



Influence of the selected physicochemical properties of the active substances of plant protection products on the results of their model exposure assessment in the surface water compartment

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ABSTRACT

The paper presents the analysis of the influence of selected physicochemical properties of the active substances of the plant protection products on the results of model exposure assessment in the Surface Water compartment. It was demonstrated that, for the compounds moderately to highly persistent in the aquatic environment, the aqueous solubility and adsorption constant K_{iOC} determine the level of exposure to them of the aquatic organisms. The relationship is such that the higher water solubility and/or lower K_{iOC} usually result in longer modelled residence times in water columns. As a result, for such compounds, the modelled exposure of the aquatic organisms dwelling in water column is higher. On the other hand, the low aqueous solubility and/or high K_{iOC} promote faster migration of the compound to the sediment phase, what in turn increases the exposure of the sediment-dwelling aquatic organisms. The aqueous solubility is correlated not only with mobility in soil, expressed as K_{iOC} , but also with lipophilicity of the compound expressed by $\text{Log}P_{ow}$ values, therefore, with bioaccumulation potential. Low solubility of the given compound in water means its higher lipophilicity and, as a result its higher bioaccumulation potential. Therefore low-mobile to immobile compounds, displaying high soil K_{iOC} values, display also low aqueous solubility and high $\text{Log}P_{ow}$ values, therefore they tend to migrate faster and to greater extent to the sediment phase, increasing risk to dwelling them aquatic organisms, as well as they display higher potential for bioaccumulation in the tissues of living organisms.

Keywords: Pesticides; Exposure assessment; Surface water; Predicted environmental concentrations; Sorption; Mobility

1. Introduction

The management of water resources, related to the increasing human activity and economic development has become one of the key issues, in particular in the context of decreasing resources of freshwater and its quality, combined with increasing demand for it. Monitoring of pesticides needs high technical effort and costly analysis, so cost-saving computer-based approaches are used to model pesticide transport and estimate pesticide loads

[1]. Mathematical programming techniques and numerical models used in it become increasingly applied and very promising in addressing this problem [2]. That fact demonstrate the research activities aimed on systematic identification and evaluation of relevant scientific publications [3]. However, although for the period 2010–2017, being the time-span of the evoked literature search activity, were identified numerous publications presenting the developed numerical modelling tools to be used in the preparation of the effective strategies for water treatment

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management, much less consideration in those publications was given to the practical applicability of such tools, including examples of such activities. In conclusion to their study, Archibald and Marshall [3] indicated the need for closer cooperation between the academic researchers and practitioners, such as decision makers responsible for water resources management, to develop effective numerical tools that could help in the development of the effective water resource management strategies.

One of the key elements of such strategies is the protection of the aquatic habitats being under constant and increasing anthropogenic pressure, such as mid-field surface water bodies, that are the receivers of the agrochemicals used on the adjacent agriculturally used areas. One group of such agrochemicals are the plant protection products, and the management strategies aimed at protecting the surface water ecosystems from their negative influence substantially rely on the outcome of the assessment of the exposure and subsequent risk performed using the numerical tools specifically designed for that purpose.

The plant protection products, commonly named pesticides, play a very important role in the global agriculture. It is estimated that the annual use around the world is 2.5 million tonnes and of which 99.9% of that load reaches the environment. It is, therefore, necessary to appropriately manage the use of the pesticides in order to minimise their impact on the environment [4], food quality [5] and drinking water quality [6,7]. This adequate management comprises the assessment of the exposure of various living organisms to the contact with the active substances of the plant protection product and the resulting risk [8,9] and, simultaneously, improve application efficiency. As it was stated by Pereira et al. [10] the more effective an application is, the less damage there will be to the ecosystem and the living organisms. The aim of this study is the analysis of the selected factors influencing the model exposure and risk assessment performed for the pesticides on the example of the model exposure assessment in the surface water (SW) compartment performed for the regulatory purposes in the EU.

The way the active substances of the plant protection products interact with the environment is determined by the method of their application. Spray application may result in pollution of the various components of the environment, including surface water bodies. Three major routes of migration of pesticides to the surface water bodies, currently taken into account in the model exposure assessment, are spray drift, runoff and drainage.

In case of the aquatic environment, the exposure to the active substances of the plant protection products is usually more limited than it is in case of the terrestrial ecosystems, mainly because of the relatively small area of the mid-field surface water bodies. The exposure and risk results from the direct contact with polluted water or is indirect, resulting from the consumption of the contaminated food. The chemicals compounds dissolved in water or present there in suspension may be directly uptaken by aquatic plants [11] or by aquatic invertebrates and vertebrates – fish and amphibians, in consequence affecting also many birds species [12]. In case of invertebrates and fish they are absorbed mainly through breathing organs (gills for fish). Other possible uptake method is the dermal absorption [13]. The potential of the

chemicals to migrate from water to the living organisms and to accumulate in tissues are determined by their hydrophobicity and lipophilicity. As in the terrestrial environment in the aquatic environment there exists a probability of the secondary poisoning through the inclusion of the pesticides to the food chain and transfer to the higher trophic levels.

The active substances of the plant protection products may also change the pH of surface water bodies, leading even to the permanent change of the character from oligotrophic to dystrophic, what in turn may result in the die-out of the certain group of aquatic organisms living there, including fish [14].

In general, the whole risk assessment for the surface water compartment and its inhabitants consists of the following stages:

- (1) Identification of the hazards;
- (2) Characterisation of the hazards;
- (3) Assessment of the exposure;
- (4) Comparison of the data concerning the hazards and the exposure and on that basis the assessment of the risk and the probability of its occurrence.

The exposure assessment – stage 3 of the whole process, is usually performed using numerical models run on the computers. The calculations carried out that way should take into account the worst-case application pattern, preferably experimental data on physical and chemical properties instead of estimated [15] and be performed using the validated modelling tools [16,17]. The outcome of such assessment is usually the values called predicted environmental concentrations – PEC. They may be calculated for both water – PEC_{SW} and sediment – PEC_{SED} compartments [18]. In addition, they may be calculated in function of time – as initial, short-term and long-term values, informing that way about the exposure profile over a certain period of time (e.g., 1 year).

The advantage of the use of the numerical computer models in the exposure assessment is that this enables to correlate several parameters characterising fate and behaviour of the given compound in the environment, such as its physicochemical properties (e.g., saturated vapour pressure, aqueous solubility), mobility characterised by the adsorption constants or coefficients and persistence characterised by the degradation rate constants, with various environmental processes and phenomena, such as migration routes, characteristic of the receiving bodies or pedo-climatic conditions.

The intrinsic physicochemical properties of the modelled compound are the factors strongly influencing their fate and behaviour in the environment and as a result also the exposure and ecotoxicological profiles [19].

In case of the exposure assessment carried out in the EU for the regulatory purposes, the tiered approach was adopted, consisting of four individual tiers, called Steps, having the increasing level of complexity with each step, reflected in the amount of input data required at each Step as well as in conservativeness of the obtained results – PEC values.

The more conservative assessment performed at lower tiers – Steps 1–2 are carried out using limited amounts of substance-specific and crop-specific input parameters,

simplified model of the receptor water body and very simple pedo-climatic scenario. As a result, the obtained PEC values are conservative and usually it becomes necessary to perform further evaluation at higher tiers.

At Step 3 broader amount of data concerning substance-specific and crop-specific input parameters is required. Also at this Step are introduced more complex models of receiving surface water bodies and pedo-climatic scenarios [20,21]. As a result, the obtained PEC values are more realistic, although they still represent the realistic worst case. Finally, the highest tier – Step 4 is based on the same principles regarding the input parameters and scenarios, but an additional factor is introduced, which is the mitigation measures lowering the exposure and the risk resulting from it, such as buffer zones. That mitigation consists of the reduction of the load of the modelled compound reaching the model water body with one of the pre-defined, common to all levels of assessment, migration routes – spray drift (taken into consideration at all Steps) and/or drainage or runoff (taking into consideration together at Steps 1–2 and separated at Steps 3 and 4).

All calculations at Steps 1–3 are performed using the validated modelling tools, developed by FOCUS. In case of the Step-4 assessment, there is no validated FOCUS tool, but a common practice is to use a SWAN tool, which is a tool helping to parameterise the standard Step 3 modelling tool in order to perform Step-4 assessment.

The aim of the present work was to determine the relationship between the selected physicochemical properties of the active substances of the plant protection products, in particular their Freundlich adsorption constant, and the magnitude and profile of exposure of the aquatic organisms modelled using the numerical tools currently used for the regulatory purposes in the EU at higher levels of assessment – mainly at tier (Step 3). The additional task was to demonstrate how and to what extent, in such modelling assessment, the selected physicochemical parameters influence the routes of migration of the modelled active substances to the receiving model water bodies.

2. Materials and methods

To perform the analysis being the aim of the study, 40 active substances of the plant protection products authorised for the use in the EU by means of listing them in the Annex of the Commission Implementing Regulation (EU) No. 540/2011 were selected. The degradation products of those compounds were not taken into consideration in this analysis.

As K_{ioc} was identified as the governing parameter in determining the exposure [22], the selected substances were divided into groups on the basis of their mobility in soil defined according to the SSLRC Mobility Classification Systems.

In line with that classification, the substances used in the analysis were divided into four following groups:

- (I) Very mobile and mobile, having $K_{ioc} < 15$ mL/g or in range 15–74 mL/g;
- (II) Moderately mobile, having K_{ioc} in range 75–499 mL/g;
- (III) Slightly mobile, having K_{ioc} in range 500–4,000 mL/g;
- (IV) Non-mobile, having $K_{ioc} > 4,000$ mL/g.

The detailed data on physicochemical properties of the active substances used in the analysis were taken from the data base “The FOOTPRINT PPDB” (Pesticide Properties Database) accessible on-line via the web address <http://sitem.herts.ac.uk/aeru/footprint/en/index.htm>. All those substance-specific parameters for each compound of concern, used as input parameters in modelling exercise are presented below in Table 1.

The modelling tool used in the assessment was FOCUS SWASH ver. 3.1 shell – a complex modelling tool comprising FOCUS PRZM, FOCUS MACRO and FOCUS TOXSWA numerical models, recommended to be used for the regulatory purposes in the EU, in the assessment of the exposure assessment in the surface water compartment at Step 3.

The calculations were performed for three FOCUS SW scenarios, identified as being relevant for Poland: D3 (ditch), D4 (pond and stream) and R1 (pond and stream). Those scenarios have the common migration route to the Surface Water bodies – spray drift (the amount of product that did not reach the target during spray application [23], while the second migration route is different – in case of D3 and D4 scenarios it is artificial drainage, while for R1 scenario the second assumed migration route is runoff. Those three scenarios were selected because they were identified to be the most relevant FOCUS SW scenarios for Poland, as country representative for Central Europe, therefore the results of that research activity could have been easily related to the real situations and used in practice in planning of the mitigation strategies and introducing mitigation measures reducing the risk to the surface water bodies resulting from the use of the plant protection products.

It shall be indicated that for some compounds, namely those having high volatility potential, the migration route concurrent with spray drift is dry deposition; however, in this analysis, in order not to complicate the whole analysis it was not taken into consideration. At the same time, it is worth of mentioning that the problem of volatilization of pesticides from soil and plant surfaces, the influence of that phenomenon on the exposure assessment and possibilities of its inclusion into currently used regulatory modelling tools was a subject of several research activities, for example, that undertaken by Mao et al. [24]. In their paper, those researchers provide the background for inclusion of the volatility phenomenon into the current regulatory models, examine the possibilities for development of sophisticated tools adequately addressing it and discuss the possible influence of the implementation of the developed modelling strategies on the existing modelling tools on the outcome of the numerical assessment.

The assessment was carried out using winter cereals as a treated crop. Two different application periods were assumed, corresponding to two different ranges of the growth stages – one for BBCH 00-09 (post sowing but pre-emergence) and BBCH 40-89 (maturation to harvest). Those periods were selected to represent two different situations regarding conditions of the treated area adjacent to the receiving water body:

- cooler and wetter period with minimal crop cover;
- warmer and drier period with full crop cover.

Table 1
Key parameters of the active substances of the plant protection products used in the study

Substance name	Key intrinsic properties								
	Physicochemical properties				Mobility – Freundlich isotherm adsorption parameters		Persistence in the environment – DT ₅₀ [d]		
	Molar weight [g/mol]	Saturated vapour pressure [Pa]	Aqueous solubility [mg/L]	LogP _{ow} [-]	K _{ioc} [mL/g]	1/n [-]	Soil	Water	Sediment
Mobility class I – very mobile and mobile compounds (K _{ioc} < 15 mL/g and K _{ioc} = 15–74 mL/g)									
Dicamba	221.04	1.67E-03	250,000	-1.88	12	1.00	4.2	40	1,000
Fosthiazate	283.35	5.60E-04	9,000	1.68	14	0.89	53	36	1,000
Florasulam	359.28	1.00E-05	6,360	-1.22	22	0.92	1.6	18	1,000
Prosulfuron	419.38	3.50E-06	4,000	1.5	23	0.9	113	50	1,000
Propoxycarbazone-sodium	420.37	1.00E-08	42,000	-1.55	28.8	0.9	61	50.7	1,000
Sulcotrione	328.77	5.00E-06	1,670	-1.7	36	0.839	25.3	9.5	1,000
Maleic hydrazide	112.1	1.00E-06	144,000	0.011	45	0.9	0.5	57	1,000
Flazasulfuron	407.37	1.33E-05	2,100	-0.06	46	0.9	8	15	1,000
2,4-D	221.04	1.87E-05	23,180	-0.83	56	0.8	14	29	1,000
MCPA	200.62	4.00E-04	29,390	0.81	74	0.68	24	13.5	1,000
Mobility class II – moderately mobile compounds (K _{ioc} = 75–499 mL/g)									
Mesotrione	339.32	5.70E-06	160	0.11	80	0.9	17	5.3	1,000
Oxasulfuron	406.41	2.00E-06	1,700	-0.81	85	0.9	10	12	1,000
Iprovalicarb	320.43	7.90E-08	17.8	3.20	106	0.9	105	54	1,000
Acetamiprid	222.67	1.73E-07	2,950	0.80	107	0.9	2.6	4.7	1,000
Amitrole	84.08	3.30E-05	264,000	-0.97	111	0.9	5	71	1,000
Ethoxysulfuron	398.39	6.60E-05	5,000	1.01	134	0.9	18	17	1,000
Flufenacet	363.33	9.00E-05	56	3.2	202	0.9	32	54	1,000
Trinexapac-ethyl	252.26	2.16E-03	10,200	-0.29	280	0.94	0.33	4.2	1,000
Iprodione	330.17	5.00E-07	12.2	3.1	373	0.93	26	30	1,000
Azoxystrobin	403.4	1.10E-10	6.7	2.5	423	0.86	279	46	1,000
Mobility class III – slightly mobile compounds (K _{ioc} = 500–4,000 mL/g)									
Linuron	249.09	5.10E-03	63.8	3	620	0.85	87	48	1,000
Phenmedipham	300.31	7.00E-10	1.8	3.59	888	0.85	37	0.2	1,000
Flumioxazine	354.33	3.20E-03	1.79	2.55	889	0.9	19	2	1,000
Picoxystrobin	367.32	5.50E-06	3.1	3.6	898	0.99	24	7.5	1,000
Zoxamide	336.64	1.30E-05	0.681	3.76	1,224	0.9	3	3	1,000
Acibenzolar-s-methyl	196.25	4.60E-04	7.7	3.1	1,285	0.78	0.5	1	1,000
Flusilazole	315.39	3.87E-05	41.9	3.87	1,664	0.9	427	1	1,000
Ziram	305.84	1.80E-05	0.967	1.65	2,023	0.9	0.05	0.25	1,000
Trifloxystrobin	408.37	3.40E-06	0.61	4.5	2,377	0.96	2	1.1	1,000
Cinidon ethyl	394.3	1.00E-05	0.057	5.4	3,262	0.9	1.3	0.1	1,000
Mobility class IV – non-mobile compounds (K _{ioc} > 4,000 mL/g)									
Benalaxyl	325.40	5.72E-04	28.6	3.54	4,998	0.9	75	38	1,000
Esfenvalerate	419.90	1.20E-09	0.001	6.24	5,300	1.07	41	30	1,000
Indoxacarb	527.83	6.00E-06	0.2	4.65	6,450	0.9	5	1.4	1,000
Aclonifen	264.66	1.60E-05	1.4	4.37	7,126	0.92	62.3	4.2	1,000
Chlorpyrifos	350.89	1.43E-03	1.05	4.7	8,151	0.9	76	5	1,000
Benfluralin	335.28	1.73E-03	0.065	5.19	10,777	0.9	38.2	0.75	1,000
Dodemorph	281.48	4.80E-04	100	4.6	25,200	0.86	41	1.3	1,000
Alpha-cypermethrin	416.30	3.40E-07	0.004	5.5	57,889	0.9	100	1.3	1,000
Pyrethrins	328.4	1.00E-06	0.001	5.9	100,000	0.9	8	44	1,000
Metiram	1088.6	1.00E-05	2	1.76	500,000	0.9	1	0.7	1,000

The purpose of such selection as to demonstrate the influence of the conditions other than the intrinsic parameters of the modelled substances on their modelled migration potential to surface water bodies and the resulting exposure profiles.

For all compounds, a single application rate – 1,000 g/ha – for both application periods was used. The assumed application method was ground spraying.

It was decided to perform the assessment only for single applications. That was done in order to limit the factors influencing the obtained results and therefore complicating the whole analysis.

All scenario- and crop-specific parameters used in calculations are additionally presented in Table 2.

The obtained results subjected to the subsequent analysis, were the maximum actual PEC values obtained in surface water – PEC_{SW} and sediment – PEC_{SED} compartments. Also analysed were the concentration profiles provided in numerical form – as PEC_{SW} and PEC_{SED} values determined and reported by the modelling tool during 100 d after the maximum PEC value was reported, and in graphical form as continuous concentration profiles in water and sediment compartments.

The characterised above numerical and graphical results returned by the modelling tool used in this research are used to define the exposure profile of the aquatic organisms dwelling in modelled surface water body, in both water column and sediment phase.

The reliability of the results was ensured by applying pre-defined in the modelling tool principle of the 90th percentile.

3. Results

The results of the model exposure assessment for the Surface Water compartment – maximum PEC_{SW} [$\mu\text{g/L}$] and PEC_{SED} [$\mu\text{g/kg}$] values for all 40 active substances subjected

to the analysis are presented in Tables 3–6. The results were divided into groups, presented in separate tables, using two key criteria – mobility in soil and BBCH growth phase of the treated crop used in simulation. The division into categories on the basis of the mobility, characterised in the previous section, resulted in creation of the four groups of results. Additionally each such group was divided into two subgroups to reflect two different growth stage of the treated model crop used in the modelling exercise – BBCH 00-09 and BBCH 40-89.

In order to indicate the dominant migration route for each modelled compound, the cells containing obtained maximum PEC_{SW} values were differently shaded – the lightest grey was used when the dominant migration route was the spray drift, medium-grey to indicate drainage as a dominant migration route and dark grey for runoff.

To identify the dominant migration route for each simulation two parameters calculated by the modelling tool were compared: the application date and the date of the maximum, both given in format “day/month/year”. The full format of those two parameters is “day/month/year/hour:minutes”, but that last element was not taken into account. That was done to simplify the analysis, because that element may introduce the additional migration route – the atmospheric dry deposition, relevant for the volatile compounds.

4. Discussion

The obtained results of the calculations confirm that the substances moderately to highly persistent in soil that have low K_{iOC} are most prone to migration to receiving surface water bodies with drainage or runoff. Both two phenomena are observed mainly in case of very mobile and mobile compounds, as well as, to lesser extent for moderately mobile compounds in soil, that is, all those having K_{iOC} in range 1–499 mL/g. For majority, those compounds drainage was observed as dominant migration route in case of D4 scenario (pond and stream). Its absence in case of D3 scenario may

Table 2
Data on application patterns used in the assessment

Parameter	Application pattern	
	I (pre-emergence)	II (pre-harvest)
Application method	Ground spray	Ground spray
Number of applications	1	1
FOCUS Crop	Winter cereals	Winter cereals
BBCH growth phase assumed in calculations	00-09	40-89
Assumed crop interception factor [%]	Calculated internally by the tool on the basis of the defined application window (on the basis of the information taken from the relevant guidelines it may be estimated to be 0%)	Calculated internally by the tool on the basis of the defined application window (on the basis of the information taken from the relevant guidelines it may be estimated to be 70% and higher)
FOCUS Scenarios used in calculations	D3 ditch	D3 ditch
	D4 pond	D4 pond
	D4 stream	D4 stream
	R1 pond	R1 pond
	R1 stream	R1 stream

Table 3

Results of the model calculations for very mobile ($K_{iOC} < 15$ mL/g) and mobile ($K_{iOC} = 15\text{--}74$ mL/g) compounds, applied to the treated crop at its growth phase BBCH 00-09 and BBCH 40-89 with indicated dominant migration route

Active substance	Key physicochemical properties			Results – PEC _{sw} [ug/L] and PEC _{sed} [ug/kg] obtained for scenario:									
	Log- P_{ow}	Aqueous solubility [mg/L]	K_{iOC} [mL/g]	D3 ditch		D4 pond		D4 stream		R1 pond		R1 stream	
				water	sedi- ment	water	sedi- ment	water	sedi- ment	water	sedi- ment	water	sedi- ment
Applied to the treated crop at its growth phase BBCH 00-09													
Dicamba	-1.88	250,000	12	6.357	0.526	0.236	0.157	5.482	0.272	0.489	0.244	36.365	1.689
Fosthiazate	1.65	9,000	14	25.787	26.451	40.528	40.816	31.034	22.062	0.610	0.432	37.202	2.769
Florasulam	-1.22	6,360	22	6.313	0.591	0.219	0.129	5.482	0.354	0.345	0.251	14.922	1.278
Prosulfuron	1.5	4,000	23	33.818	49.515	59.520	75.301	40.205	38.586	0.658	0.579	41.172	3.537
Propoxycarba- zone – sodium	-1.55	42,000	28.8	14.994	19.139	32.838	46.768	26.542	22.585	0.667	0.651	42.024	3.908
Sulcotrione	-1.7	1,670	36	6.687	2.049	6.883	9.447	9.845	6.816	0.621	0.579	41.102	4.542
Maleic hydra- zyne	0.011	144,000	45	6.313	0.819	0.219	0.294	5.482	0.483	0.219	0.287	4.167	0.288
Flazasulfuron	-0.06	2,100	46	6.319	0.850	0.620	0.981	5.482	0.583	0.583	0.557	36.455	4.078
2,4-D	-0.83	23,180	56	6.313	1.160	1.763	4.341	5.481	2.100	0.634	1.114	40.107	5.692
MCPA	-0.81	29,390	74	6.311	1.776	2.454	7.782	5.481	5.163	0.645	1.730	43.150	8.270
Applied to the treated crop at its growth phase BBCH 40-89													
Dicamba	-1.88	250,000	12	6.359	0.645	0.219	0.093	5.482	0.260	2.969	1.216	28.824	2.824
Fosthiazate	1.65	9,000	14	14.359	12.703	8.625	12.703	6.379	5.262	3.235	1.722	31.641	3.615
Florasulam	-1.22	6,360	22	6.359	0.867	0.219	0.867	5.482	0.354	2.455	1.167	23.867	1.143
Prosulfuron	1.5	4,000	23	22.463	31.527	17.143	31.527	11.434	12.041	3.167	2.175	30.857	4.155
Propoxycarba- zone – sodium	-1.55	42,000	28.8	11.236	11.768	7.919	11.768	5.670	5.935	3.088	2.337	30.049	4.432
Sulcotrione	-1.7	1,670	36	6.425	1.482	5.482	1.482	0.717	1.180	0.618	0.578	40.888	4.520
Maleic hydra- zyne	0.011	144,000	45	6.359	1.223	0.219	1.223	5.482	0.483	0.957	0.969	7.999	1.924
Flazasulfuron	-0.06	2,100	46	6.359	1.204	0.219	1.204	5.482	0.486	2.651	1.671	26.076	4.775
2,4-D	-0.83	23,180	56	6.359	1.723	0.219	1.723	5.481	0.667	2.575	3.029	25.003	6.004
MCPA	-0.81	29,390	74	6.358	2.649	0.219	2.649	5.480	0.945	2.173	3.447	21.330	7.687



 Spray drift
 Drainage
 Runoff

be explained by the fact that of all FOCUS SW scenarios that one is known to be least prone to drainage. Runoff as a dominant migration route was observed for practically all compounds belonging to the characterised above group in case of R1 (pond and stream) scenario. The only exception from that rule was observed for maleic hydrazide, the compound although being mobile in soil ($K_{iOC} = 45$ mL/g), displaying very low persistence in that compartment – $DT_{50} = 0.5$ d. Hence, for that compound the spray drift was identified as the dominant migration route in all scenarios used in the assessment.

Also important in case of the compounds belonging to the above two mobility groups is their good aqueous solubility, promoting faster migration of the toxic compounds to the water bodies. That good solubility in combination with

low K_{iOC} usually results in longer residence times of those compounds in water column. That in turn prolongs the duration of the exposure to them of the aquatic organisms dwelling in water column.

On the other hand, low aqueous solubility increases the lipophilicity of the compound, expressed by the value of $\text{Log}P_{ow}$ (octanol/water partition coefficient). The compounds having $\text{Log}P_{ow} \geq 3.0$ have a higher affinity to lipid tissue of the living organisms, hence display higher tendency for bioaccumulation in the aquatic organisms and to the secondary poisoning resulting from inclusion and transfer within the food chain.

Slightly mobile substances, having $K_{iOC} = 500\text{--}4,000$ mL/g even if highly persistent in soil, were demonstrated to be much less prone to be transferred to the surface water

Table 4

Results of the model calculations for moderately mobile (K_{foc} 75–499 mL/g) compounds, applied to the treated crop at its growth phase BBCH 00-09 and BBCH 40-89, with indicated dominant migration route

Active substance	Key physicochemical properties			Results – PEC _{sw} [ug/L] and PEC _{sed} [ug/kg] obtained for scenario:									
	Log- P_{ow}	Aqueous solubility [mg/L]	K_{foc} [mL/g]	D3 ditch		D4 pond		D4 stream		R1 pond		R1 stream	
				water	sediment	water	sediment	water	sediment	water	sediment	water	sediment
Applied to the treated crop at its growth phase BBCH 00-09													
Mesotrione	0.11	160	80	6.316	0.960	1.891	1.066	5.482	1.538	0.575	0.516	39.504	5.537
Oxasulfuron	−0.81	1,700	85	6.313	1.070	0.798	1.482	5.482	0.979	0.575	0.682	36.396	5.254
Iprovalicarb	3.2	17.8	106	6.411	1.587	8.507	19.911	10.755	8.323	0.648	1.150	40.540	6.393
Acetamiprid	0.8	2,950	107	6.312	1.166	0.219	0.152	5.481	0.688	0.354	0.385	20.639	3.368
Amitrole	−0.97	264,000	111	6.312	1.209	0.224	0.626	5.481	0.706	0.511	0.988	28.506	4.646
Ethoxysulfuron	1.01	5,000	134	6.312	1.306	2.465	5.360	5.481	3.343	0.563	0.914	34.583	6.030
Flufenacet	3.2	56	202	6.312	1.567	5.206	15.610	8.005	7.463	0.523	1.457	29.971	6.086
Trinexapacethyl	−0.29	10,200	280	6.311	1.586	0.219	0.187	5.481	0.814	0.219	0.245	4.166	0.437
Inprodione	3.1	12.2	373	6.311	1.843	3.018	10.284	5.480	5.492	0.573	1.974	19.953	4.826
Azoxystrobin	2.5	6.7	423	6.310	2.231	11.012	52.293	14.765	25.080	0.803	3.801	18.696	5.127
Applied to the treated crop at its growth phase BBCH 40-89													
Mesotrione	0.11	160	80	6.359	1.090	0.219	0.071	5.482	0.554	2.331	1.298	23.839	5.774
Oxasulfuron	−0.81	1,700	85	6.359	1.558	0.219	0.180	5.482	0.613	2.299	1.782	22.600	5.690
Iprovalicarb	3.2	17.8	106	7.100	5.542	4.741	14.290	5.482	6.133	2.370	3.313	22.687	6.412
Acetamiprid	0.8	2,950	107	6.358	1.621	0.219	0.129	5.481	0.657	1.624	1.029	16.471	4.982
Amitrole	−0.97	264,000	111	6.358	1.820	0.219	0.407	5.481	0.676	1.994	3.027	18.755	5.618
Ethoxysulfuron	1.01	5,000	134	6.358	1.936	0.220	0.437	5.481	0.734	2.036	2.222	19.655	6.471
Flufenacet	3.2	56	202	6.358	2.385	0.612	2.253	5.481	0.948	1.749	3.414	16.290	7.088
Trinexapacethyl	0.29	10,200	280	6.357	2.227	0.219	0.161	5.481	0.810	0.219	0.243	4.186	1.165
Inprodione	3.1	12.2	373	6.357	2.871	0.340	1.449	5.480	0.925	1.252	2.582	11.395	7.508
Azoxystrobin	2.5	6.7	423	6.355	3.626	3.480	18.230	5.479	8.777	1.042	4.372	9.069	8.449



 Spray drift
 Drainage
 Runoff

bodies either with drainage (in D3 and D4 scenarios) or with runoff (in R1 scenario). For the substances classified as non-mobile in soil – those with $K_{foc} > 4,000$ mL/g, regardless of their persistence in soil, the spray drift was demonstrated to be the dominant migration route to the receiving surface water bodies for all three FOCUS scenarios used in the analysis. The resulting maximum PEC_{sw} and PEC_{sed} values were lower.

The correlation between high K_{foc} value and the low aqueous solubility of the given compound is very important in case of the exposure of the sediment-dwelling organisms. Such compounds in water column quickly give saturated solutions and tend to relatively rapidly migrate to the sediment phase. As a result, because of the short residence time of such compound in water column the exposure to it of the aquatic organisms dwelling there is short, while the sediment dwellers are exposed to it for much longer period. Moreover, the compounds that migrate to the sediment may accumulate there.

At the same time, it has to be indicated that the assumed in calculations persistence in sediment – $DT_{50} = 1,000$ d in many cases is not a measured value, but a regulatory default recommended to be used by the current Guidelines in case the measured value is not available. This is a common approach in case the only available experimental value characterising the true degradation rate of the given compound is the whole-system DT_{50} value (for water and associated sediment), the sediment phase DT_{50} could not have been determined and available water DT_{50} is a dissipation value informing about the rate of migration to the sediment phase and, possibly, of the true degradation. For that reason, such values cannot be used in modelling to avoid a so-called “double-counting”.

In the model exposure assessment for the surface compartment performed using FOCUS modelling tools, the application period plays a very important role. Being correlated determines the amount of the given active compound that reaches the soil surface and may be

Table 5

Results of the model calculations for slightly mobile (K_{ioc} 500–4,000 mL/g) compounds, applied to the treated crop at its growth phase BBCH 00-09 and BBCH 40-89, with indicated dominant migration route

Active substance	Key physicochemical properties			Results – PEC _{sw} [ug/L] and PEC _{sed} [ug/kg] obtained for scenario:									
	Log- P_{ow}	Aqueous solubility	K_{ioc} [mL/g]	D3 ditch		D4 pond		D4 stream		R1 pond		R1 stream	
				water	sediment	water	sediment	water	sediment	water	sediment	water	sediment
Applied to the treated crop at its growth phase BBCH 00-09													
Linuron	3	63.8	620	6.307	2.498	2.452	16.476	5.476	7.861	0.923	5.286	12.939	4.048
Phenmedipham	3.59	1.8	888	6.304	1.679	0.218	0.116	5.474	1.008	0.409	0.405	8.529	4.079
Flumioxazine	2.55	1.79	889	6.306	2.341	0.218	0.348	5.476	1.030	0.498	1.088	8.512	2.838
Picoxystrobin	3.6	3.1	898	6.309	2.135	0.519	1.963	5.478	1.586	0.695	1.839	10.248	3.054
Zoxamide	3.76	0.681	1,224	6.303	2.583	0.218	0.379	5.473	1.079	0.218	0.585	4.161	1.527
Acibenzolar-s-methyl	3.1	7.7	1,285	6.294	2.732	0.217	0.301	5.465	1.103	0.217	0.464	4.154	0.547
Flusilazole	3.87	41.9	1,664	6.300	2.522	0.856	3.568	5.470	9.992	0.598	1.255	5.551	5.065
Ziram	1.65	0.967	2,023	6.297	1.929	0.218	0.087	5.468	0.896	0.218	0.145	4.156	0.505
Trifloxystrobin	4.5	0.61	2,377	6.299	2.513	0.218	0.227	5.470	1.054	0.218	0.325	4.158	0.898
Cinidon ethyl	5.4	0.057	3,262	6.287	1.277	0.218	0.040	5.459	0.670	0.217	0.072	4.149	0.565
Applied to the treated crop at its growth phase BBCH 40-89													
Linuron	3	63.8	620	6.353	4.256	0.657	5.301	5.476	2.383	0.751	4.377	6.089	9.083
Phenmedipham	3.59	1.8	888	6.350	1.163	0.218	0.053	5.474	0.754	0.218	0.394	4.180	9.787
Flumioxazine	2.55	1.79	889	6.352	3.132	0.218	0.216	5.470	1.009	0.429	0.775	4.604	7.493
Picoxystrobin	3.6	3.1	898	6.355	3.360	0.219	0.405	5.478	0.978	0.748	1.327	6.733	8.360
Zoxamide	3.76	0.681	1,224	6.349	4.043	0.218	0.323	5.473	1.070	0.268	0.842	4.180	7.890
Acibenzolar-s-methyl	3.1	7.7	1,285	6.340	3.610	0.217	0.236	5.465	1.076	0.217	0.325	4.173	2.809
Flusilazole	3.87	41.9	1,664	6.346	3.228	0.337	1.427	5.470	3.941	0.267	0.869	4.178	11.812
Ziram	1.65	0.967	2,023	6.343	1.456	0.218	0.066	5.468	0.824	0.218	0.145	4.156	0.505
Trifloxystrobin	4.5	0.61	2,377	6.345	3.296	0.218	0.185	5.470	1.031	0.218	0.468	4.177	7.416
Cinidon ethyl	5.4	0.057	3,262	6.333	0.692	0.218	0.029	5.459	0.565	0.217	0.072	4.149	0.565

	Spray drift
	Drainage
	Runoff

subsequently transferred to the receiving water body with drainage or runoff. Additionally, at higher tiers – Step 3, where more complex pedo-climatic scenarios are used, this factor may further influence the migration potential of the compound via drainage or runoff, because of the correlation with simulated weather conditions – temperature, which is one of the drivers of persistence of the compound in soil, and the precipitation, important in terms of migration, but also, to some extent, being the driver of the soil persistence of modelled compound.

In case of this analysis, two application periods in relation to the treated crop – winter cereals, growth stages were selected:

- at BBCH 00-09, being post-sowing, but pre-emergence stages occurring in late summer and in autumn depending on the FOCUS scenario from early September until

late November; further called Application pattern I;

- at BBCH 40-89, being maturation to harvest stages occurring in late spring to mid-summer – depending on the FOCUS scenario from May to early August; further called Application pattern II.

The applications following the Application pattern I result in situation with no crop cover to very little crop cover, with very limited crop interception, so in practice they are bare-soil applications. As a result, almost the whole applied amount, reduced by the fraction migrating with the spray drift, reaches the soil surface. Therefore, that whole amount is potentially prone to migration, either with drainage or with runoff.

In case of the Application pattern II, when the crop cover is dense, the actual amount reaching the soil surface is significantly lower than the application rate reduced by

Table 6

Results of the model calculations for non-mobile ($K_{iOC} > 4,000$ mL/g) compounds, applied to the treated crop at its growth phase BBCH 00-09 and BBCH 40-89, with indicated dominant migration route

Active substance	Key physicochemical properties			Results – PEC _{sw} [ug/L] and PEC _{sed} [ug/kg] obtained for scenario:									
	Log- P_{ow}	Aqueous solubility [mg/L]	K_{iOC} [mL/g]	D3 ditch		D4 pond		D4 stream		R1 pond		R1 stream	
				water	sediment	water	sediment	water	sediment	water	sediment	water	sediment
Benalaxyl	3.54	28.6	4,998	6.272	3.133	0.217	1.808	5.446	1.179	0.359	5.208	4.140	8.998
Esfenvalerate	6.24	0.001	5,300	6.295	2.767	0.218	0.940	5.466	1.107	0.451	3.242	4.156	5.100
Indoxacarb	4.65	0.2	6,450	6.261	2.926	0.216	0.406	5.436	1.132	0.216	0.654	4.132	3.197
Aclonifen	4.37	1.4	7,126	6.261	3.083	0.216	0.800	5.436	1.165	0.217	2.225	4.132	10.661
Chlorpyrifos	4.7	1.05	8,151	6.247	3.093	0.216	0.873	5.424	1.164	0.216	2.371	4.122	11.584
Benfluralin	5.19	0.065	10,777	6.226	2.233	0.215	0.187	5.405	0.961	0.214	0.446	4.108	4.039
Dodemorph	4.6	100	25,200	6.068	2.951	0.206	0.444	5.266	1.112	0.205	1.399	3.997	21.738
Alpha cypermethrin	5.5	0.004	57,889	6.075	2.945	0.207	0.440	5.273	1.112	0.207	1.576	4.004	27.256
Pyrethrins	5.9	0.001	100,000	6.075	3.193	0.207	2.407	5.273	1.162	0.207	3.094	4.004	8.584
Metiram	1.76	2	500,000	6.075	2.733	0.207	0.256	5.273	1.067	0.207	0.453	4.004	0.637
Benalaxyl	3.54	28.6	4,998	6.318	6.220	0.217	1.601	5.446	1.178	0.249	3.894	4.159	24.114
Esfenvalerate	6.24	0.001	5,300	6.341	5.134	0.218	0.808	5.466	1.105	0.355	2.041	4.175	11.762
Indoxacarb	4.65	0.2	6,450	6.307	4.387	0.216	0.310	5.436	1.112	0.216	0.759	4.151	11.589
Aclonifen	4.37	1.4	7,126	6.307	5.601	0.216	0.663	5.436	1.158	0.217	1.625	4.151	26.951
Chlorpyrifos	4.7	1.05	8,151	6.293	5.402	0.216	0.713	5.424	1.153	0.216	1.401	4.141	16.366
Benfluralin	5.19	0.065	10,777	6.271	1.810	0.215	0.140	5.405	0.891	0.214	0.462	4.127	9.323
Dodemorph	4.6	100	25,200	6.113	4.480	0.206	0.334	5.266	1.091	0.205	1.581	4.016	37.694
Alpha cypermethrin	5.5	0.004	57,889	6.120	4.449	0.207	0.332	5.273	1.091	0.207	2.373	4.023	60.224
Pyrethrins	5.9	0.001	100,000	6.120	6.368	0.207	2.045	5.273	1.158	0.207	2.510	4.023	13.502
Metiram	1.76	2	500,000	6.120	3.348	0.207	0.190	5.273	1.031	0.207	0.404	4.023	6.149

 Spray drift
 Drainage
 Runoff

the amount migrating with the spray drift. That is due to the fact that the treated crop retains a fraction of the applied amount – crop interception factor, the parameter increasing with the growth of the treated crop, reaches its highest levels. For the purpose of this analysis, it was estimated that at least 70% of the application rate was intercepted by the treated crop, what resulted in only about 30% reaching the soil surface (comparing with almost 100% of the amount reaching the soil surface). As a result, the amount of the applied substance potentially available for the migration with drainage or runoff is much lower.

The obtained results seem to confirm the above analysis. It was noticed that the majority of the maximum PEC values were higher for the Application pattern I than for the Application pattern II, regardless of the pedo-climatic scenario, type of receiving water body and mobility group to which the modelled compounds belonged.

At the same time, it has to be indicated that the values of the predicted environmental concentrations depend on several factors of similar importance – intrinsic properties of the modelled compound, simulated climatic conditions

forming a part of the pedo-climatic scenario used in the assessment, characteristic of the soil assumed in simulation, also being a part of the pedo-climatic scenario used in the assessment, type of the model receiving surface water bodies.

The application pattern, and more precisely the application time, may be correlated with some of them, directly – with simulated climatic conditions on the treated field and in the receiving surface water body, or indirectly – with intrinsic properties of the modelled compound such as mobility and persistence in the environment (in soil compartment) through the simulated climate conditions.

The influence of the assumed climatic conditions, correlated with the application time, on the resulting exposure profile in surface water bodies, maximum PEC values, identified dominant migration route and concentration profile (individual peak concentrations) has two aspects – that resulting from the precipitation pattern and that from the temperature (air and soil) distribution.

It shall be indicated that of the three migration routes assumed within the FOCUS models for calculating PEC values at Step 3 only that via spray drift is at present

independent of the weather conditions occurring on the treated site during application and after the event. That is due to the fact how the spray drift is defined at present within the FOCUS SW evaluation schemes and what factors are used in that definition.

Therefore the amount of the given compound reaching the water body adjacent to the treated model field via that route depends only on the application rate and the distance from the edge of the treated field to the edge of the receiving model water body. That factor is related to the characteristic of the receiving water body and may be reflected in the values of the obtained results – in D4 and R1 scenarios, in which two types of the receiving water bodies are defined, the resulting maximum PEC_{SW} values were higher in stream, what may be attributed to the fact that the distance from the edge of the treated field to the edge of the surface water body is, at Step 3 and for Winter cereals as a treated crop, 1.5 m for stream and 3.5 m for pond. Also higher than for pond are the PEC_{SW} values in case when the receiving water body is ditch, for which, in case of the modelled crop Winter cereals, the above mentioned distance is 1.0 m. This relationship becomes clearly visible in case when, for all scenarios used in model exposure assessment spray drift is the dominant migration route, but is also observed when other two migration routes occur and are of similar or greater relevance in performed modelling.

The situation is more complex in case of the two remaining migration routes – drainage and runoff. For those two routes, application timing, climatic conditions and the compound's intrinsic properties lay an important role in the determination of their relevance in the migration of the active substances to the surface water bodies.

The role of the application time, in addition to already characterised related to it crop cover (which determined the fraction of the applied compound reaching the soil surface, becoming therefore potentially available for migration with drainage or runoff), determines also the climatic conditions on the treated field at and after the application – precipitation and temperature of soil and air.

The relationship between precipitation and migration with drainage, or, in particular runoff, seems to be more obvious – the amount and frequency of rainfall is a driver of the intensity of runoff and drainage on the modelled site, independently of whether it was treated with the plant protection product or not, so it decides how for the given compound its mobility, determined by means of the adsorption constant K_{iOC} translates itself into the migration to the adjacent water body and resulting exposure profile.

At the same time it has to be indicated that soil characteristic also plays here an important role. That was demonstrated for drainage, for which two pedo-climatic scenarios were used – D3 and D4. In case of runoff, another factor, additional to soil characteristic, is important – the slope of the field. Inclusion into the analysis of the other FOCUS scenarios would demonstrate that relationship more clearly, however that was beyond the scope of the present research.

For the second climatic factor – temperature of soil and air on the treated field, such straightforward relationship cannot be easily found. The migration of the given compound

via drainage or runoff is related to the soil and air temperature assumed in the modelling indirectly – through the persistence of that compound in soil.

When the modelling tool is parameterised for the intrinsic properties of the modelled compound, one of such inserted properties is its persistence in soil, expressed as the average soil DT_{50} . That value has to be inserted as normalised value, that is, converted to as if measured at standard conditions – temperature $T = 20^{\circ}C$ and soil moisture content of 10 kPa (pF2).

The reason for this practice is the fact that the degradation of the active substances in soil, as well as in the surface water compartment is assumed, for the modelling purposes, to be biologically mediated (enzymatic) process, performed by the microorganisms. It is, therefore, strongly correlated with the temperature and in case of soil with soil moisture content. As it was already indicated, the modelling tool used in this research has inbuilt weather files, forming a part of the pedo-climatic scenarios. Therefore, during the modelling calculations, because of the assumed climatic files, the tool calculates the instantaneous (daily) transformation rate constant, the variable dependent on the daily temperature and soil moisture defined in the scenario using the Arrhenius (for temperature) and Walker (for moisture content) equations. That determines the amount of the compound potentially available for migration with runoff or drainage on the given day.

The influence of the temperature on the process of degradation is such that with lowering of the temperature it slows down, while the increase of the temperature increases also the pace of the degradation (what is in line with the thermodynamic principles of the kinetics). In the modelling practice that means that the given compound when applied in autumn, because of the lower temperatures, is available for longer and in greater amounts for migration with drainage or runoff, than it is in case of late spring and summer applications.

Similarly can be characterised the influence of the second weather-related factor driving the rate of degradation in soil of the active substances of the plant protection products – soil moisture. In case it is too low, the degradation slows down. However, the influence of that factor on the rate of degradation is lesser than that of the temperature.

As a result, it may be stated that in autumn, when the temperatures, in real situation and in reflecting it modelling are lower than in autumn, the degradation is slower, what to some extent is reflected in the obtained results – the maximum PEC values and the probability that either drainage or runoff dominates over the spray drift as a migration route of the applied active substances of the plant protection products increases.

However, the nature of modelling is complex and several factors influence the migration of the given active compound to the surface water bodies and hence the concentration profiles. Therefore also other factors driving the phenomenon of concern should be taken into consideration alongside the characterised above parameters.

Analysing the factors defined within the pedo-climatic scenarios that influence the migration with drainage or runoff the type of soil should also be mentioned, as it affects the relevance of both drainage and runoff. For example on

sandy or loamy soils surface water is more dominant [25]. Soil properties, in particular texture, organic carbon content and pH, may be considered as influencing the mobility of the given compound in the soil profile. In combination with weather conditions they can render the chemical more or less prone to migration with the drainage flux, for the same application period assumed. That was demonstrated by the results obtained in scenarios D3 and D4. It is worth mentioning that among FOCUS SW D scenarios may be indicated those that are more drainage-sensitive due to the predefined pedo-climatic conditions, e.g. D1 and D2 scenarios.

Also type of soil is one of the determinants for runoff in case of R scenarios, however in case of those scenarios of the similar, if not greater importance is another landscape-related factor – land's slope.

Finally, it shall be indicated that the type of the receiving water body plays an important role in the obtained results. That is due not only to the already discussed issue of the distance from the edge of the treated field to the edge of the receiving water body, but also on how the receiving water body is defined. In case of smaller ditch and stream, the obtained PEC_{SW} values may be higher than for pond, and they usually tend to be higher for stream than for ditch. That relationship is reversed in case of the sediment phase – the lowest PEC values are usually observed for stream and the highest in pond, with those for ditch standing in-between, what is due to the characteristic of the water body – its flow rate and the thickness of the sediment.

5. Conclusions

Modelling with FOCUS SW numerical tools showed that the level of exposure of the aquatic organisms to the active substances of the plant protection products is correlated with the aqueous solubility of those compounds and their mobility in the environment expressed by the Freundlich adsorption constant K_{iOC} . That relationship, clearly visible in case of the compounds moderately persistent and persistent in the environment, and in particular in its aquatic component (surface water bodies) is such that the higher is aqueous solubility and lower is the K_{iOC} of the given compound, the longer is its residence in water phase. Such compounds also more slowly and to lesser extent migrate to the sediment phase. In contrast, the higher and faster migration from water column to the sediment phase is correlated with low aqueous solubility of the given compound and its low mobility, expressed by the high K_{iOC} value. Therefore, the compounds highly soluble in water and highly mobile in the environment (with low K_{iOC} values) usually pose a higher threat to the aquatic organisms present in the water column, while low soluble in aqueous solutions or miscible with water compounds with high K_{iOC} values (slightly mobile and non-mobile) pose a more serious threat to the sediment dwellers.

The moderately mobile compounds usually stand in-between and may pose an equally serious threat to both aquatic organisms present in the water column and to the sediment dwellers.

It was demonstrated that in the modelling exposure assessment the magnitude of the exposure of the aquatic

organisms to the active substances of the plant protection products significantly depends on the assumed application pattern, in particular on the application time, method of application and growth phase of the treated crops. Also the number of applications, factor not taken into account in this research activity, is known to influence the values of calculated PEC.

In practice, it was stated that the calculated PEC_{SW} and PEC_{SED} values were higher for the applications occurring in autumn (Application pattern I) than in those occurring at late spring and summer (Application pattern II). That was due to the following factors:

- the weather conditions assumed for each simulation on the basis on the weather files inbuilt in the modelling tool – in case of the Application pattern I the application occurred during the period with higher precipitation and lower temperatures decreasing with time, while the weather conditions during and after the application within the Application pattern II may be characterised as drier and warmer;
- the crop cover assumed by the tool for each application pattern – in case of the Application pattern I the application was on the bare soil or with minimal crop cover, while for Application pattern II it was performed onto the full canopy.

When the influence of various factors on the migration routes was analysed it was stated that the spray drift as a migration route is independent of the physicochemical properties of the modelled compounds and of the weather conditions. It is, however, dependent on the application method, type of water body assumed in calculations and the distance between the edge of treated field and that of the receiving water body.

In contrast, the migration with runoff and drainage is strongly correlated with the intrinsic properties of the modelled compounds – their mobility in the environment, expressed as K_{iOC} , persistence in soil – the soil DT_{50} value, and aqueous solubility, correlated with K_{iOC} .

Other factors identified in this research as influencing the migration of the given compound to the receiving water body are:

- application timing in relation to weather conditions – autumn and winter applications, in comparison to late spring and summer/early autumn applications, represent worse case because of the higher level of precipitation and lower, decreasing temperatures;
- application times with regard to the crop cover – autumn applications again represent worse case comparing with the late spring and autumn applications, because the former occur onto bare soil or onto fields with minimal crop cover, while for the latter the assumed crop cover is practically “full canopy”;
- type of soil on the treated field.

It has to be indicated that, although all listed above factors, including the intrinsic properties of the compounds of concern, were identified for model exposure assessment, they also play a key role in reality.

When the results of the performed model exposure assessment were examined in relation to the analysed intrinsic properties of the active substances of the plant protection products – the adsorption constant K_{iOC} , characterising their mobility in the environment, and the aqueous solubility, the following conclusions were drawn:

- for the compounds with short soil DT_{50} (low persistence in soil) and high K_{iOC} values (low mobility) the main identified migration route to the surface water bodies, regardless of the application time, is via spray drift;
- the compounds that display good solubility in water and aqueous solutions, have low K_{iOC} values – in range of 1–499 mL/g (classified as very mobile, mobile and moderately mobile), and that are persistent in soil, are generally prone to migration to surface water bodies with drainage, as it was demonstrated in case of tested D scenarios, or with runoff, as shown by the results of the tested R1 scenario; the migration with drainage in D scenarios is lower for applications at later growth stages of the treated crop;
- substances belonging to the group of slightly mobile compounds – having $K_{iOC} = 500$ – $4,000$ mL/g, even if persistent in soil (having long DT_{50} values) are less prone to migration to surface water bodies with runoff than those characterised in the previous bullet point, while the drainage as a migration route is for them practically not observed;
- for the substances with $K_{iOC} > 4,000$ mL/g (non-mobile compounds), regardless of their persistence in soil and FOCUS scenario (including the type of receiving water body) spray drift becomes the predominant, if not the sole migration route to the receiving water body

On that basis was drawn the general conclusion that the, regardless of the other assumptions used in modeling, the PEC_{SW} and PEC_{SED} values tend to decrease with the decreasing mobility of the compound in the environment.

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