound	Number of positive hits	Frequency of occurrence (FO) [%]	AA-EQS [µg/L]	mean MEC [µg/L] / water body	MAC-EQS [µg/L]	maximum MEC [µg/L]	PNEC (present in literature) [µg/L]	Critical toxicity endpoint of aquatic organisms	RQ max	Level of risk
Butylate[†]	10	4.9	–	–	–	0.13	1.88[o]	acute algae 96 h EC_{50}	0.07	Low
Myclobutanil	1	0.5	–	–	–	0.08	1.1[c]	acute crustacean LC_{50}	0.07	
Dichlorprop	2	1.0	–	–	–	0.03	0.5 l	acute fish 96 h EC_{50}	0.06	
Disulfoton sulfoxide[M†]	1	0.5	–	–	–	0.01	0.2 l (disulfoton)	chronic invertebrate 4 d LC_{50}	0.05	
AMPA[M]	21	10.5	– [3]	–	– [3]	3.0	80[p]	provisional	0.04	
Dimethomorph	1	0.5	–	–	–	0.02	0.5[q]	acute invertebrate NOEC	0.04	
Metalaxyl	2	1.0	–	–	–	0.3	8.03[c]	acute crustacean LC_{50}	0.04	
Propiconazole	11	5.4	–	–	–	0.05	1.36[d]	chronic fish 21 d NOEC	0.04	
Cyproconazole	12	5.9	–	–	–	0.02	0.6[d]	chronic algae 120 h NOEL	0.03	
MCPA	2	1.0	–	–	–	0.03	1.4[d]	chronic plant 14 d NOEL	0.02	
Nicosulfuron	4	2.0	–	–	–	0.03	1.43[i]	acute algae 96 h EC_{50}	0.02	
2,4-D	6	3.0	–	–	–	0.04	2.7[i]	acute algae 7d EC_{50}	0.015	
Simazine[†]	1	0.5	1.0	0.0056	4.0	0.01	0.7[b]	chronic fish 21 d NOEC	0.014	
Thionazin[†]	1	0.5	–	–	–	0.06	5 l	chronic algae 96 h NOEC	0.012	
Boscalid	7	3.4	–	–	–	0.02	2.32[d]	chronic fish 97 d NOEC	0.008	
Penconazole	2	1.0	–	–	–	0.05	6[r]	not known	0.008	
Mecoprop	1	0.5	– [4]	–	– [4]	0.01	6[p]	provisional	0.001	
Fenuron[†]	1	0.5	–	–	–	0.01	7 l	chronic algae 10 d EC_{10}	0.0001	

Ecotoxicological data and the predicted no-effect concentrations (PNECs) were collected from the literature or calculated using databases [EnviroTox, PPDB] as described in the methods (indicated in the superscript). The maximal Risk Quotient (RQ max) values were calculated and characterized the level of risk. Insecticide and repellent residues are in bold and italics, herbicide residues are in bold, fungicide residues are in italics

FO% frequency of occurrence, *AA-EQS* annual average environmental quality standard, MAC-EQS maximum allowable concentration environmental quality standard (according to the 2013/39/EC), mean MEC calculated average concentration values (according to 2009/90/EC), maximum MEC—maximum measured environmental concentration for each compound. n. a. not applicable, EQS—not listed as a priority substance in the field of water policy according to Directive 2013/39/EC

[†] the banned pesticide residues in Hungary during the investigation period. [*]sum of the enantiomer/isomer composition of metolachlor. [M]a metabolite of the active substance of pesticide

[a] [39]; [b][9]; [c][40]; [d][33]; [e][41]; [f][42]; [g][43]; [h][44]; [i][36]; [j][45]; [k][46]; [l][37]; [m][47]; [n][32].; [o][48]; [p][49]; [q][14]; [r][50].

[1] the sum of cyclodiene pesticides; [2]DDT total comprises the sum of the isomers; [3]this substance is not a priority substance but one of the other pollutants for which the EQS are identical to those laid down in the legislation that applied before 13 January 2009. [4]possible identification as priority substances or priority hazardous substances according to Directive 2008/105/EC [38]

periods (while it was 1.73 µg/L in the spring and 2.9 µg/L in the autumn seasons).

During springtime (from March to May), waters were less polluted. In the watercourses, desethyl-atrazine, metolachlor, and terbuthylazine were dominant while Lake Balaton was dominated by DEET. The spatial distribution of other compounds was relatively even. The pesticide-composition of the waters had changed in autumn (September–October): butylate, cycloate, desethyl-atrazine, and AMPA became dominant, while glyphosate practically disappeared and DEET drastically decreased (Figs. 3, and 4.).

The average number of detected compounds per season was significantly different ($p \leq 0.05$). The cumulative concentrations of the detected compounds per season and sampling sites showed a considerable level of variation in surface waters (Figs. 3, and 4, Additional file 1: Table S2). In general, results revealed that the highest concentrations correspond to agricultural and domestic applications; therefore no considerable differences were observed in the seasonal distribution and diversity of the detected compounds between 2018 and 2019. Glyphosate, terbuthylazine, metolachlor, AMPA and DEET were the most frequent pesticides in both years.

In all seasons, the treated effluent water of the WWTP presented the most diverse pesticide- composition. In the sediment samples, the cumulative presence of AMPA was remarkable during the years (Figs. 3 and 4).

Geographical distribution of pesticides

The watercourses have been divided into territorial units for northern- and southern catchment areas, Lake Balaton, and Révfülöp WWTP subsequently, and the data were analysed monthly.

In 75 water samples from Lake Balaton, 15 compounds were detected—5 herbicides, 3 fungicides, 6 insecticides, and 1 insect repellent residue. The occurrence of the herbicide terbuthylazine was more than 50%, while insect repellent DEET with the highest maximal concentration at 0.41 µg/L was detectable from 20% of the samples. 2,4′-DDT and three insecticide metabolites (4,4′-DDE, 4,4′-DDD, and 3-hydroxy carbofuran) could be identified only once in a sediment sample.

In the 97 water samples originating from the inflow and outflow streams, 34 compounds (21 herbicides, nine fungicides, four insecticides, and one repellent residue) were identified, most often DEET, terbuthylazine (FO% $\geq$ 30), desethyl-atrazine and metolachlor (FO% $\geq$ 20). Bentazone, AMPA, atrazine, and cyproconazole were also detected in more than 10% of the samples collected at 8 points over 3 years. Totalling 36 sediment samples, three compounds, mostly AMPA (FO% $\geq$ 40); 4,4′-DDE; and glyphosate have occurred (Additional file 1: Fig. S3).

In the northern catchment area, two inflowing watercourses, Lesence (point "11") and Tapolca (point "11/B") streams have been examined. From the water of the Lesence stream, desethyl-atrazine was detected 12 times out of 15 (80% occurrence rate) with concentrations ranging from 0.01 µg/L to 0.04 µg/L. AMPA and DEET were prominent and peaked in September 2018 and July–August 2019 (with 0.2 µg/L and 0.46 µg/L, 0.14 µg/L, respectively). In the sediment of the Lesence stream, AMPA has also been found in four cases at lower concentrations (0.05–0.12 µg/L in aqueous extract). In the neighbourhood of Lesence stream, water samples of the Tapolca stream contained twice as many pesticides with the dominance of atrazine and desethyl-atrazine (FO% = 86.7 and 93.3), which were detectable practically during the whole monitoring period. From June to August, AMPA, glyphosate, and DEET were detectable in 13–40% of the samples at concentrations above 0.2 µg/L. Dimethomorph, fluazinam, propiconazole, and tebuconazole fungicides could be detected occasionally even in May and June. AMPA was detectable in one-third of the sediment samples of the Tapolca stream at a concentration range of 0.11–0.31 µg/L. Traces of 4,4′-DDE (0.01 µg/L) were detected in the sediment samples on two occasions (August 2018 and March 2019) (Additional file 1: Fig. S2).

In the southern coastal watercourses (Zala River mouth, point "17"; Nyugati-övcsatorna, point "18"; Balatonfenyvesi-nyomóárok, point "23"; Pogányvölgyi-víz, point "29"; Irmapuszta effluent, point "32" and effluent water of Sió-Canal, point "S1") the distribution pattern of the compounds showed a wide diversity compared to the northern region with twice as many detected chemicals. In summary, 20 herbicides, seven fungicides, three insecticides, and one insect repellent residue have polluted these water samples. In 2018 and 2019, the dominance of AMPA and glyphosate were definitive with average concentrations of 0.3–0.85 µg/L, at one time (July 2019) reaching the level of 2.0 µg/L. Like in the northern region, seven fungicides had shown high abundance, and DEET was detectable during the summer sampling periods (May, July, and August). At the same time, atrazine and desethyl-atrazine occurred in only two and one sample, respectively. The occurrence frequency of bentazone was 73%. Indeed, about half of the samples contained a combination of metolachlor and terbuthylazine. The banned butylate and cycloate compounds were also notable with 0.11 and 0.21 µg/L mean concentrations. AMPA was the only detectable component in the sediments (with a maximum average concentration of 0.175 µg/L) (Additional file 1: Fig. S2). July 2019 provided the highest cumulative concentration values of the substances, contributed mainly by AMPA, glyphosate, and DEET.

Acetamiprid, an insecticide, could be detected at a concentration of 0.31 µg/L solely in July. May 2018 provided the other extremity when no pesticide compounds were detectable.

In the treated water of the Révfülöp wastewater treatment plant (WWTP), 25 different compounds were identified: 11 herbicides, nine fungicides, four insecticides, and one insect repellent (DEET). June 2019 had proved to be the most charging month, in which 12 of the 25 compounds were detected at a total concentration of 1.84 µg/L, including AMPA with the highest individual concentration of 1.6 µg/L, detectable only in this month. The most abundant herbicides were atrazine and terbuthylazine, the former with a notable (0.45 µg/L) concentration. The most frequently occurring compound was propiconazole (detected in 77.8% of the effluent samples), followed by tebuconazole and imidacloprid. From June to October, the number of pesticides showed a declining trend (Additional file 1: Table S3). In the entire sub-catchment area, carbendazim, fludioxonil, linuron, metalaxyl, metribuzin, myclobutanil, propoxur, simazine, and terbutryn were identified only in the effluent water of Révfülöp WWTP.

Environmental risk assessment of pesticide and insect repellent compounds

Results of the environmental risk assessment are summarized in Table 1 including the total number of hits, the frequency of occurrence, and the measured maximum MEC values of the pesticides detected in Lake Balaton, and its sub-catchment area during the investigation period. RQ max values were calculated from maximum MEC and PNEC values. Environmental quality standard values (AA-EQS and MAC-EQS) for each compound were collected based on the Directive 2013/39/EC and compared to the mean MECs and maximum MECs. According to EC Directive 2009/90/EC, if the concentration of the priority substances (nine pesticides) were below the LOD in each sample, the measurement results were set to half of the given LOD value to calculate mean MECs.

According to the ERA, 18 compounds represent a high level of ecological risk (RQ $\geq$ 1), and eight of them are banned in Hungary (and in the EU). Three chemicals are the transformation products of formerly banned parent compounds. Endrin posed the highest ecological risk for aquatic ecosystems with an RQ max value of 7.38E + 05 followed by metolachlor (26 hits, RQ max = 110), 4,4'-DDE (1 hit, RQ max = 27.1), thiabendazole (5 hits, RQ max = 20.8), carbendazim (1 hit, RQ max = 20), imazalil (1 hit, RQ max = 13.3), azoxystrobin (6 hits, RQ max = 11.5), tebuconazole (14 hits, RQ max = 6.0), glyphosate (9 hits, RQ max = 5.6), atrazine (17 hits, RQ max = 4.5), imidacloprid (8 hits, RQ max = 4.4) desethyl-atrazine (31 hits, RQ max = 2.8), and terbuthylazine (74 hits, RQ max = 2.7). Among them, DEET is a recurrent substance with an overall frequency of occurrence of 35%. Over 66% of the 53 detected pesticides represent a possible high or medium ecological risk for aquatic ecosystems. 18 chemicals pose a low risk to the environment [16 active substances of pesticides (four banned) and two metabolites].

Figure 5 shows the average RQs and their related specific region (territorial isolation) on a grouped XY graph chart, illustrated separately in descending order. The level of risk varied among different sampling regions and presented a given predictable spatial distribution. In general, the southern catchment region posed five high-, 13 medium-, and 13 low-risk compounds (six out of the eight watercourses). The results also show that the substances with high risk emerged from WWTP and Lake Balaton with seven and eight matches. Overall, the outcomes from WWTP triggered the second-highest number of risk substances (Σ = 25 compounds—seven high, seven medium, and 11 low). In the northern catchment region, imidacloprid, tebuconazole, and glyphosate pose a high risk besides the medium risk of desethyl-atrazine fluazinam, isoproturon, and atrazine (data in detail are shown in Additional file 1: Table S4).

Discussion

This study documents the first monitoring data of multi-pesticide residues by time-series analysis of the water basin of the largest shallow lake (Lake Balaton) in Central Europe. In Hungary, the arable land ratio is over 50% (the largest besides Denmark), and concurrently, the number of monitoring sites (surface waters) per 100 km^2 of arable land is the lowest. According to the Waterbase, the EEA's database on the status and quality of European water status and quality, Hungary reported 17 detected pesticides from monitoring sites in the period between 2007 and 2017, which may be linked to the measurement of priority, "obsolete" substances as required by EWFD and Directive 2008/105/EC [38, 51]. According to our results over 3 years, 53 out of the investigated 456 compounds were identified in water and six in sediment samples. To our best knowledge, no former study analysed as many pesticides simultaneously as this study.

The rapid increase in the number of pesticide residues from spring to summer was following seasonal trends during the excessive agricultural usage and application patterns as previously described by Konstantinou et al. [52] and Chow et al. [53].

Our theories that the differences in pesticide concentrations and diversity between regions (northern- and southern catchments, Lake Balaton and the Révfülöp

WWTP) are related to varying flow conditions of watercourses, the dilution potential of Lake Balaton due to its large mass of water, the various land use, variable weather conditions [53], the effects of WWTPs that are directly discharging effluents into the watercourses representing major point-source for pesticide load [54], and mainly the pesticide use that prevail in the area. However, no clear differences were observed between the regions over the years.

DEET was the most frequently detected compound in Lake Balaton and its sub-catchment region correlating with the seasonal application. To prevent insect and mosquito bites, DEET is one of the most frequently used repellents all around the world and is ubiquitously present in aquatic environments such as surface waters and wastewater effluents at a range from 0.003 µg/L to 2.51 µg/L [55–61]. The potential classification of DEET under Regulation (EC) No. 1272/2008 could mean that insect repellent products containing more than 10% DEET cannot be available to the public in the EU. It is slightly toxic (100–200 mg/L) to aquatic organisms and birds [62]. Still, as reported in previous studies, DEET can alter the regulation of androgen receptor genes and results in a decreased hepatosomatic index in adult female fathead minnows (*Pimephales promelas*) at a concentration of 0.6 µg/L [63]. Moreover, it has a weak haemolytic potential toward human erythrocytes at 1–5 mM (dilution of 0.02–0.1%) [64].

The primary and regular occurrence of atrazine and desethyl-atrazine in water bodies raises the possibility that this pesticide is still used more than 10 years after its banning in Hungary or could correlate with the contamination of the northern catchment area described by Székács et al. [24] and Maloschik et al. [25] originating from past industrial activities. In the case of other s-triazine herbicides, the results support previous findings that terbuthylazine has been frequently detected in freshwaters in several EU countries such as Italy [65, 66], Spain [1, 67, 68], Greece [14], or Portugal [69]. The importance and excessive usage of terbuthylazine have increased since atrazine was banned, and approximately 278–310 tons of active substance (the fourth largest amount of active ingredient) were sold and used annually in Hungary from 2018 to 2019 [70]. Terbuthylazine is a chemical of emerging concern that can pose a similar risk to atrazine due to its moderate persistence and high bioaccumulation rate (log K_{ow} = 3.4) under reductive conditions and with stability against aqueous hydrolysis [36, 69]. In addition to acting as an endocrine disruptor [71, 72], terbuthylazine has sub-lethal effects on anurans at environmental concentrations (0.003–0.3 µg/L) [73]. These adverse effect concentrations coincide with the applied values (0.02–0.72 µg/L) in the worst-case and typical exposure scenarios. Nevertheless, PNECs protect the most sensitive trophic levels of organisms (even if it is at a lower trophic level) and the functions of aquatic ecosystems [74].

Although R-metolachlor is banned in the European Union since 2002 [75], the racemic S-isomer is still used with the third-largest amount of pesticides sold in Hungary. S-metolachlor is one of the most frequently detected herbicides, similar to other international studies [12, 76, 77].

In recent years, the presence of AMPA and glyphosate has become widespread in surface and groundwaters surrounding agricultural catchment areas (including soils and sediments) in increasingly critical concentrations (AMPA: 0.656–49.4 µg/L; glyphosate: 3–387 µg/L) and frequency (15–80% of the total samples) [17, 78–81]. Similarly, we found glyphosate (sold in the highest volume over the 6 years) [70], and AMPA regularly, with maximum concentrations of 3.0, and 2.0 µg/L respectively. Glyphosate at a lower concentration (1 µg/L) than the detected maximum value was proved to cause morphological changes and metabolic disruptions in generation F2 on rainbow trout (*Oncorhynchus mykiss*) [82]. Contrary to other research [81, 83], the presence of AMPA was more frequent than glyphosate in both water and sediment. The probability that the herbicides detected in sediments could pollute the groundwater aquifers is comparatively high [24]. The appearance of a high concentration of AMPA (1.6 µg/L) in the effluent of Révfülöp WWTP can be associated not only with the degradation of glyphosate but also with the use of phosphoric acid type detergents, especially during dry seasons [84].

In addition to herbicides, azole fungicides were detected in a high number and concentration (0.0004–3.023 µg/L) in the influent and effluent of WWTPs as well as in natural surface waters (lakes, rivers) all around the world [77, 85–88]. Accordingly, FO% values for tebuconazole, propiconazole, and cyproconazole were $\geq \sim 5\%$ in the examined water samples of our study. These compounds are stable to aqueous hydrolysis and moderately persistent in an aquatic environment with high log K_{ow} (3.09–3.7) [36]. Tebuconazole is also widely used in Hungary: about 273.0–247.0 tons of active ingredient was sold in the years 2018 and 2019 (fifth in the sales ranking) [70].

DDT isomers and metabolites, as lipophilic compounds, are known to have high log K_{ow} values, consequently, they tend to be strongly adsorbed on sediment organic matter with long-lasting persistence [36]. Their occurrence is not unexpected after more than 50 years of restriction. They were detected in a sole water sample (B-11/B, Szigliget-basin) only one time in 2018, while

their total sum of mean concentration [according to the 2009/90/EC Directive] (0.0005 µg/L) did not exceed the AA-EQS limit (0.025 µg/L) for all DDT isomers set by the Directive 2013/39/EC. MAC-EQS is marked as not applicable in the case of 4,4′-DDT. However, the measured concentration of 4,4′-DDT in 2018 was twofold higher (maximum MEC: 0.021 µg/L) than the allowed AA-EQS (0.01 µg/L) for inland surface waters including rivers, lakes, and related artificial or heavily modified water bodies, which should be protected against short-term pollution peaks. Along with these residues, atrazine, diuron, endrin, isoproturon, simazine, and terbutryn also have EQS values, which they did not exceed, either in average or maximum concentrations. Overall, environmental quality standard values are established only for nine pesticides from the 53 detected compounds. According to the EQS Directive, the surface water EU Watch List (WL) is developed under the EWFD. The WL should be updated every 2 years to obtain high-quality EU-wide monitoring data on potential water pollutants that may pose a significant risk in aquatic environments and to determine the EQS levels. Terbuthylazine and DEET are not listed either in the 1st WL [42] or in the reviewed 1st WL and recommendations for the 2nd WL report [46], and according to the report proposing new substances for the 3rd Watch List [89], they are not potential candidates to be monitored in surface waters. However, they were present in 74 and 71 samples, respectively, from 33 sites and should be reviewed and considered by the EWFD just as it was performed regarding the azole fungicide group [89].

In the present study, seven of the 18 high-risk pesticides had risk ratio values above ten. Moreover, it is alarming that only five out of 18 have an AA-EQS value and their status might have to be reconsidered in the future. Following the environmental risk assessment, the majority of pesticide residues in Lake Balaton sub-catchment area seem to represent a high and medium risk to local biota even though only certain aquatic algae, invertebrate and crustacean species are affected. Our results provide a chance for the Hungarian decision-makers to update the priority lists of chemical substances. The monitoring of priority substances should be undertaken not just in the Lake Balaton sub-catchment area, but in all national river basins.

On the northern and southern coast of Lake Balaton, there are two and three sites, respectively, designated as drinking-water sources by the Hungarian Decree No. 6 of 2002. (XI. 5.) KvVM on the pollution limits for surface waters designated as drinking-water sources (under 98/83/EC). According to this legislation, the concentration of individual and total pesticides allowed in surface waters assigned as drinking water sources are 0.1 µg/L and 0.5 µg/L, respectively, the same as for drinking waters (established by the 98/83/EC). However, none of the legislation specifies or determines the list of compounds or the number of pesticides for monitoring, while currently 454 active substances are approved in the EU. According to the current legislation, 'only those pesticides which are likely to be present in a given supply need be monitored'. These gaps are of great concern, especially considering that during our work, we have identified numerous pesticides posing medium or high environmental risks that have long been banned in the EU; therefore, they are not necessarily expected to be present in surface waters. On the other hand, many of the detected pesticides, such as glyphosate, terbuthylazine, metolachlor (surpassed the EU limit of 0.1 µg/L and 0.5 µg/L), and tebuconazole are widely used (and consequently the most frequently detected) with high environmental risk and are also under-represented in the current relevant legislation lists. Additionally, the prioritisation of DEET in Lake Balaton catchment area should be encouraged.

Our results can be used to prioritise and identify the unregulated and uncontrolled pesticide residues discharged into the aquatic ecosystems. In the case of these compounds, it is suggested to collect EU-wide monitoring data to support future prioritization activity.

Conclusion

Our 3-year period monitoring is the first comprehensive study on over 450 pesticide compounds in Lake Balaton and its sub-catchment area. Due to the ongoing agricultural and domestic processes in the area, the presence of the detected compounds corresponds with their continuous or increased application. Effluent water from WWTP can play an important role in the complexity of pesticide loads and may influence the water quality of Lake Balaton. The occurrence of long-banned pesticides in the watercourses in the northern area (including protected ecological systems) is worrisome and suggests the prohibited use and/or hidden supply of these chemicals and their release into the environment. The number of the detected compounds not listed in any of the related legislations highlights the need to regularly monitor not just the prioritized pesticides but as many as possible, regardless of their current legal status. Being a 'seasonal substance', DEET was detectable in each sampling point in summer; the cumulative concentration and distribution showed appreciable spatial–temporal changes through the seasons. Based on the worst and general state RQs, the emerging pesticides glyphosate, metolachlor, tebuconazole, and terbuthylazine occasionally presented at least a medium risk in the studied area during the whole investigation period. In the future, the durable surface

water monitoring of these substances is strongly recommended to reach a more comprehensive dataset for supplementary environmental impact assessment and meta-analysis of projects.

Abbreviations

AA-EQS: Annual average environmental quality standard; AF: Assessment factor; AMPA: Aminomethylphosphonic acid; ANOVA: One-way analysis of variance; DEET: Diethyltoluamide; d.w.: Dry weight; EQS: Environmental quality standard; ERA: Environmental risk assessment; EWFD: European water framework directive; FO%: Frequency of occurrence in percentage; GC–MS: Gas chromatography-mass spectrometry; HPLC–MS: High-performance liquid chromatography-mass spectrometry; LOD: Limit of detection; MAC-EQS: Maximum allowable concentration environmental quality standard; MEC: Measured environmental concentration; NOEC: No observed effect concentration; PNEC: Predicted no effect concentration; RQ: Risk quotient; TLVs: Threshold limit values; WL: Watch list; WWTP: Wastewater treatment plan.

Supplementary Information

The online version contains supplementary material available at https://doi.org/10.1186/s12302-022-00630-2.

Additional file1: Figure S1. The land cover/land use of the Lake Balaton, and its sub-catchment area. **Figure S2.** Detected pesticides and their metabolites at the period from April 2018 to August 2020 in water samples (A1, B1, C1) and sediment samples (A2, B2, C2) of the northern influent watercourses (Lesence stream – A1, A2 and Tapolca stream – B1, B2) and of the influent, effluent watercourses at southern catchment area in average concentrations (C1, C2) by monthly. **Figure S3.** Frequency of occurrence of the detected pesticides, their metabolites, insect repellent in water (A1 and B1) and sediment (A2 and B2) samples of Lake Balaton and northern and southern watercourses. **Legend**: † - the banned pesticide residues in Hungary during the investigation period. * - sum of the enantiomer/isomer composition of metolachlor. M – a metabolite of the active substance of pesticide. **Legend:** Labelling in **bold** the detected compound name indicating herbicide residues. Labelling in *italic* the detected compound name indicating fungicide residues. Labelling in ***bold and italic*** the detected compound name indicating insecticide and repellent residues. **Table S1.** Sample points name, type, and name of the body of water are analyzed according to town/area and geographic coordinates. **Table S2.** Cumulative concentrations (µg/L) of the detected compounds in water- and in sediment (below the **bold line**) samples at each sampling point in spring, summer, and autumn seasons during the 3 years of investigation period. **Table S3.** Results of the chemical analyses of the effluent discharge of Révfülöp wastewater treatment plant (WWTP) monthly at northern catchment region. **Table S4.** The number of positive hits, minimum-, average-, and maximum concentrations of the detected pesticides and insect repellent in the whole investigation period (2017-2020) at each sampling region (Northern catchment area, Southern catchment area, Lake Balaton, and Révfülöp WWTP). The RQ means, RQ max values and the level of risk are calculated as described in the methods.

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Author contributions

GT: conceptualization, investigation, formal analysis, visualization, writing—original draft, review & editing. JH: conceptualization, formal analysis, investigation, writing—original draft, review & editing. SS: conceptualization, project administration, resources, writing—original draft, review & editing, supervision. PH: investigation. MF: investigation. JR: investigation. BG: investigation. EK: investigation writing—review & editing. IS: visualization and investigation. BU: project administration, funding acquisition, resources. BK: project administration, funding acquisition, resources. All the authors read and approved the final manuscript.

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Availability of data and materials

The data used and analysed during the current study are available from the corresponding author on reasonable request.

Declarations

Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Competing interests

The authors declare that they have no competing interests.

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