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Pesticides in Small Agricultural Catchments in the Czech Republic

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ABSTRACT
Generally, pesticides are the products containing at least one chemical substance which should protect plant or plant products against pests/diseases. Among them, the most important ones are herbicides, followed by insecticides and fungicides. As a result of intensive agriculture techniques, large amounts of pesticides are applied on agricultural soil. They remain and degrade in soil, but they can enter water bodies and negatively affect water quality and the aquatic ecosystem. The article deals with the level of pesticide load in soil, bottom sediment and surface water in chosen agriculture catchments in the Czech Republic. Results revealed that the main general problem is glyphosate and its metabolite AMPA, although their application has been constrained for several years. Furthermore, the difference in contents of chosen parent pesticide substances and their metabolites in soils and waters were pointed out.

Keywords: soil, sediment, water, glyphosate, AMPA, parent pesticides, metabolites.

INTRODUCTION

Intensive farming in the Czech Republic brings a wide spectrum of pesticides into the arable land. They partly remain in soil, are degraded and partly transported to water bodies. Besides agricultural land, there are also point pesticide sources (e.g. municipalities) as a potential risk of surface waters pollution, but the study aims at agricultural non-point sources. In a catchment, there are two main ways of material transport: water erosion (surface runoff), infiltration and subsequent subsurface runoff. Transport by water erosion is an extensive problem in the Czech Republic. Due to large blocks of arable land, steep slopes and soil erodibility, about 50% of the agricultural land is threatened by the aforementioned soil degradation process. Subsurface runoff can be accelerated on leachy soils and with ameliorative drainage. Subsoil drainage was built in the Czech Republic in the last century to extend agricultural land and obtain higher yield and consequently, it extends to about 25% of arable land now (Kulhavý and Fučík 2015).

Although the currently used pesticides (CUPs) are not persistent in the environment, they can still accumulate in soil and water, as a result of their repeated use ("pseudo persistence"), since their degradation is slower than their input (Hvězdová et al. 2018). Moreover, the degradation products of CUPs can remain in the soil for a long time and can have similar negative effects on ecosystems as the original substance (Halešová et al. 2021). This happens despite the sophisticated process of risk assessment which must be done for each active substance and product as a part of authorization to ensure compliance with European rules (Regulation EC No. 1107/2009). Since groundwater contamination can pose a direct risk for humans and it is relatively better described (e.g. Kodeš et al. 2016, Syafrudin et al. 2021) than contamination coming in soil, a system of limit values for concentrations of selected CUPs in groundwater has been developed in many countries and also at the EU level (Regulation EC No. 1107/2009). For soil, however, such limits are not established in any country, even though the toxicity of CUPs in the soil has been proven in many experiments, especially for soil microorganisms (e.g. Tripathi et al. 2020).

Earlier studies presumed that the transport of CUPs is dependent mainly on surface runoff (Kladivko et al. 2001); however, at present, with improved monitoring systems, it has also been demonstrated that a significant role could be played by shallow subsurface runoff, including drainage runoff (e.g. Sandin et al. 2018). A significant role in the transport of pesticides is played by soil preferential pathways such as macropores (Tediosi et al. 2013) and, in light-textured, mid to highly permeable soils, also by cracks and clefts. The rate of preferential flow during rainfall-runoff events (RREs) can be so high that in such situations, the physical-chemical properties of pesticides together with soil characteristics lose their significance for leaching (Doppler et al. 2012). Any accelerated runoff markedly reduces the time of pesticide reaction with the environment (effect on the target organisms, sorption or degradation in soils / crops) and can lead to the direct and immediate leaching of the parent compound into waters.

Although many studies focusing on the transport of pesticides from soil to water were conducted with valuable results (Doppler et al. 2012, Bundschuh et al. 2014; Székács et al. 2015; Lefrancq et al. 2017, …), the processes influencing the dynamics of pesticide washing out and leaching are still not completely understood. The aim of this study was to contribute to the knowledge of real pesticide load levels in soils, sediments and surface waters in small agricultural catchments and show differences in concentrations and occurrence of parent substances and metabolites in monitored media.

MATERIAL AND METHODS

Research on pesticides in soil, sediment and surface water has been proceeding in three experimental catchments since 2019: Černičí (in Křemešnická highlands), Němčice (Drahanská highlands) and Uhřice (Litenčická highlands) (Fig. 1). They represent different natural conditions of the Czech Republic (Table 1).

Sampling and analytical methods were unified in all three catchments. The pesticide concentrations in soils were monitored in two transects covering the basic slope zones of each catchment. Samples were collected as mixed takings from 5 sites from the topsoil four times per year (April, June, August, October) and twice per year also

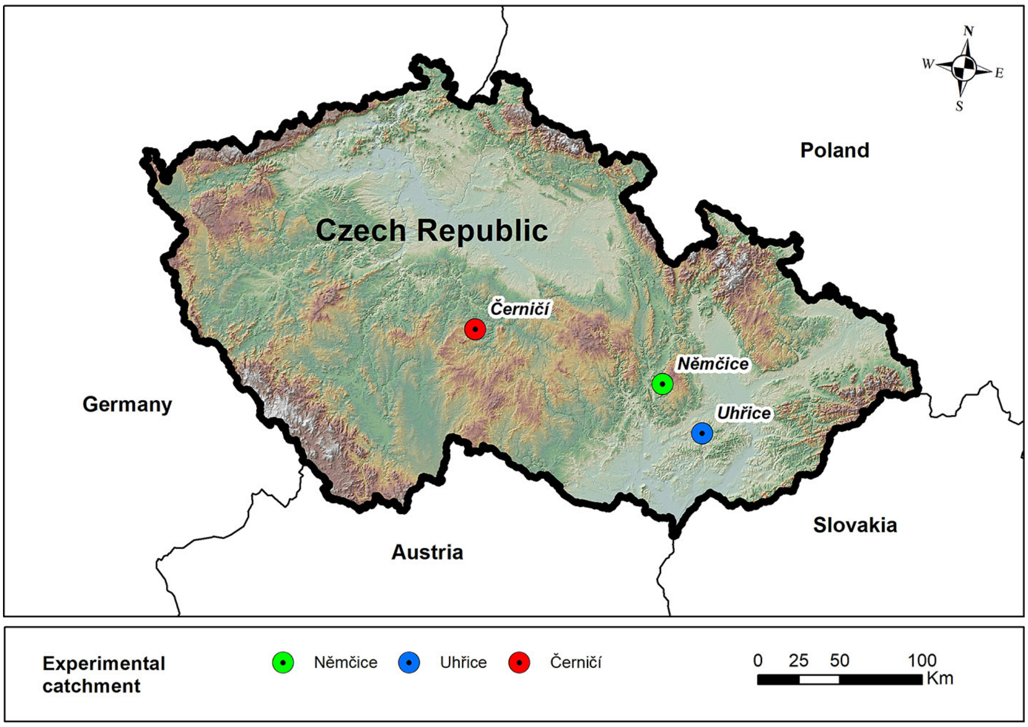

Figure 1. Location of the experimental catchments

Table 1. Characteristics of the experimental catchments

Catchment	Area (ha)	Altitude (m) / slope (%)	Aver. precip. year total (mm)	Aver. year temp. (°C)	Geology	Soil types (WRB)	Arable land (%)
Černičí	138	520 / 6.0	720	7	Crystallinium	Cambisol, Stagnosol	75
Němčice	347	606 / 7.3	650	6	Kulm, debris, granodiorites	Cambisol, Luvisol	50
Uhřice	2570	350 / 9.3	600	8	Neogen, loess	Chernozem, Regosol	55

from subsoil (at the beginning and end of the growing season).

The pesticide concentrations in bottom sediments were monitored at the gauging profile of the stream and in the reservoir closing the catchment. Samples were taken manually every month during vegetation seasons.

The samples of surface waters were taken at a gauging profile in the stream and from the reservoir. The sampling regime at the stream profile (and monitoring of drainage waters in Černičí) differed according to the season and hydrological situation at the time. During prevalent baseflow and slow interflow, samples were collected manually at monthly intervals. During distinctive rainfall-runoff events (RREs), sampling was done using automated samplers ISCO at intervals from 5 min to 1 hour (acc. to flow dynamic and season). Reservoir water was sampled manually at 1-month intervals.

The samples of all monitored media (water, soil, sediments) were analysed for the content of the entire range of pesticide substances, including their selected metabolites. Within the monitoring period assessed here (2019 – 2021), 1,056 samples were taken and analysed (details in Table 2, Fig. 2–4).

LCMSMS equipment (Water Aquity UPLC and Xevo TQ-S) was used for analyses of pesticides in solid and liquid matrices. About 150

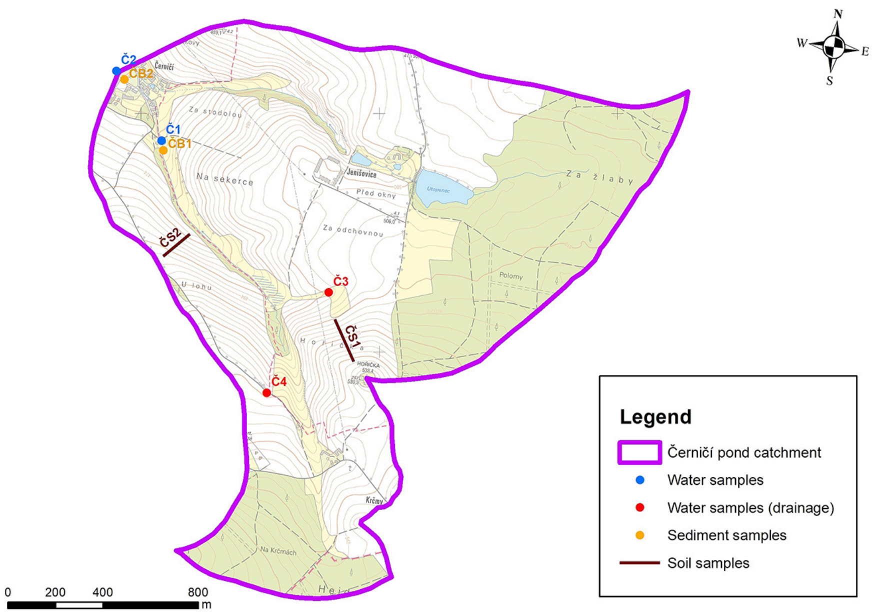

Figure 2. Černičí – monitored places

Table 2. Summary of taken samples

Catchment	Soil	Sediment	Surface water	Drain water
Černičí	74	68	266	88
Němčice	100	64	257	0
Uhřice	87	56	84	0
Sum of samples	261	188	607	88

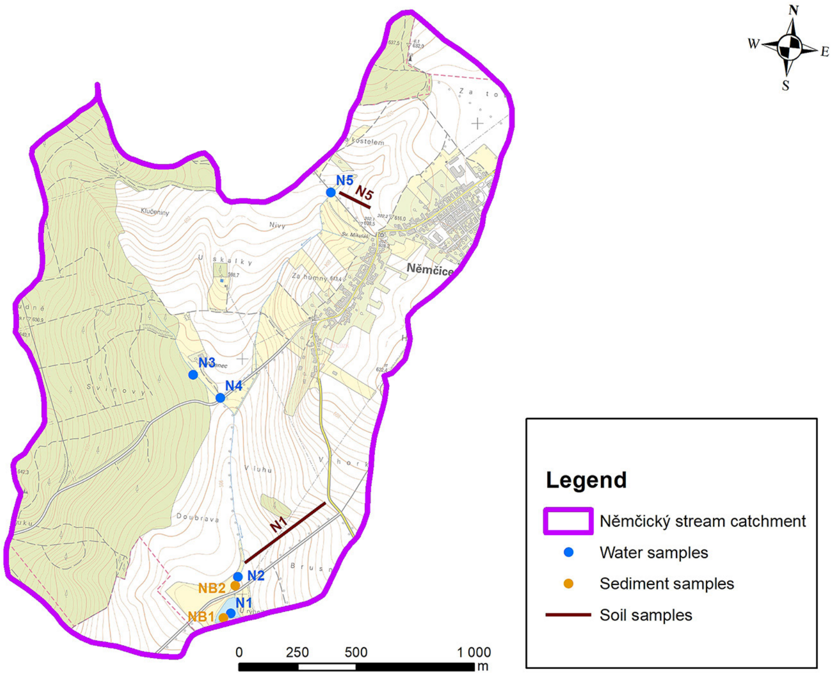

Figure 3. Němčice – monitored places

pesticides were analysed in earthen matrices (sediments, soil) as part of seasonal monitoring, especially active components of plant protection agents but also their degradation products, which tend to absorb onto soil particles. Approximately 300 pesticides, including their polar metabolites, were measured in liquid matrices (surface water) as part of the full screening. The ranges of regularly monitored pesticides and their metabolites were selected based on several criteria within the risk analysis of the occurrence of pesticide substances in each location of interest. The risk analysis included the data on the consumption of plant protection products in the given locations, pesticide full screening during seasonal applications, and assessment of the physicochemical and

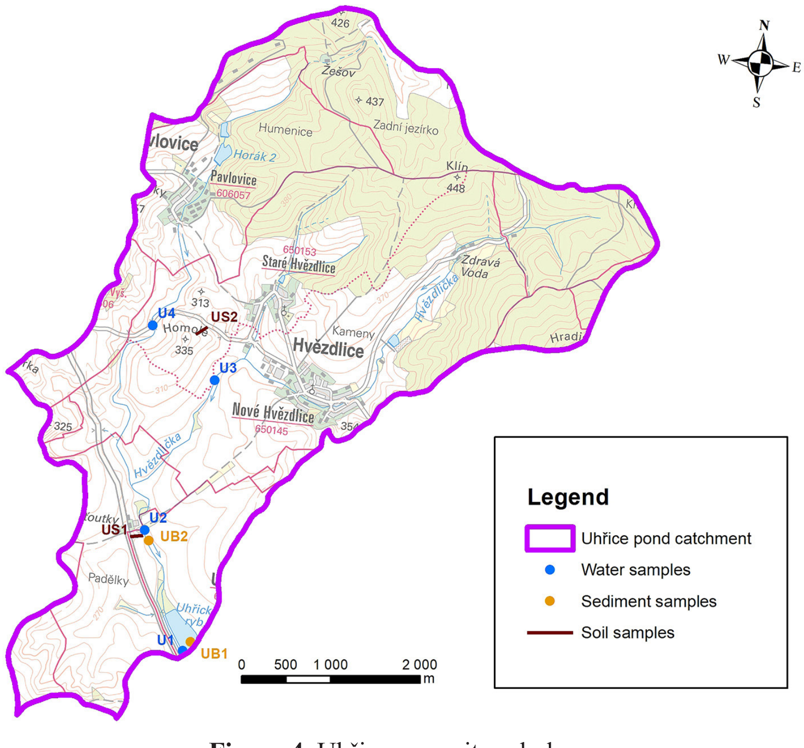

Figure 4. Uhřice – monitored places

toxicological properties of pesticides. The monitored pesticide substances included representatives of azole pesticides, triazine pesticides, chloracetanilide, amide, carbamate, phenoxyalkane pesticides, chloridazone, urea, neonicotin, organophosphorus and other unclassified pesticides.

RESULTS AND DISCUSSION

The obtained results reflect different conditions of the three catchments. Crops and the related spectrum of applicated protective agents are one of them: corn and beet dominate in Uhřice, cereals and rape in Černičí and Němčice, resulting in detection of different pesticide substances in soils and other monitored media. Parent substances are accentuated in bold in Tables 3 – 11 with results, current letters were used for metabolites.

The Černičí catchment (Fig. 2) has the largest rate of tile drained lands (29% of the total area), that is why the drainage waters there are monitored in addition to other media. Subsurface runoff probably plays a significant role in pollutants transport in system soil – in this case, water body (Fučík et al. 2017).

The concentrations of pesticide substances in the soils of the Černičí catchment were significantly higher in the topsoil. The cumulative concentrations ranged from 22 to 2 214 µg/kg, with an average value of 320 µg/kg. A total of 26 pesticide substances were detected, but most of them in very low concentrations. Parent substances were commonly detected with an average concentration value of 190 µg/kg.

The most common soil-bound substances were glyphosate, diflufenican, epoxiconazole and tebuconazole (Table 3). Of the metabolites, AMPA was clearly the dominant one with an average concentration of 150 µg/kg. Often detected was also terbuthylazine-hydroxy, which is a metabolite from triazine metabolites group typically occurring in soil. Glyphosate and its metabolite AMPA represented on average 65% of the total pesticide concentration in the sample. In the subsurface soil layer, pesticide concentrations had approximately three times lower values than in the topsoil. Of the metabolites, AMPA was almost exclusively present, and the composition of the parent compounds was similar to that of the topsoil, but at much lower concentrations.

The monitored bottom sediments contained almost exclusively glyphosate and its metabolite AMPA (Table 4). The value of pesticide concentrations in stream and reservoir sediments differed significantly due to their different characteristics. The sandy sediments in the stream bind pesticides significantly less than the fine-grained materials in the pond sediment. Only AMPA was detected here in all samples with an average concentration of 14.7 µg/kg. The concentrations of pesticides were significantly higher in reservoir sediment,

Table 3. Average concentrations of the main pesticides in soils (Černičí)

Pesticide	Topsoil			Subsoil		
	Detection [%]	Av. conc. [µg/kg]	Stand. dev. [µg/kg]	Detection [%]	Av. conc. [µg/kg]	Stand. dev. [µg/kg]
Diflufenican	81	21.6	38.4	33	6.1	19.8
Epoxiconazole	95	10.3	9.9	33	2.4	5.0
Glyphosate	99	41.3	45.2	68	11.8	17.7
AMPA	100	149.3	97.6	100	45.3	55.9
Tebuconazole	80	23.8	46.9	15	2.1	6.4
Terbuthylazine-hydroxy	94	7.8	3.7	63	4.9	4.3

Table 4. Average concentrations of the main pesticides in bottom sediments (Černičí)

Pesticide	Stream bottom			Reservoir bottom		
	Detection [%]	Av. conc. [µg/kg]	Stand. dev. [µg/kg]	Detection [%]	Av. conc. [µg/kg]	Stand. dev. [µg/kg]
Alachlor	0	0	0	67	9.3	6.6
AMPA	100	14.7	9.3	100	111.0	23.7
Glyphosate	45	4.9	6.8	100	110.1	57.1
Terbuthylazine-hydroxy	7	0.3	0.9	17	2.4	5.7

in addition to AMPA (av. 111 μg/kg), the parent glyphosate (av. 110 μg/kg) was also present in the reservoir sediment in all samples collected. The herbicide alachlor (forbidden in EU since 2008) was also frequently detected.

A total of 55 substances were detected in the drainage waters monitored in the Černičí catchment, 24 parental compounds and 31 metabolites. The summary concentrations ranged from 1.3 to 20.1 μg/l, depending mostly on the actual hydrologic conditions in the monitored drainage sub catchment. Prevailing substances in the drainage runoff were persistent metabolites of chloroacetanilide herbicides (av. 4.1 μg/l). Often detected was also metabolite 1,2,4-triazole (av. 0.2 μg/l). Parental compounds in higher concentrations were detected only during storm events. Their composition and concentrations depended on the actual crop in the drainage group sub catchment and actual spraying.

The surface runoff in the closing profile of the stream is mainly composed of the drainage runoff of individual drainage groups, where different soil management with the application of various pesticides takes place. This is reflected in the vivid composition of pesticides in surface runoff. A total of 81 substances were detected, the most significant are presented in Table 5. The summary concentrations ranged from 1.1 μg/l to 27.2 μg/l (av. 3.49 μg/l). Overall, metabolites (Fig. 9) dominated the surface runoff with an average concentration of 2.63 μg/l (from 0.63 μg/l to 5.81 μg/l). Of these substances, the predominant ones were the chloroacetanilide herbicides, with an average concentration value of 2.56 μg/l (mostly metolachlor ESA and metazachlor ESA). Other common pollutants were metabolites of azole pesticides in the form of 1,2,4-triazole (av. 0.13 μg/l) and metabolites of terbuthylazine (av. 0.05 μg/l). The parent compounds were predominantly present during the RREs. The summary values ranged from 0 μg/l (during prevailing baseflow) to 25.92 μg/l (during peak flow early after spraying). Most of parental substances were detected during single event only; that is why they are not mentioned in Table 5. Herbicides MCPA (one single RRE happened early after spraying) and bentazone were detected in the highest concentrations.

The pond in the village of Černičí was monitored as a recipient of all flowing waters. The summary concentrations of pesticides ranged from 1.50 μg/l to 5.87 μg/l (av. 3.39 μg/l). A total of 97 pesticide substances were detected, mostly at low concentrations. The total concentration consisted mainly of metabolites (Fig. 7–9). In addition to the metabolites of chloracetanilide herbicides (1.44–3.44 μg/l), high concentrations of the metabolite AMPA (av. 0.16 μg/l) were also detected. Other metabolites (Table 5) were presented often, but their concentrations were considerably lower.

Table 5. Average concentrations of chosen pesticides in surface water (Černičí)

Pesticide	Stream (reg. monitoring)			Stream (storm events)			Reservoir		
	Detection [%]	Av. conc. [μg/l]	Stand. dev. [μg/l]	Detection [%]	Av. conc. [μg/l]	Stand. dev. [μg/l]	Detection [%]	Av. conc. [μg/l]	Stand. dev. [μg/l]
1,2,4-triazole	97	0.099	0.052	100	0.160	0.115	85	0.048	0.047
Acetochlor ESA	97	0.031	0.011	95	0.024	0.014	100	0.048	0.019
Alachlor ESA	100	0.370	0.217	100	0.147	0.111	100	0.257	0.119
AMPA	7	0.001	0.005	40	0.020	0.031	96	0.160	0.120
Atrazine-2-hydroxy	100	0.013	0.005	95	0.015	0.006	100	0.025	0.022
Atrazine-desethyl	93	0.005	0.002	30	0.001	0.002	65	0.004	0.009
Bentazone	53	0.041	0.078	73	0.455	1.551	62	0.034	0.075
Glyphosate	7	0.002	0.009	15	0.015	0.058	77	0.103	0.168
Chloridazon-desphenyl	77	0.045	0.037	63	0.021	0.019	73	0.061	0.047
Chloridazon-methyl desphenyl	80	0.025	0.018	45	0.012	0.015	50	0.030	0.083
Metazachlor ESA	100	1.035	0.605	100	0.585	0.524	100	0.986	0.417
Metazachlor OA	100	0.101	0.062	100	0.072	0.059	100	0.133	0.055
Metolachlor ESA	100	1.016	0.695	100	0.619	0.244	100	0.690	0.473
Metolachlor OA	97	0.391	0.332	100	0.216	0.220	100	0.259	0.186
Terbuthylazine-hydroxy	100	0.029	0.010	100	0.043	0.014	100	0.081	0.079

From parentals, only glyphosate was detected in the most of samples (77%), its av. concentration was 0,10 µg/l. Other parental compounds (esp. bentazone and tebuconazole) were detected only seldom after RREs, so they are not mentioned in Table 5.

The Němčice catchment (Fig. 3) features short steep slopes of arable land falling directly to the stream. The dominant transport process here is surface runoff (Honek et al. 2020).

On average, the sum of all detected pesticides in one topsoil sample reached 663.9 µg/kg, and for subsoil – 227.1 µg/kg (Fig. 5). The soils in the Němčice catchment are the most heavily loaded with AMPA (Table 6). This metabolite of glyphosate was detected in almost all soil samples and its concentrations (topsoil av. 161 µg/kg) are the highest comparing to other studied pesticide matters. Glyphosate concentrations (topsoil av. 81 µg/kg) in soil persist although its application has been constrained since 2019 (MZE 2018). Table 6 presents the substances detected in more than 50 % of soil samples. It is apparent that average concentrations of all are higher in topsoil than subsoil. The residues of azole pesticides (epoxiconazole and tebuconazole) were found in soil samples. They give rise to the metabolite 1,2,4-triazole, which is mobile in the soil and thus contaminates waters.

While up to 19 pesticide substances were often detected in one soil sample, the spectrum in the bottom sediments was narrower (max. 9 substances). The average pesticides sum was 316.9 µg/kg in the stream bottom sediment and 263.5

Table 6. Average concentrations of the main pesticides in soils (Němčice)

Pesticide	Topsoil			Subsoil		
	Detection [%]	Av. conc. [µg/kg]	Stand. dev. [µg/kg]	Detection [%]	Av. conc. [µg/kg]	Stand. dev. [µg/kg]
AMPA	97	160.7	104.4	88	125.4	98.1
Glyphosate	96	81.0	104.9	81	34.6	31.3
Diflufenican	87	61.2	88.1	69	14.9	21.0
Epoxiconazole	89	11.0	10.1	88	8.3	7.3
Tebuconazole	58	18.4	41.5	44	4.7	12.0

Table 7. Average concentrations of the main pesticides in bottom sediments (Němčice)

Pesticide	Stream bottom			Reservoir bottom		
	Detection [%]	Av. conc. [µg/kg]	Stand. dev. [µg/kg]	Detection [%]	Av. conc. [µg/kg]	Stand. dev. [µg/kg]
AMPA	100	258.7	108.5	100	205.3	88.8
Glyphosate	100	49.8	46.9	100	35.6	34.4
Dimethachlor ESA	72	0.8	1.1	79	2.4	4.7
Metazachlor ESA	56	0.2	0.3	57	0.3	0.4
Metolachlor ESA	78	0.9	0.8	79	1.8	2.2

Table 8. Average concentrations of chosen pesticides in surface water (Němčice)

Pesticide	Stream (reg. monitoring)			Stream (storm events)			Reservoir		
	Detection [%]	Av. conc. [µg/l]	Stand. dev. [µg/l]	Detection [%]	Av. conc. [µg/l]	Stand. dev. [µg/l]	Detection [%]	Av. conc. [µg/l]	Stand. dev. [µg/l]
1,2,4-Triazole	100	0.198	0.064	100	0.131	0.056	100	0.141	0.064
AMPA	100	0.310	0.174	100	0.721	0.435	100	0.336	0.162
Atrazine-2-hydroxy	96	0.008	0.004	92	0.007	0.004	100	0.020	0.017
Dimethachlor ESA	100	0.415	0.330	96	0.118	0.144	100	0.452	0.363
Glyphosate	61	0.037	0.038	93	0.255	0.360	78	0.055	0.059
Metazachlor ESA	100	0.105	0.112	96	0.042	0.049	100	0.096	0.104
Metolachlor ESA	100	0.601	0.361	100	0.148	0.132	100	0.526	0.358
Terbuthylazine-hydroxy	100	0.014	0.006	99	0.024	0.013	100	0.049	0.044

µg/kg in the reservoir sediment (Fig. 6). AMPA and glyphosate appeared in all sediment samples, next often detected were different from soils (Table 7). The most significant contaminant of the sediments was AMPA (stream av. 259 µg/kg) and its concentrations were lower than in soil; glyphosate had the opposite profile.

Surface waters in the Němčice catchment obtained max. 50 pesticide substances (av. sum about 2.2 µg/l), predominantly metabolites in the vast majority of samples (Fig. 7–9). The average concentration of persistent relevant metabolite 1,2,4-triazole was 0.198 µg/l (Table 8). Other detected metabolites are not considered to be relevant. Table 8 shows a good conformity between concentrations in reservoir water and stream water from monthly monitoring. During storm events (RREs), outflow carries markedly higher amounts of AMPA (0.721 µg/l = the highest av. concentration through all water samples) and glyphosate, which are the most significant pollutants in soils and sediments. This relates to water erosion, soil washing and swirling bottom sediments.

The Uhřice catchment (Fig. 4) is the largest among the experimental catchments. Here are sloped blocks of arable land but also wide flat alluvial zones that retard even dam erosion runoff to the water bodies (Konečná et al. 2022). The soil (Chernozems – Table 1) retention and sorption capability here are better than in the other catchments (e.g., according to Pignatello 2022). Due to intensive growing of crops like corn, beet, and sunflower, the spectrum of herbicides is wider here. Moreover, the topsoil pesticides average sum 996.6 µg/kg (Fig. 5) is the highest comparing the other catchments, the value for subsoil was 160.4 µg/kg. Table 9 shows analysis results for 8 matters with detection in more than 50% topsoil samples. Likewise in the other catchments, the highest concentrations in topsoil were obtained for glyphosate (topsoil av. 181 µg/kg) and its metabolite AMPA (topsoil av. 108 µg/kg). The next highest concentrations were obtained for active substances of azole pesticides, epoxiconazole and tebuconazole.

Maximum of nine pesticide substances were positively detected in bottom sediments, but four of them were detected in more than 50% of samples. Their concentrations were higher in the sediments from the stream than from the reservoir (Table 10) and the main contaminants are again AMPA and glyphosate. A sample of the stream bottom sediment contained approximately 204.7 µg/kg of pesticides (as a sum), reservoir sediment 114.1 µg/kg (Fig. 6).

Table 9. Average concentrations of the main pesticides in soils (Uhřice)

Pesticide	Topsoil			Subsoil		
	Detection [%]	Av. conc. [µg/kg]	Stand. dev. [µg/kg]	Detection [%]	Av. conc. [µg/kg]	Stand. dev. [µg/kg]
AMPA	100	107.8	126.0	79	24.4	40.2
Azoxystrobin	82	60.8	112.5	24	4.5	12.1
Boscalid	55	11.0	30.9	21	12.0	2.6
Epoxiconazole	83	56.8	94.6	58	12.9	27.9
Glyphosate	93	181.2	472.7	64	27.5	67.9
Chloridazon-desphenyl	88	54.4	124.4	91	46.8	91.7
Metazachlor ESA	70	4.4	21.5	36	0.6	1.2
Metazachlor OA	70	7.0	40.6	24	0.1	0.3
Tebuconazole	83	73.8	127.7	30	6.6	16.4

Table 10. Average concentrations of the main pesticides in bottom sediments (Uhřice)

Pesticide	Stream bottom			Reservoir bottom		
	Detection [%]	Av. conc. [µg/kg]	Stand. dev. [µg/kg]	Detection [%]	Av. conc. [µg/kg]	Stand. dev. [µg/kg]
AMPA	100	127.5	47.4	81	65.7	40.7
Glyphosate	100	65.0	30.8	75	40.5	38.3
Chloridazon-desphenyl	100	10.8	6.0	31	2.1	3.4
Metazachlor ESA	54	0.3	0.5	31	0.7	0.9

Table 11. Average concentrations of chosen pesticides in surface water (Uhřice)

Pesticide	Stream (reg. monitoring)			Stream (storm events)			Reservoir		
	Detection [%]	Av. conc. [μg/l]	Stand. dev. [μg/l]	Detection [%]	Av. conc. [μg/l]	Stand. dev. [μg/l]	Detection [%]	Av. conc. [μg/l]	Stand. dev. [μg/l]
1,2,4-triazole	94	0.054	0.024	75	0.046	0.033	76	0.012	0.012
Acetochlor ESA	41	0.028	0.029	100	0.015	0.002	86	0.017	0.013
AMPA	100	1.306	0.838	100	0.253	0.095	100	0.481	0.292
Atrazine-2-hydroxy	100	0.036	0.022	100	0.020	0.008	100	0.038	0.025
Fluazifop	59	0.007	0.007	100	0.012	0.004	81	0.023	0.025
Glyphosate	94	0.524	0.545	100	0.065	0.036	62	0.037	0.037
Chloridazon	100	0.013	0.007	100	0.010	0.004	95	0.006	0.003
Chloridazon-desphenyl	100	2.721	2.658	100	1.265	0.265	90	0.722	0.423
Chloridazon-methyl desphenyl	100	0.261	0.107	100	0.248	0.026	81	0.136	0.095
Metolachlor ESA	82	0.032	0.031	100	0.020	0.003	86	0.015	0.008
Terbuthylazine-hydroxy	100	0.013	0.009	75	0.006	0.004	100	0.017	0.013

In the Uhřice catchment, up to 42 pesticide matters were positively detected in one sample of surface water. Most significant of them were chosen for Table 11. The highest average concentration was obtained for chloridazon-desphenyl (2.7 μg/l) from stream water regular monitoring. This metabolite is also the main contaminant of the reservoir water. The concentrations of AMPA were on the second place. The non-presence of azole pesticides in water is probably caused by their degradation in soils. The half-life of azole pesticides is about 1.5–4 months (Regulation EU No. 528/2012) and, as it was described above, the Uhřice is an area with lower erosion runoff to the water bodies. Better water quality in reservoir (av. pesticides sum 2.4 μg/l) comparing the stream monitoring value (7.5 μg/l) is documented by Figure 7.

Although there are significant natural differences among the studied catchments, glyphosate and AMPA appears in all of them. Limited use of glyphosate in EU was approved until 15 Dec. 2022. (Commission Regulation EU 2017/2324). Spectrum of other pesticides in soils, sediments and water differs. To compare the results from the 3 studied catchments, sum of all pesticide substances was chosen (Fig. 5–9).

The amount of pesticides in topsoil is the highest in the Uhřice catchment, av. content is about 1000 μg/kg (Fig. 5). Stream sediments in the

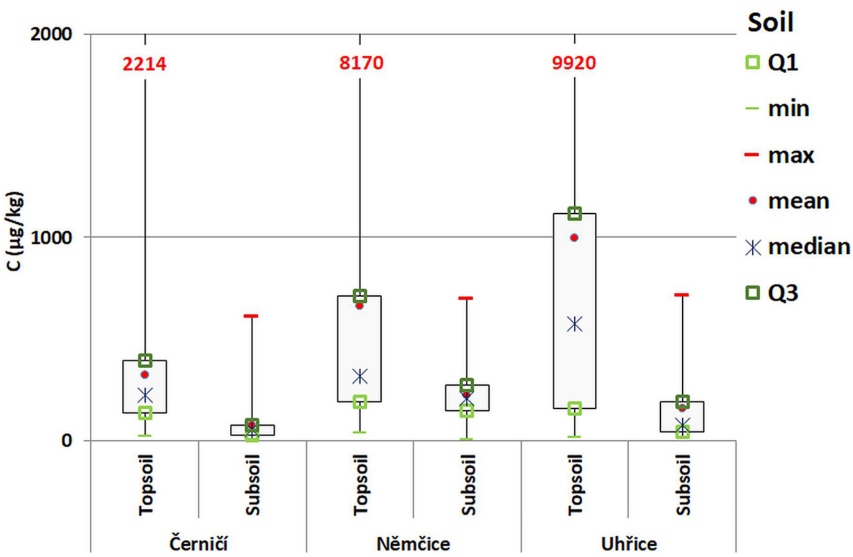

Figure 5. Pesticides sum in soils

Černičí are sandy, so they do not bind nutrients or contaminants. There are more fine particles in the stream sediments in Němčice and Uhřice catchment and the higher content of pesticides in them is apparent from Figure 6. The average sum of pesticides in subsoil is quite similar in all 3 reservoirs. It was mentioned above that the farming intensity and pesticides using is the highest in the Uhřice catchment. However, this catchment is the largest and transport of matters is retarded by the character of relief, good soil properties and the stream length.

Surface waters in the Černičí catchment seemed to be more polluted with pesticide substances than the Němčický catchment. Although their natural characteristics are similar, the state presented in Figure 7 is due to the significant influence of the drainage waters in the Černičí catchment. Amelioration systems here accelerate material transport from soil to surface water (Doležal, Kvítek 2004). The highest pesticide sum was obtained for stream waters in the Uhřice catchment from regular monitoring. Water quality in the Uhřice reservoir is visibly better. Considering the results from the bottom sediments, good self-cleaning ability of the flow can be stated. Moreover, the dense reed growth at the inlet of the reservoir apparently has a strong filtering function (Konečná et al. 2022).

Figures 8 and 9 document the differences in the transport of pesticides obtained from regular monitoring and from RREs. Higher concentrations of metabolites are characteristic of the

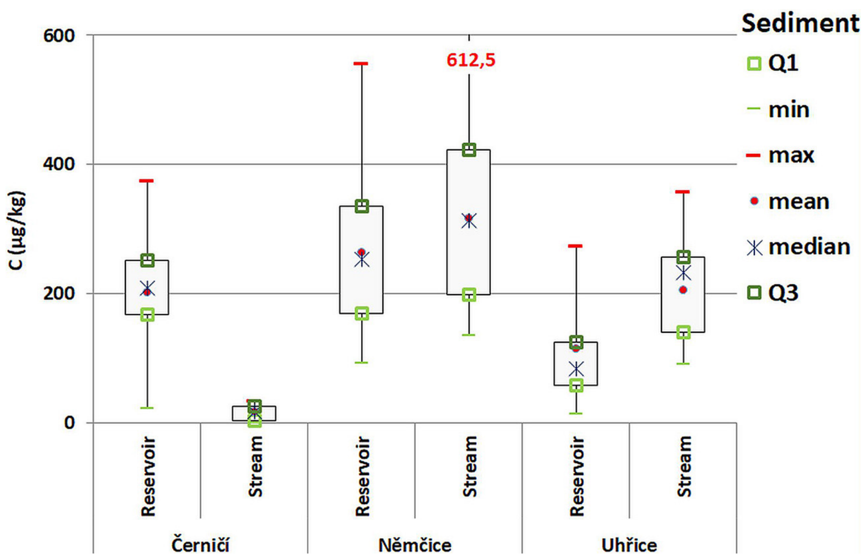

Figure 6. Sum of pesticides in bottom sediments

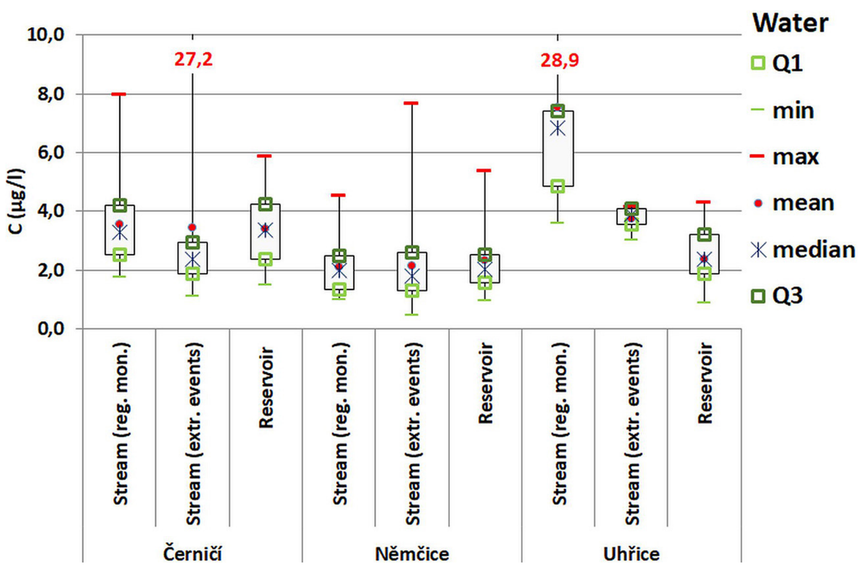

Figure 7. Sum of pesticides in surface waters

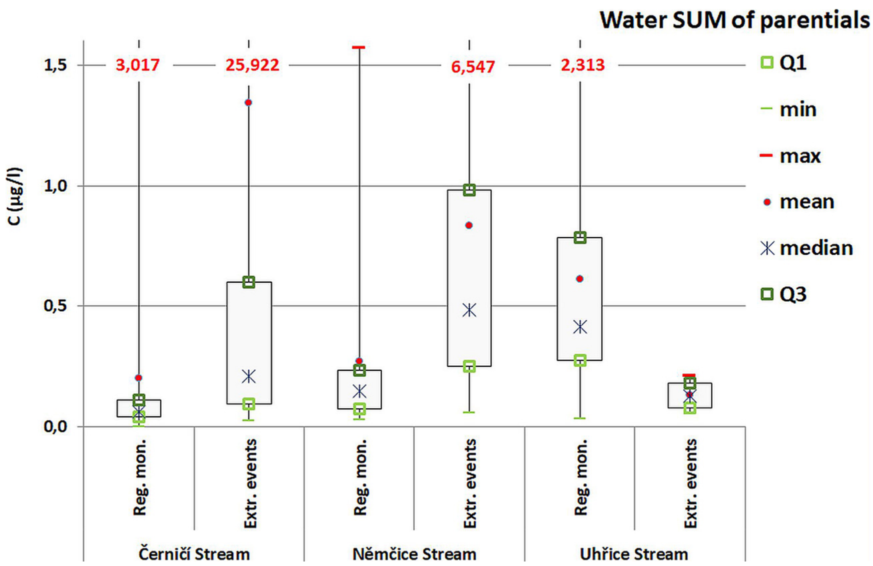

Figure 8. Sum of parent pesticide matters in surface waters

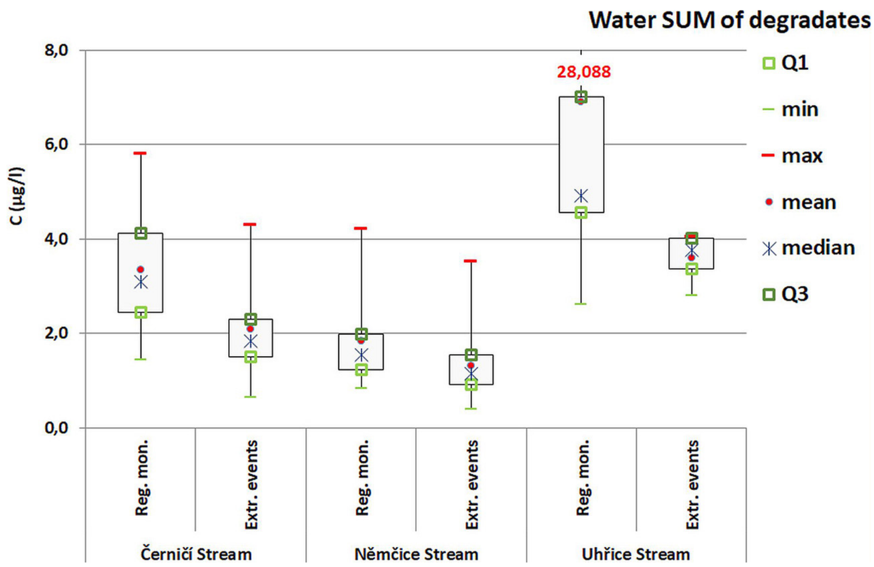

Figure 9. Sum of degraded pesticide matters (metabolites) in surface waters

general flow described by regular monitoring. During storm events, as a consequence of intensive soil erosion and washing-out processes, more parent pesticide matters were detected in the streams. The Černičí and Němčice catchments have gauging equipment allowing continual recording of RREs hydrological data and sampling of flood waters. Extreme events in the Uhřice stream were sampled only through monthly monitoring, which is why the Uhřice stream results in Figures 8 and 9 are dissimilar to the Černičí and Němčice streams. This knowledge illustrates how both monitoring systems (regular and aimed at RREs) are important for obtaining complex and critical results and conclusions of research on pesticide transport in the soil – water system.

CONCLUSIONS

The soils in the studied catchments contain mainly parent pesticide matters. Glyphosate, epoxiconazole and tebuconazole were detected in all sites. It agrees with the results of national and EU soil monitoring (Poláková, Kosubová 2021, Silva et al. 2018). Of the metabolites, the most often detected is AMPA. All pesticide concentrations in topsoil were markedly higher than in subsoil. The physical-chemical characteristics of the topsoil play a key role in the processes of pesticide binding, degradation and leaching (e.g. Kodešová et al. 2010, Pérez-Lucas et al. 2019). During soil erosion, the substances can be transported with the topsoil particles into water bodies. Vašíčková et al. (2019) drew attention to the ecotoxicity risk for soil organisms and agroecosystem functions, esp. for triazine, chloracetanilide, epoxiconazole, atrazine and others.

The pesticide spectrum in bottom sediments is narrower than in topsoil and metabolites occurred more often. Concentrations are related to the sediment structure – sandy sediments cannot bind substances as well as loamy or clayey sediments. Where loamy sediments were in the stream, the detected pesticide concentrations in reservoirs were lower than in stream bottoms.

Metabolites dominated over parent substances in surface waters. A lot of them (atrazine, 1,2,4-triazole, …) represent a risk for water ecosystems (de Souza et al. 2020). Parental compounds were detected mostly during RREs. A prerequisite for their leaching is that the rainfall-runoff episode occurs relatively shortly after their application. Zajíček et al. (2018) found out that the concentrations in drainage waters decreased until approximately two months after spraying and then almost absented. Water quality in reservoirs and streams in small catchments were similar especially during baseflow periods. In the larger catchment (Uhřice), pesticide retention in the reservoir water was better than in the stream. The self-cleaning ability of flow could probably have been better applied here.

It is important to mention that the active substance glyphosate and its metabolite AMPA do not occur in surface water, comparing the findings in solid matrices. This herbicide glyphosate is a polar, highly soluble substance, which are features that favour the pollution of the aquatic system. Even though its persistence is relatively short compared to other pesticides (it has a half-life that ranges from 2 to 91 days), when it is absorbed onto soil particles or sediment, glyphosate persists for longer and it may last up to 215 days (Silva et al. 2018). Its degradation product aminomethylphosphonic acid (AMPA) is considered the most important metabolite. AMPA is more persistent than glyphosate, with a higher half-life ranging from 76 to 240 days in soil.

The degradation product of epoxiconazole and tebuconazole is 1,2,4-triazole. This metabolite is a common metabolite of all azole pesticides, and it is considered toxicologically relevant. By Commission regulation (EU) 2021/2204, 1,2,4-triazole was included in REACH among carcinogenic, mutagenic, or toxic substances for reproduction. This metabolite is persistent in the environment and is a potential hazard for groundwater contamination (Halešová et al. 2021).

Therefore, it is necessary to pay close attention both to parent substances and metabolites in the environment, considering the transport processes in agricultural catchments and potential mutual influences of various environment components.

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