DYNAMIC MODELLING OF PESTICIDES UPTAKE BY TRITICUM SPP. ANATOMICAL COMPARTMENTS

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Abstract

Since world population is growing and expansion of arable land is limited, cropping intensity and yield must be increased. Pesticides are widely used as a solution, being used to control unwanted pests potentially damaging crop yield levels and wheat quality. However, it is widely known that pesticides are hazardous substances that could reach also non-target areas or living systems, such as wheat grown for consumption. Through this study we proposed to build a model that allow to simulate how used pesticides are uptake by wheat and which compartments bioaccumulate them in higher yields.

Key words: *bioconcentration modelling, diuron, multicompartiment modelling, time evolution modelling, Triticum spp*

1. INTRODUCTION

Modern agriculture requires substantial input of pesticides to soils to control weeds and insects. While pesticides usage in farmland has brought great benefits to crop production, they simultaneously generate great concerns linked to the contamination to ecosystems and food safety [1–6]. Most pesticides can accumulate in water systems [7], pollute the air and soil [8,9], and in some cases have other dramatic environmental effects as weakening the natural ecosystems and threatening biodiversity upon which human survival depends [10–13]. Pesticides, also have been linked to a wide range of human hazards, ranging from short-term impacts such as headaches and nausea to chronic impacts like cancer, reproductive harm, and endocrine disruption [14–16].

Thus, contamination of pesticides (or their transformation products) to soil has become one of the environmental problems throughout the world. Their use can damage agricultural land by (i.) harming beneficial insect species, soil microorganisms, and worms which naturally limit pest populations and maintain soil health; (ii.) weakening plant root systems and immune systems; (iii.) reducing concentrations of essential plant nutrients in the soil such nitrogen and phosphorous; (iv.) bioconcentrate in plant species thus favoring their biomagnification through food web chain to higher trophic levels; etc.

Although many pesticides have been banned or restricted in use and quantity through law, even in our days a large number of pesticides and their by-products (metabolite-, degradedcompounds) are detected as contaminants in soil-plant-water systems [17, 18]. On the other hand, due to continuously increasing demand for food products, new agrochemicals have been developed and are extensively used in farmland to control the diseases and increase the yields. Because of that, for the approved pesticide there are regulations on how to be used, in which quantity and frequency could be applied on the fields, and so on [10]. But even in that case they could be accumulated in plant species that are intended for human consumption [19–21].

As vegetable food forms (including crops, vegetables, fruits, etc.) form a major part of the diet of human beings, and also of cattle, sheep, etc., the contamination of plants with banned or approved pesticides will have a large influence on the total daily intake of them. In this work the diuron (a used and approved herbicide) bioconcentration was modelled in wheat (Triticum aestivum) through its anatomical development in time.

The main goal was to find a suitable modeling approach based on experimental data through out to could predict the diuron concentration in any anatomic compartment of wheat whatever stage of its development. Such estimates will help risk assessors, decision makers to regulate the pesticides for a safer manner of production and use, as well farmland managers to adjust their farming procedure (pesticide use) in order to assure a safe crop production.

2. MATERIALS AND METHODS

2.1. Sampling strategy

Wheat samples were collected from the same infield located near Turda city (460340 1500N, 230460 4500E). Our sampling strategy was based on the wheat growth cycle considering the Zadocks system classification. Samples were collected on the following days: 14, 35, 69, 82, 98, 127 and 139, starting from the moment of sowing. These days represent the beginning of the main stages of wheat development in terms of its anatomical evolution in time (see Table 1).

Time (days)	**Stage (anatomo-physiological development)**	**Characterization (general description)**
14	Germination/Tilling	Starting from the germination process beginning, includes germination, seedling establishment and first leafs production; Tillering and head differentiation: appearance of main leaves on the main shoot, initiation of heads on the main shoot tillers;
35	Node formation (Leaf strongly erect)	Stem and head growth: each stem internode up wheat becomes progressively longer;
60	Boot	The flag leaf sheath encloses the growing head;
82	Heading	Head emergence-as the stem continues to elongate, the head is pushed out of the flag leaf sheath;
98	Flowering/Grain filling	Flowering (pollination) begins in the head, starting first with the florets in the central spikelets; Flowering progresses both up and down the spike;
127	Ripening	Kernel begins accumulating starch and protein rapidly and its dry weight increases in a nearly linear manner; Most of the final weight of the kernel is accumulated;
139	Maturity	Growth of the kernel declines into grain filling and its weight approaches a maximum attained at physiological maturity;

Table 1. Wheat sampling days considering its major anatomo-physiological development stages.

2.2. Sample collection

Wheat samples were carefully uprooted, and the soil loosely adhering to the roots (rhizosphere soil) were removed by gently shaking and collected carefully as sample. They were stored at −4 ◦C until analysis. Three replicates of wheat samples were collected and analyzed at each time point. In order to eliminate possible results adulteration due to particulate deposition on plant surface, wheat plants were then thoroughly washed with running tap water to remove airborne dust and soil particles. Then, the major anatomical compartments as root, stem, leaves and wheatear of each samples were separated and measured carefully as follows: (i.) root length was measured from the point of attachment of the stem

base to the tip of the tap root after that it was separated from the rest of sample; (ii.) shoot length were measured from the stem base to the tip and divided according this; (iii.) the stem was measured from the base to its upper end; (iv.) leaves were measured and separated from the stem starting from their lower base (contact with stem) to their external end and grouped carefully on nodes; (v.) wheatear was measured and separated from stem. All these anatomical part were sectioned in segments of about 5 cm (starting from the bottom to the top of the specified anatomical component), homogenized and 8 analysed in triplicate. Wheat tissue water content was determined by constant weight-drying in an oven at 70 °C for 24 hour before analysis, and the concentration was expressed on a dry weight basis.

2.3. Extraction and derivatization step of diuron and its transformation products

These sample preparation steps consisted of followings: Prior to extraction, the tissue samples of mentioned anatomical parts (roots, stems, leaves, and wheatear) were chopped into small pieces, then transferred into a mortar and thoroughly grounded. Then 1.5 g of sample was transferred in a 20 mL headspace vials which contain 1.125 g NaCl and 7 mL water at pH 2 (adjusted with H3P O4). After that, each vials was sealed with a screw cap having a Teflon lined rubber septum. According with method described by [41] a polydimethylsiloxane- divinilbenzene (65µm PDMS/DVB; Supelco) SPME fibre was used for extraction. Firstly SPME fibre was exposed in the headspace mode to 10µL of PFBBr (derivatising agent) and heated at 50◦C for 10 min. Diuron and its metabolite/degraded compounds were extracted from sample aliquots headspace (which was stirred through all the process) by PDMS/DVB fibre over 45 hour at 50 °C. After that the fibre was introduced in the GC injector and the analytes desorbed for 5 min at 250 °C.

2.4. GC-MS analysis

A Focus GC with DSQ II mass spectrometer (Thermo Fisher Scientific Inc.) equipped with a split/splitless injector was used to perform the analysis. A TR-5 MS (5% diphenyl-95% dimethylpolysiloxane; 30 m x 0.32 mm x 0.25 mm film thickness) capillary column was used for diuron and its metabolite/degraded compounds separation from the sample extract. Helium was used as carrier gas with 2mL · min−1 flow rate. Injection was made in splitless mode (5 min) with the temperature set at 250◦C. MS detector and transfer line temperature were set at 250 and 200◦C respectively. The GC oven temperature program applied for column was 80◦C (2 min), increased at 160◦C ·min−1 (2 min), and increased again with 10◦C ·min−1 until 240◦C and hold for 10 min. The MS was used in SIM mode both for qualitative and for quantitative analysis. Three ions were monitored both for diuron as well for its major metabolite/degraded compounds. Diuron and its degraded compounds from rhizospheric soil were analysed under similar condition as described before.

2.5. Modelling approaches

2.5.1. Model hypothesis

Our modelling concept was based on two major hypothesis which refer to (i.) main routes throughout diuron is bioconcentrated in wheat cultivars, and (ii.) diuron biogeochemical behavior under wheat-environment interaction. (i.)First hypothesis-the main rout of diuron bioconcentration in wheat cultivars is soil to root transfer followed by its transfer from root to other plant parts (anatomical compartment). Diuron has a water solubility of it ∼ 42mg ·L −1 and a $\log_{KOW}$ of 2.68 at room temperature. The Henry's Law constant of 2.7 · 10−6 atm m3 ·mol−1 indicates that it is non-volatile, while its half-life in soil, 90-180 days, indicates that its presence in wheat surrounding soil media cover the entire development period of it-including its maturity, even until harvesting. Considering the diuron chemical properties, our model was built considering the hypothesis that the major rout through that wheat can be uptake by wheat is soil to root transfer. Thus, in our modeling concept we have been neglected the vapor/gas uptake from ambient air and particulate deposition on plant surfaces as routes of diuron uptake by wheat. (ii.)Second hypothesis-although diuron is a stable pesticide. which include its main physico-chemical properties) it's structure suffer changes both in environment (degradationdegradates formation) as well in wheat body (metabolism-metabolites formation). It is known that in plant species, diuron is metabolized via N-demethylation of the nitrogen atom and hydroxylation at position 2 of the benzene ring. The predominant metabolite is 3.4-dichloroaniline (DCA) followed by 3.4-dichlorophenylurea (DCPU) and

N-(3.4-dichlorophenyl)-N-methylurea (DCPMU). Based on this knowledge, our experimental data was extended both on diuron concentration as well on its major metabolite concentration (DCA) and degradate compounds fromed in soil (DCPU, DCPMU) in order to get a more realistic view on this pesticide bioconcentration in wheat body during its entire development time.

2.5.2. Reaction-diffusion model for diuron bioconcentration

Considering the nature of the problem, firstly, a reaction-diffusion model was formulated for diuron (as well its major metabolite, DCA) bioconcentration modelling through wheat (Triticum sp.) anatomical evolution in time. The model, described by eq. 1, illustrate the diuron concentration diffusion rate through the entire wheat body, considering its evolution in time.

$$\frac{\partial C}{\partial t} + \frac{L'(t)}{L(t)} C = D \frac{1}{L(t)^2} \cdot \frac{\partial^2 C}{\partial x^2} + R(C) \quad (1.)$$

where L(t) is length of domain; D is the diffusion coefficient and R(C) is the reaction term.

Boundary condition of the model were:

$$U(0,t) = 1, t \in (0,\infty) \quad (2.)$$

$$\frac{\partial U(L,t)}{\partial x} = 0 \quad (3.)$$

and the initial condition was:

$$U(x,0) = 0, 0 \leq x \leq L(t)$$

The approach was to consider the eqs. (1, 2, 3), as an inverse problem with known C and to compute D and R(C) from measurement data.

2.5.3. Modelling using multiple linear regression approach

During the approximation $\partial^2 C/\partial x^2$ from input data using reaction-diffusion model for diuron bioconcentration estimation, we obtain very small values, which suggest that eqs.(1,2,3), is an inappropriate model for our purposes. Considering that and the pattern of our experimental data we proposed to use a multiple linear regression approach for our DCMU bioconcentration estimates. We construct our model based on multiple predictor variable and parameter estimates for each predictor variable. The coefficient values for each predictor are the slope estimates. The general form of the model is described as:

$$Y = \beta_0 + \beta_1 \cdot x_1 + \cdots + \beta_k \cdot x_k + \epsilon \quad (4.)$$

where Y is the response variable and $x_1, \ldots x_k$, are independent variables. $\beta_0, \beta_1, \ldots, \beta_k$ are fixed (but unknown) parameters. Sometimes, design matrices might include information about the constant term. However, *fitlm* or *stepwiselm* by default includes a constant term in the model. ε is a random variable called residuals (representing the error) and which is normally distributed with mean 0 and having a variance of σ σ_ϵ^2.

2.6. Software and statistical approaches

Proposed models approach were constructed and implemented using Matlab (Matlab 2013, version B, MathWorks Inc.). The statistical analysis was carried out by one-way of ANOVA (Statistical toolbox from Matlab).

3. RESULTS

3.1. Wheat parameters time dependence

This study involved the examination of wheat samples considering its anatomo-physiological development in time. In order to could develop the optimal modeling approach for diuron bioconcentration modelling the main physical, chemical and physiological parameters were measured also in laboratory. A summary of main parameters variation according with main evolution stage are presented in table 2.

Stage	Total height [cm]	ϕ_{stem} [cm]	Leaf dimension length/width [cm]	$\chi^{(*)}$ [%]	$W_C^{(**)}$	$ET^{(***)}$ [%]
1	16.62	0.3	16.5/0.65	9.12	7.88	22.35
2	22.48	0.7	24.75/0.62	8.29	9.26	19.05
3	62.14	0.6	37.25/0.75	9.05	11.27	20.11
4	78.22	0.6	46.5/0.86	7.68	13.45	18.35
5	84.15	0.4	49.75/0.9	8.02	16.55	15.67
6	96.12	0.35	26.75/0.8	7.15	18.27	9.02
7	105.02	0.35	33/1	6.53	19.25	7.14

Table 2. Main characteristics of wheat considering its major development stage (data represent the average value obtained through multiple wheat samples analysis, n=7 for all parameters).

$^{(*)}\chi$ – crop hydration coefficient;

$^{(**)}W_C$ – saturated hydration coefficient;

$^{(***)}$ ET- evaporation-transpiration coefficient

The data presented in table 2 revealed a linear increasing in value of WC and ET coefficients, respectively, considering all development stages while wheat hydration coefficient present an irregular behavior through major development stages. Water and lipid content, which are also morpho-functional parameters with significant influence of wheat uptake potential were determined for all anatomical compartment during their evolution in time (see 3). It was observed that water content decrease during anatomical evolution in all major anatomical compartments of wheat while lipid content present an irregular behavior during root, stem and leaves main development stage. Only in case of wheatear could be observed a slightly increases during its development in time.

Stage	Water content (%)				Lipid content (%)			
	Root	Stem	Leaves	Wheatear	Root	Stem	Leaves	Wheatear
1	46.5	65.2	41.6	-	0.78	0.28	0.59	-
2	42.8	51.8	35.2	-	0.72	0.25	0.51	-
3	35.6	46.3	31.4	-	0.65	0.31	0.48	-
4	27.1	38.5	28.8	-	0.63	0.38	0.51	-
5	22.8	32.5	26.2	14.5	0.66	0.46	0.53	0.95
6	18.9	28.9	17.9	11.2	0.71	0.41	0.47	1.15
7	17.5	22.5	15.2	9.5	0.72	0.35	0.39	1.05

Table 3. Water and lipid content in main anatomical parts of wheat under their major development stage (all data presented in 3 represent the average value obtained through multiple wheat samples analysis, n =7 for all parameters)

3.2. Occurrence of diuron in wheat cultivars

Wheat is a stable food for a large section of the population in many countries and is one of the most important stable foods for humans worldwide [44]. With a production of 680 million tons in 2013, wheat contributes with approximately 30% to the world's average crop consumption. In Romania 5715429.24 tons of wheat was cultivated during the period of 1993-2013 [45]. Furthermore, wheat is grown on more arable land than any other commercial crops with an ever increasing due to a continuously growing global population. Since expansion of arable land is limited, cropping intensity and crop yield must be increased [46]. Considering its importance (is a basic food) and continuously increasing demand, agrochemicals have been and are extensively used to control the diseases and increase the yields. This is the case of diuron use, which is a broad-spectrum herbicide widely utilized in agriculture. In Romania is often used as a potency reference herbicide to assess effects of non-target species due to its effectiveness at low concentrations. The vast majority of the usage is in wheat (51%) and barley (21%) industries, with sugar representing the third highest usage amounts (6.5%).

Although for efficient usage is enough even small quantities, diuron is an herbicide with a relatively long soil half-life of 75 days; field trials however, report a range from 20 to 231 days [47, 48]. At this moment only a very few studies have investigated the presence of diuron in landscape soils as well its incorporation in crops, cultivated species that is supposed that need to be protected in their evolution by this herbicide. Also even fewer have investigated its bioconcentration in wheat through its anatomical development in time. Therefore, an understanding of the diuron behavior in agricultural land field as well its potential to accumulate and bioconcentrate in cultivated species is needed to help optimize its use in agriculture as well as determining (through modeling) the appropriate doses of diuron applied to these soils to avoid the risk of cultivated crop contamination.

In our studied agricultural land, diuron was detected between 16.2-168.1 [$\mu g \cdot kg^{-1}$]. In the wheat samples corresponding rizosphere soil its concentration was ranged between 4.92-83.14 [$\mu g \cdot kg^{-1}$]. Major degradation compounds as DCPMU andDCPU were also detected, which prove that this herbicide possess a history of use in the studied land field. Diuron was detected in 90% of the sample while DCPMU and DCPU (as primary degradate compounds of diuron in soil) were detected in roughly 60%.

This made us wonder if diuron is also reflected in the wheat grown on the studied landscape. Specifically, the combination of potency and longevity, raised concerns that diuron was having accumulative effects even on emergent crops as those intended for protection as wheat. After laboratory analysis of diuron in wheat samples, it was observed that both diuron as primary compound as well its major metabolite in plant species, DCA, were detected in relatively significant concentrations 4.

Stage	Concentration (ng·kg^{-1})							
	Diuron (parent compound)				**3.4-dichloroaniline (principal metabolite)**			
	Root	*Stem*	*Leaf*	*Wheat ear*	*Root*	*Stem*	*Leaf*	*Wheat ear*
1.	68.1	10.1	16.2	-	83.1	16.2	21.3	-
2.	54.3	15.4	18.6	-	78.2	21.5	34.5	-
3.	56.2	15.6	26.6	-	69.5	28.3	46.7	-
4.	51.8	21.7	26.3	-	62.8	37.6	58.8	-
5.	47.3	24.3	26.9	9.4	56.2	41.2	63.5	16.5
6.	43.8	24.5	25.9	7.4	43.8	46.3	70.2	18.9
7.	38.9	23.4	30.3	4.9	34.1	48.9	73.6	20.6

Table 4. Average amount of diuron and its principal metabolite in wheat main anatomical compartments during its morpho-functional development (n=7)

Analyzing data recorded in 4 we could observe that in root samples the diuron and DCA amount tend to be similar, which suggest that the metabolizing process is started at this anatomical compartment. In root, minor differences are observed at the first development stages after that until to maturity the diuron breakdown reach the equilibrium. If we look at upper anatomical part of wheat, we could observe that the ratio between diuron (as parent compound) and DCA (primar metabolite of diuron in wheat) is dramatically changed. The parent compound significantly decreases once that the metabolite compound increase, suggesting that the metabolizing process of diuron is almost completed. These results sustain that both our hypothesis are correct and building our model approaches on that basis is consistent with experimental data.

3.3. Reaction-diffusion model for diuron-wheat interaction description

Through this work we start the diuron bioconcentration modeling using a reaction-diffusion equation based approach (see eq.1). Considering the diuron concentration data obtained from laboratory analysis it was observed a uniform and almost linear growth of concentration reporting it to crop height evolution in time where the graph exhibit small oscilations. It may be possible also that due to this reason when we estimated the second order partial derivatives ∂ 2C ∂x2, we obtained small values, which made this model to be improper for diuron bioconcentration modelling in case of wheat samples. Perhaps the slow variation of diuron concentration in relation to the wheat anatomo-physiological evolution in time could be also attributed to wheat simplest geometry and not just only to its physiological characteristics. Considering the inadequacy of this model application due to an almost linear behavior of diuron concentration reported to wheat anatomical evolution in time (height/growing), in the following we have proposed to use multiple linear modelling approaches.

3.4. Diuron bioconcentration modelling through multiple linear regression models

Three major models were developed using multiple linear regression modeling approach for diuron bioconcentration in wheat. These models are: (i.) linear model with interaction for strain; (ii.) linear model with interaction for strain including diameter variation during anatomical evolution in time; and (iii.) linear model that interlink strain and leaves.

Linear model with interaction for strain

In case of diuron bioconcentration modeling in wheat strain we proposed the following model:

$$Y = \beta_0 + \beta_1 \cdot X_1 + \beta_2 \cdot X + \beta_3 \cdot X_1 : X_2 \qquad (5)$$

where: Y represent the diuron concentration; X_1 is time considering evolution stages and it is expressed as days; X_2 represent the wheat strain height at the corresponding evolution time and it is expressed in cm; $X_1 : X_2$ represent the time:height interaction.

This model was selected as the optimal modelling approach after several attempts and their performance in statistical terms. Outliers were determined using Cooks distance (see Figure 1) but analyzing no significant differences were observed through interference analysis about parameters (ANOVA F-test), thus in the following we dropped outlier removal.

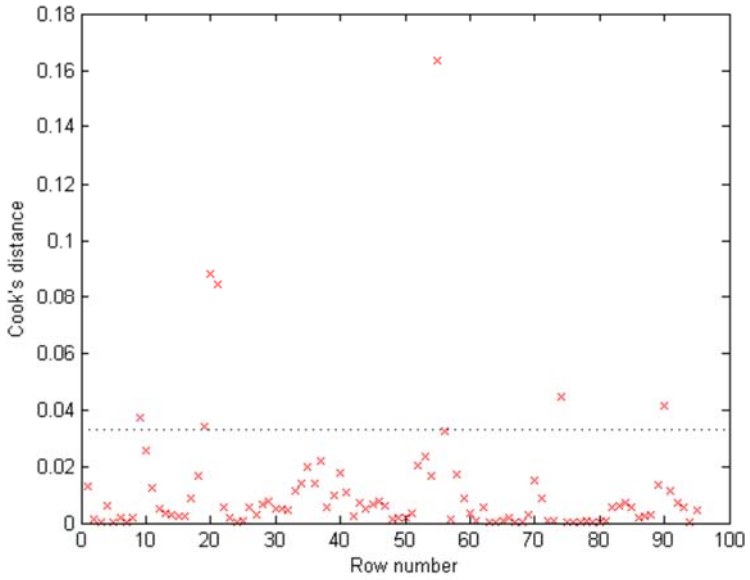


Figure 1. Case order plot of Cook's distance

Considering the statistical performance data and the feedback from ANOVA (see 6) we propose as the optimal model the following eq. 6:

$$Y = 6.5217 + 0.23963x1 + 0.13907x2 - 0.0035623x1x2 \quad (6)$$

where:

In table 5 estimate represent the coefficient estimates for each corresponding term in the model;

SE is the standard error of the coefficients;

tStat is the t-statistic for each coefficient to test the null hypothesis that the corresponding coefficient is zero against the alternative that it is different from zero, given the other predictors in the model;

pValue is for the F statistic of the hypotheses test that the corresponding coefficient is equal to zero or not;

ANOVA pValue is for the F-test on the model.

	Estimate	**SE**	**tStat**	**pValue**	**ANOVA pValue**
(intercept)	6.5217	1.5011	4.3446	3.621e-05	-
X_1	0.23963	0.014801	16.19	1.5494e-28	6.7897e-23
X_2	0.13907	0.042473	3.2743	0.001499	8.693e-37
X_1x_2	-0.0035623	0.00036204	-98396	5.523e-16	5.523e-16
R^2	0.861	Adjusted R^2	0.857		
F statistics vs. constant model	188	pValue	6.56e-39		

Table 5. Multiple linear regression model with interaction - strain

$$y = 6.5217 + 0.23963x_1 + 0.13907x_2 - 0.0035623x_1x_2$$

Similar procedure was applied for Linear model with interaction for strain including diameter; Linear model interlinking strain and leaves;

In this work diuron bioconcentration over time were estimated by multiple linear regression approximation over time (implemented in Matlab) on the different anatomical compartment domain where diuron concentration occurs at different amount for the differently aged crops. The R-squared value of our models were 0.861, 0.856 and 0.787 for (i.) linear model with interaction for strain; (ii.) linear model with interaction for strain including diameter variation during anatomical evolution in time; and (iii.) linear model that interlink strain and leaves, respectively. The distribution coefficient of diuron (dispersion rate) from root to stem was established at 0.046 and represent de numeric value of the diuron amount that disperse across the unit area (root compartment subdivision) per day from a certain position in the spatial domain (stem). Simulation were performed over experimental data set (amount, time period).

3.5. Model validation

Our proposed approaches for the mentioned three cases were validated. For each model we used a training set as well a validation set obtained from laboratory analysis of diuron concentration. The training sets were used for modelling while the validation set were used for the chosen approaches validation which included prediction performing, R^2 completion and finally the check of model significance arias using t-test:

$$T = \sqrt{\frac{R^2(n-p-1)}{1-R^2}}$$

Considering the following hypothesis (i.) H_0: $R^2 = 0$ and (ii.) H_1: $R^2 \neq 0$, when p-value < α the H_0 was rejected.

Those, the obtained coefficient values were interpreted as how much of a unit change in Y will occur for a unit increase in a particular X predictor variable, given that the other variables are held constant. The t-test was applied on each individual coefficient in order to test their significance in the presence of all other variables used in our model. We used α of 0.05 to perform this test, with the p-value less than α when we reject the null hypothesis and decide that the slope differs from zero. Those, our condition is that the variable is a significant linear predictor. From ANOVA table output the p-values of 0.000 shows that we would reject the null hypothesis that all the slopes equal 0 and conclude that at least one

of the slopes differs significantly from zero. However, this does not tell us how many differ and/or which ones differ.

4. DISCUSSIONS

Modelling diuron bioconcentration in wheat anatomy through time development

Despite the benefit of diuron use in wheat production (eliminate the negative impact of perennial broadleaf and grassy weeds) its use must be controlled because an important fraction of it is uptake or (metabolized) by wheat, presenting a potential hazard risk.

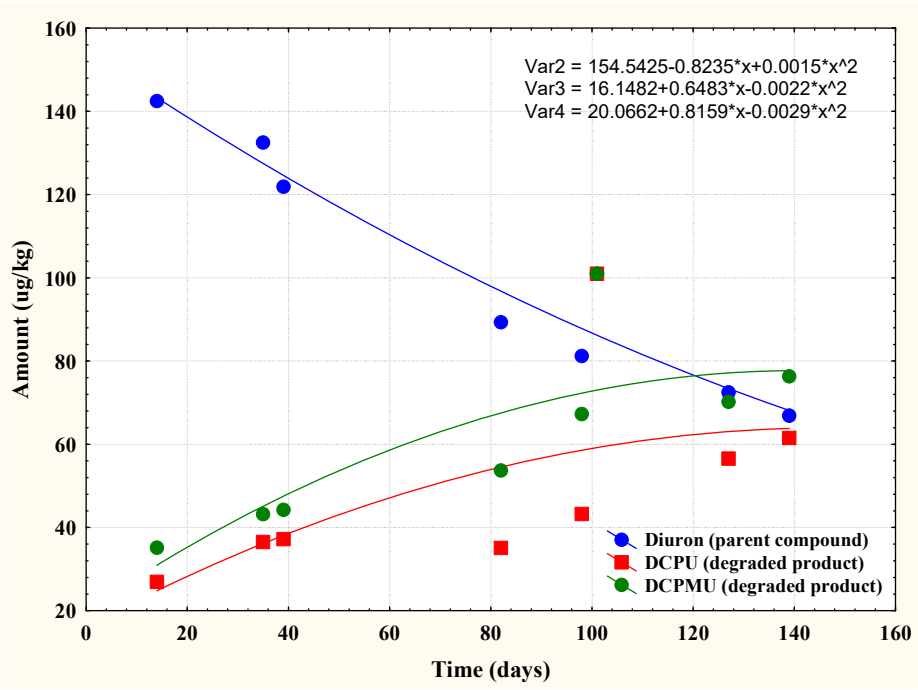


Figure 2. Diuron and its degradation by-products behavior in the monitored farmland during our study period

Moreover, upper trophic level organisms can accumulate these chemicals through food web chain. The tendency of living organisms to bioaccumulate is measured by the bioconcentration factor which is formally defined as the equilibrium ratio of the concentration of the substance in the exposed organisms (wheat in our case) to the concentration of the substance bioavailable in the surrounding environment (agriculture land). Bioconcentration factor is important to indicate the future response of cultivars as wheat to a toxic substance (as diuron), but also to evaluate the biomagnification process (e.g. the accumulation of chemical in the trophic chain due to dietary adsorption).

Unfortunately, the experimental determination of bioconcentration factor is time consuming, difficult, expensive and measuring the bioconcetrantion factor of the many thousands of chemical substances that are of potential interest, simply is not possible. Since experimental data are not available for all chemicals in use, many researchers tend to use estimation methods to supply the missing data. Numerous correlations have been developed relating bioconcentration factor values to then-octanol-water partition coefficient (logP). Unfortunately, not all the bioconcentration factor values have always a good correlation with logP with any kind of compound, and the application of these methods is limited by the availability of parameter data. For diuron case, estimation based on chromatographic data (experimental measurement) is also a time and financial consuming techniques. Those the necessity do develop

numerical methods that could offer such data are imminent for decision makers, safety assessors and agriculture managers.

In our work we determined for diuron the compartment-specific degradation/metabolizing residence times T deg met,i = HL ln(2) which was derived from the degradation/metabolizing half-life HLi of the diuron in the i-th compartment (wheat anatomical compartments) based on the measured experimental data. Degradation half-lives of diuron in soil were derived also from the measured experimental data, referring to it as parent compound as well to it degradates as DCPU and DCPMU (see 3). However, persistence is not exclusively related to degradation or metabolization in wheat organism. Instead, the system dynamics is rather related to the overall residence time in a compartment, considering both metabolizing and transfer processes with the latter often being dominant especially in soil. Analyzing the obtained data, it was observed that the higher persistence was obtained in leaves compartment (see 3).

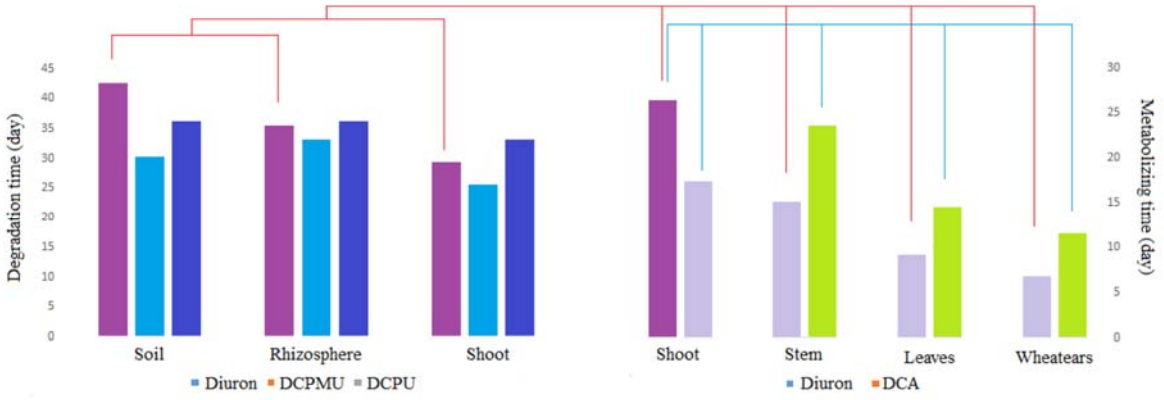


Figure 3. Diuron and its degradates/metabolite species compartment specific residence time

CONCLUSIONS

Pesticides, as diuron, are widely used in conventional agriculture to obtain a better yield for crops. GC-MS analysis of diuron revealed its presence both in soil samples as well in cultivated wheat samples. Moreover, its major degradate compounds as DCPU and DCPMU were also 21 detected in soil and rhizospheric soils samples collected from the monitored agricultural land.

The principal metabolite compound of diuron was detected also in all anatomical compartment of wheat during its evolution in time. Development of mechanistic models are particularly important in furthering the understanding of the uptake process. These models offer insight not only into what could be important factors that govern plant uptake but also help to guide risk assessors, decision makers and farmers to improve harvests safety status.

Through this work, three major models were developed using multiple linear regression modeling approach for diuron bioconcentration in wheat. These models are: (i.) linear model with interaction for strain; (ii.) linear model with interaction for strain including diameter variation during anatomical evolution in time; and (iii.) linear model that interlink strain and leaves. Those, diuron bioconcentration over time was estimated by multiple linear regression approximation over time (implemented in Matlab) on the different anatomical compartment domain where diuron concentration occurs at different amount for the differently aged crops.

The R-squared value of our models were 0.861, 0.856 and 0.787 for (i.) linear model with interaction for strain; (ii.) linear model with interaction for strain including diameter variation during anatomical evolution in time; and (iii.) linear model that interlink strain and leaves, respectively. The distribution

coefficient of diuron (dispersion rate) from root to stem was established at 0.046 and represent the numeric value of the diuron amount that disperse across the unit area (root compartment subdivision) per day from a certain position in the spatial domain (stem). Simulation were performed over experimental data set (amount, time period).

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