E3S Web of Conferences **285**, 03007 (2021) https://doi.org/10.1051/e3sconf/202128503007
ABR 2021

Derivation of pesticide aged sorption parameters from laboratory incubation data

Victoria Kolupaeva*

All-Russia Research Institute of Phytopathology, 143050, Bolshie Vyazemy, Russia

Abstract. The results of the incubation laboratory experiment showed that the decomposition of cyantraniliprole is bi-phasic and the rapid decomposition in the period after the application of the pesticide is accompanied by a subsequent slowdown of this process. The use of the bi-exponential equation increased the accuracy of the description of the dynamics of decomposition of cyantraniliprole, as evidenced by the static indices. The bi-exponential equation coefficients were used to calculate the parameters of non-equilibrium sorption. The obtained parameters served as input data for the PEARL model. Modelling the migration of cyantraniliprole with considering aged sorption, showed a significant decrease in the predicted concentrations of the pesticide in percolate.

1 Introduction

The degradation of pesticides in soil does not always occur with a constant rate. Often, a period of fast degradation is followed by a slowdown in the rate of the process [1,2]. One of the reasons for this phenomenon is considered to be the nonequilibrium (aged, time-dependent) sorption of pesticides. Sorption of pesticides, along with degradation, defines their fate in the environment. The degree of pesticide sorption affects their concentration in the soil solution [3] and so determines the availability of the pesticide for plants and microorganisms [4], the susceptibility of the pesticide to migration [5]. To estimate the parameters of non-equilibrium sorption, it is recommended to use incubation studies with the extraction of the pesticide with an organic solvent and an aqueous solution of calcium chloride [6]. However, it is also possible to roughly calculate the indices of aged sorption from a standard degradation study from bi-exponential equation [6]. The aim of the work was: to fit bi-exponential kinetics to degradation data and to receive the parameters of bi-phasic degradation; from the parameters of the bi-exponential model and parameters from standard batch sorption data to calculate the parameters for non-equilibrium sorption; with pesticide fate model PEARL 4.4.4 to assess the influence of the calculated sorption parameters on cyantraniliprole leaching.

* Corresponding author: v.kolupaeva@vniif.ru

2 Methods

2.1 Pesticide and soil

Cyantraniliprole is a second-generation insecticide, it belongs to the class of anthranilamides and is used on a wide range of crops against sucking pests and thrips. It is medium persistent and medium mobility active substances: $DT_{50geomean\ lab.}$ = 34.4 days and $K_{oc\ average}$ = 241 ml/g [7]. The soil is soddy-podzolic silt loam with 1.5% of organic carbon and pH = 6.

2.2 Degradation study and analytical detection

The degradation study was carried out in accordance with the OECD methodology [8]. Quantitative determination of cyantraniliprole content in soil was performed by high performance liquid chromatography (HPLC) in accordance with the methodological guidelines [9]. Detection limits of cyantraniliprole were 2.5 μg/kg.

2.3 Estimation of the bi-exponential equation parameters

Degradation cannot always be described by the first-order kinetics. Rapid initial pesticide disappearance is often accompanied by a slower decrease. This is commonly named to as bi-phasic nature of pesticide decomposition. One of the ways to describe the bi-phasic decomposition of pesticides is to use a bi-exponential model (eq. 1):

$$C = C_o * [g \exp(\lambda_1 t) + (1-g)\, exp(-\lambda_2 t)] \tag{1}$$

where C - total amount of chemical present at time t (μg kg^{-1}); C_0 - total amount of chemical applied at time t=0 (μg kg^{-1}); g - fraction of pesticide in fast compartment (-); k_1 - rate constant in fast compartment (day^{-1}); k_2 - rate constant in slow compartment (day^{-1}). The system consists of two first-order equations. Unfortunately, there is no analytical solution to this equation for calculating degradation endpoints; for this, an iterative procedure should be used. This can be done, for example, using the goal-seek function in Excel or Degradation Kinetics Software (FOCUS_DEGKIN v2), which was developed by the FOCUS working group, implemented in the Excel, and is available for download [10].

2.4 Assessment of goodness of fit

Differences between experimental and calculated values were assessed using the residual sum square (equation 2), scaled root mean square error (equation 3), coefficient of determination (equation 4), model efficiency (equation 5) and chi-square (χ2) statistics (equation 6):

$$\text{RSS} = \sum_{i=1}^{n}(O_i - P_i)^2 \tag{2}$$

$$\text{SRMSE} = \frac{1}{\bar{O}}\sqrt{\frac{1}{n}\sum_{i=1}^{n}(O_i - P_i)^2} \tag{3}$$

$$CD = \frac{\sum_{i=1}^{n}(O_i - \bar{O})^2}{\sum_{i=1}^{n}(P_i - \overline{O)}} \tag{4}$$

$$ME = \frac{\sum_{i=1}^{n}(O_i - \bar{O})^2 - \sum_{i=1}^{n}(P_i - \bar{O})^2}{\sum_{i=1}^{n}(O_i - \overline{\bar{O})}} \quad (5)$$

$$\chi^2 = \sum \frac{(O_i - P_i)^2}{(\frac{err}{100} * \bar{O})} \quad (6)$$

where O_i and P_i are observed and calculated values respectively, $\bar{O}$ - average of experimental values, n -number of measurements.

2.5 Aged sorption parameters calculation

k_t and k_{des} can be calculated on the basis of g, λ_1 and λ_2 at the equation 1 (equations 7 and 8):

$$k_{des} = \frac{\lambda_1 \lambda_2}{g\lambda_1 + (1-g)\lambda_2} \quad (7)$$

$$k_t = g\,\lambda_1 + (1-g)\lambda_2 \quad (8)$$

where k_{des} is the desorption rate coefficient (d^{-1}), k_t is the degradation rate coefficient (d^{-1}).

For the calculation of f_{NE}, the soil water content and the linear equilibrium sorption coefficient ($K_{L,EQ}$) are also needed (equations 9 and 10).

$$\Phi = \frac{g(1-g)(\lambda_1 - \lambda_2)^2}{\lambda_1 \lambda_2} \quad (9)$$

$$f_{NE} = \Phi \frac{W+-K_{L.EQ}}{K_{L.EQ}} \quad (10)$$

where f_{NE} is the factor for describing the ratio between the equilibrium and non-equilibrium Freundlich coefficients (-), W is the gravimetric water content of the incubation system, defined as volume of water divided by mass of dry soil (0.24 L kg^{-1}), and $K_{L,EQ}$ is the linear equilibrium sorption coefficient (from bath equilibrium sorption experiment [11]).

2.6 Model PEARL

Calculations of pesticide concentrations in leachate were carried out using the PEARL model, which is used when registering pesticides in the EU and the Russian Federation, and using standard scenarios for Moscow region. The PEARL model [12] describes the water flow by the Darcy law and the Richards' equation and the transport of pesticides in the soil by the convection – dispersion - diffusion equation.

3 Results and discussion

Table 1 presented the values of the parameters of the bi-phasic degradation of cyantraniliprole. The parameters were calculated using the FOCUS_DEGKIN v. 2 program, achieving the lowest RSS values. As can be seen from Table 2, the best agreement between the calculated and experimental values was obtained for the variant where the fraction of the pesticide available for rapid degradation (in the equilibrium phase) is 0.3, and the DT50 value of the fast phase is 6.6 days and the slow phase is 121.6 days.

Table 1. Bi-exponential equation and aged sorption parameters for cyantraniliprole. Predicted concentration in groundwater leachate

g (-)	λ_1 (day^{1})	λ_2 (day^{-1})	k_{des} (day^{-1})	k_t (day^{-1})	DT50 (day)	Φ (-)	f_{NE} (-)	C_{gw} (μ L^{-1})
0.2	0.1810	0.0088	0.0401	0.0397	17.45	4.47	4.65	0.00
0.3	0.1054	0.0057	0.0174	0.0345	20.11	4.14	4.31	0.02
0.4	0.0725	0.0047	0.0107	0.0318	21.80	3.24	3.37	0.04
0.5	0.0543	0.0028	0.0053	0.0285	24.31	4.43	4.61	0.08
0.6	0.0433	0.0006	0.0010	0.0262	26.44	17.44	18.16	0.00
0.7	0.0315	0.0001	0.0001	0.0221	31.43	65.73	68.45	0.00
0.8	0.0224	0.0001	0.0001	0.0179	38.72	55.38	57.67	0.00
1.0*	0.0139	0.0000	0.0000	0.0139	49.90	-	1	2.49

* - first-order equation variant.

Also, the data in Table 2 show that for values of g from 0.2 to 0.6, values of statistical parameters were satisfactory, and also for all variants of calculation except of g = 0.8, the calculated values of $\chi2$ were lower than the table values at a significance level of $\alpha = 0.05$, which suggested that all these options for solving the bi-exponential equation are acceptable. The calculated values of the sorption parameters are presented in Table 1. It should be noted that the values of k_{des} and k_t decreased with an increase in the amount of pesticide in the equilibrium phase (g), and the values of the distribution coefficient between the nonequilibrium and equilibrium phases (f_{NE}) first slightly decreased from g = 0.2 to g = 0.4, and then increased significantly.

Table 2. Statistical characteristics of fitting degradation experimental data to bi-exponential model

g	$\chi2$*	RSS	SRMSE	CD	ME
0.2	4.16	44.90	0.04	0.98	0.98
0.3	2.50	16.18	0.02	1.02	0.99
0.4	2.83	20.80	0.03	1.02	0.99
0.5	3.69	35.25	0.04	0.98	0.99
0.6	4.50	52.55	0.04	0.96	0.98
0.7	6.65	114.71	0.07	0.81	0.97
0.8	9.65**	244.67	0.10	0.64	0.94
1.0***	9.74	454.46	0.13	0.66	0.89

* - $\chi2_{tabl}$ equal 9.16 for bi-exponential equation (three fitted parameters) and 11.07 for first-order equation (one fitted parameters).
** - $\chi2_{calc} > \chi2_{tabl.}$
*** - first-order equation variant.

It is known that non-equilibrium sorption of pesticides leads to a decrease in the mobility of pesticides in the soil. Using the PEARL model, the 80% percentile of the average annual values of the cyanthraniliprole concentration in the groundwater leachate at a depth of 1 m was calculated (Table 1). The simulation results showed that if aged sorption is taken into account, then the predicted pesticide concentrations in percolate were significantly reduced.

4 Conclusion

The study of cyantraniliprole degradation in laboratory incubation experiment revealed that insecticide kinetics had a pronounced two-stage character - rapid decomposition at the beginning with slowing down later. The use of the bi-exponential equation to describe the dynamics of degradaion of cyantraniliprole significantly increased the accuracy in comparison with the first-order equation. The best fit of the model with experimental data was at g (the fraction of the pesticide in the fast phase) equal to 0.3. The parameters of the bi-exponential equation were used to determine the indicators that characterize the process of time-dependent sorption. For the variant with g = 0.3, k_{des} was equal to 0.0174 d^{-1} and f_{NE} is equal to 4.31. Modeling with the PEARL model confirmed that non-equilibrium sorption was an important process influencing the behavior of a pesticide in soil. So, in this case, the predicted concentrations of the pesticide in the leachate decreased by more than 100 times compared with the option where only equilibrium sorption was taken into account.

References

1. D. I. Gustafson, L. R. Holden, Environ. Sci. Technol. **24**, 1032 (1990)
2. J. J. Pignatello, Adv. Agron. **69**, 1 (2000)
3. R. D. Wauchope, S. Yeh, J. B. H. J. Linders, R. Kloskowski, K. Tanaka, B. Rubin, A. Katayama, W. Koerdel, Z. Gerstl, M. Lane, J. B. Unsworth, Pest Manag. Sci., **58,** 419 (2002)
4. M. Alexander M, Environ. Sci. Technol. **34**, 4259 (2000)
5. A. Walker, M. S. Rodriguez-Cruz and M. J. Mitchell, Environ. Pollut. **133**, 43 (2005)
6. Statement on the FERA guidance proposal: ‘Guidance on how aged sorption studies for pesticides should be conducted, analysed and used in regulatory assessments’ (FERA, 2012). EFSA J. **13(7)**, 4175 (2015)
7. PPDB - Pesticide Properties Database URL: https://sitem.herts.ac.uk/aeru/ppdb/en/
8. Test No. 307: Aerobic and Anaerobic Transformation in Soil. URL: https://www.oecd-ilibrary.org/environment/test-no-307-aerobic-and-anaerobic-transformation-in-soil_9789264070509-enL
9. V. Kolupaeva, A. Kokoreva, A. Belik, P. Pletenev, Open Agriculture. **4**, 599 (2019)
10. Degradation Kinetics Software. URL : http://esdac.jrc.ec.europa.eu/
11. V. Kolupaeva, I. Nyukhina, A. Belik, E3S Web of Conferences. **169** (2020)
12. Pearl version 1.1. User Manual. RIVM report 711401008, Alterra report 29. 2000. 144 p.