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EFFECT OF WINE INDUSTRY WASTE ON PESTICIDE DEGRADATION IN SOIL

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ABSTRACT: Dissipation kinetics of insecticide neonicotinoids belongs to chemical groups dinotefuran and flonicamid was studied in black soil and amended with red wine waste and white wine waste at the rate of 1% and 5%. The rate of degradation in soil and amended soil was in the order of sterilized black soil < black soil < red waste 1% < red waste 5% <white waste1% < white waste 5% with half-life ranging between 1-2 days for flonicamid and 20-30 days for dinotefuran. The dissipation behavior of flonicamid and dinotefuran insecticides followed 1st and 1st+ 1st order rate kinetics Comparison of the degradation rate in natural against sterilized soil suggests that, microbial degradation might be the major pathway of pesticide dissipation

KEYWORDS: Insecticides, wine waste, soil, dissipation rate kinetics, half-life.

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1. INTRODUCTION

The application of large number of pesticides are used in modern agriculture for control various insect pest population. The varieties and consumption of pesticides have been increasing as increased human population and crop production, therefore misuses of pesticides become more and more serious problem as environmental point of view [1]. The repeated application of pesticides may reaches in soil activity creates imbalance of soil which kills the pests and destroy the micro-organisms which are required for soil fertility and productivity [2]. There is a growing interest in the utilization of the wine waste generated by the wine making industry. The addition of wine waste in soil is a good alternative to increase the soil fertility. The application of amendment to soil increase adsorption of chemicals, reduces mobility and increase degradation [3]. The pomace is solid material containing skin, seed and pulp produced in large quantity during wine production [4], which is cheap, eco-friendly, easily available and safe for soil. The application of wine waste increases percentage of organic matter. [5], which are responsible for enhancement of the microbial activity within a soil, help to stimulate microorganism population. Dinotefuran and flonicamidare systemic insecticides belonging to group neonicotinoids used to control sucking and chewing insect pest such as aphids, whiteflies, leaf plant-hoppers, thrips, micro lepidoptera and coleopteran. These systemic insecticides are applied as foliar spray which get absorbed by root system [6]. Dinotefuran have high water solubility 39,830 mg/L and low partition coefficient (Kow 0.283) [7], while flonicamid have water solubility 5,200 mg/L with low partition coefficient (Kow 0.263) [8]. The application of wine waste in soil is a type of organic amendment with significant importance from the environmental point of view, which is helpful for increasing microbial biomass. By Knowing fate and behavior of dinotefuran and flonicamid in soil it is clearly indicate that, there is need of application of wine waste in soil. The objective of current work was to study the effect of white and red wine waste on dissipation of flonicamid and dinotefuran in amended soil and black soil.

2. MATERIALS AND METHODS

2.1. Chemical

The agricultural formulation of dinotefuran (Token 20% WG) was obtained from United Phosphorus Limited. (Mumbai, India) and flonicamid (ULALA 50% WG) obtained from Indofil. (Gujarat, India). The certified reference standard of dinotefuran and flonicamid were purchased from Dr. Ehrenstorfer GmbH, Augsburg, Germany (>99% purity), Chemical Industries. Ltd, Osaka, Japan). All other solvents and reagents used were of LC-MS grade or equivalent purity (Sigma-Aldrich India, Bangalore).

2.2. Soil Sampling

For the laboratory study, the black soil samples were collected at a depth of 0-10 cm from the top soil layer from the farm of ICAR- National Research Centre for Grapes, Pune, India. The soil was air dried prior to the laboratory experiment and sieved to a maximum particle size of <2 mm for experimental study. The physico-chemical properties such as pH, conductivity and organic carbon of soil were estimated by using standard methods. The soil types belonged to the textural class clay with physiochemical properties are described in the table 1.For the amendment study, White (Sauvignon Blanc) and red (Cabernet Sauvignon) grapes were collected from Sula wineries located in Nasik region of Maharashtra (India). Afterwards grapes were processed for wine and the winery by-products (Pomace) for two varieties were collected for further study.

2.3. Soil Preparation

The degradation study was performed with six different sets which include black soil, sterilized black soil, two sets of black soil amended with white wine waste (Sauvignon Blanc) and two sets of black soil amended with red wine waste (Cabernet Sauvignon). Sterilization was performed to explore the abiotic rate of degradation of selected insecticides in soil by autoclaving the soil at 100 ºC for 1hr. The amended soil was prepared by adding red and white wine waste at the rate of 1% and 5% level on dry weight basis and also separate to black soil (approximately 1 kg). Further, 200 g of each soils were taken and different treatments were applied. The moisture content in the soil was maintained at field capacity level by checking every week throughout the experimental period.

2.4. Degradation study

Degradation experiment for dinotefuran and flonicamid insecticides were carried out separately. The application rate of flonicamid for the study on black soil, amended soil and sterilized black soil were 1 and 10 mg/kg and for dinotefuran the application rate were 1 and 5 mg/kg. Samples were drawn at 0, 1, 3, 5, 7, 10, 15, 30, 45 and 60th days of interval and analysis was carried out using LCMS-MS.

2.5. Extraction of sample

Flonicamid: Soil sample (5g) was drawn in 25 ml centrifuge tube separately and acetonitrile 10 mL was added to it as extraction solvent. The mixture was vortexed for 2 mins and to it dried 4 g magnesium sulphate and 1 g sodium acetate was added followed by vortexing again for 2 min. The sample was centrifuged at 2000 rpm for 5 min and supernatant was collected, filtered with 0.22 µ nylon filter and analysed in LC-MS/MS.

Dinotefuran: Soil sample (10 g) was taken in a 25 mL centrifuge tube and extracted with 10 mL 80% methanol by vortexing. Afterwards the sample was centrifuged at 2000 rpm for 5 min. The supernatant was then filtered with 0.22 µ nylon filter and the analysis was carried out on LC-MS/MS.

2.6. LC-MS/MS analysis

The calibration standards (6 levels) ranging between 0.01- 0.5 mg/mL were prepared by successive dilutions of the intermediate standard (10 mg/mL) in methanol: water (1:1, v/v). The LOD was set at signal to noise (S/N) of ≥3, whereas the LOQ was set to a signal with S/N≥10 pertaining to the quantifier MRM. The analysis of flonicamid and dinotefuran were carried out using high performance liquid chromatography (HPLC) (Waters 2695 separation module) hyphenated to triple quadrupole (Quattro Premier, Waters Corporation, Milford, USA) mass spectrometer equipped with electron spray ionization (ESI) probe. An aliquot of 10 µL was injected via autosampler. The column oven temperature was maintained at 25ºC. The analysis of flonicamid was done using an eclipse plus

C_{18} column (4.6×150mm, 5µm; Merck India Ltd., Mumbai), with the mobile phase composed of A: methanol: water (10:90, v/v) with 0.5% Formic acid) and B: methanol: water (90:10, v/v) with 0.5% Formic acid. The elution was done in gradient elution mode at the flow rate of 0.8 mL/min. The gradient programme consisting 0-1 min/10 % B, 5.0-10 min/98 % B, 11-15 min/15% B gave elution of flonicamid at 3.49 min. Flonicamid quantification was done considering 230.2 $[M+H]^+$ >173.9 transition and 230.2 >147.8 transition was taken for confirmation. Dinotefuran analysis was conducted with Purosphere column (4.6×150 mm, 5µm; Agilent technology) with mobile phase flow rate of 0.3 mL/min. The mobile phase was composed of A: H_2O (water) 100% with 0.5% formic acid + 20mm Ammonium formate and B: 100% ACN (acetonitrile) with gradient 0-0.5 min/15% B, 3.0 min/ 60% B, 3.5-6 min/ 15% B. The LC-MS/MS analysis was performed in positive polarity by multiple reaction monitoring (MRM) with mass transition 203.3 $[M+H]^+$ >129 selected for quantification and 203.3>113.3 for confirmation of dinotefuran.

2.7. Data analysis

The time-wise residue dissipation data was analyzed using the curve fitting software Table curve 2D v 5.01. Equation parameters, regression equation, half-life were calculated by the software. The different models used are listed below:

1^{st} order: $[A]_t = [A]_1 . \exp(-k_1 . t)$ (1)

$1^{st} + 1^{st}$ order model: $[A]_t = [A]_1 . \exp(-k_1 . t) + [A]_2 . \exp(-k_2 . t)$ (2)

In the above equations, $[A]_t$ is the concentration (µg kg^{-1}) of A at time t (days) and $[A]_{1\&2}$ are the initial concentrations of A at time 0 degraded through 1^{st} or 1^{st}+ 1^{st} order process. The symbols k_1 and k_2 are the degradation rate constants equation 1 and 2. Since the 1^{st}+ 1^{st} order model cannot be described in a differential form, DT_{50} could only be calculated by an iterative procedure. The equation parameters and DT_{50} for all kinetic models were calculated by using commercially available program Table Curve 2D (v 5.01).

3. RESULTS AND DISCUSSION

The linearity of the calibration curve was established in the range 0.01-5 mg $kg^{-1}$with correlation coefficient (R^2) of the calibration curve >0.99. For matrix matched calibration also, the R^2 was >0.99. The LOD and LOQ were decided as 0.082 and 0.274 mg kg^{-1} for dinotefuran and 0.010 and 0.034 mg kg^{-1} for flonicamid. The kinetics of the residue data was evaluated by fitting the data into 1^{st} and 1^{st}+ 1^{st} order kinetics model. In dinotefuran the rate of degradation was very fast at the beginning following 1 + 1st order kinetics were 30, 27, 26, 25, 24 and 21 days for sterilized soil, black soil, red wine waste1%, red wine waste 5%, white wine waste1% and white wine waste 5% respectively. In flonicamid the rate of degradation following 1st order kinetics. The persistence of flonicamid was very low in the amended soil of 1% and 5% white wine waste, 1% red wine waste and 5% red wine waste (WW1, WW5, R W1 and RW5), which was present only for 3 days after application. The calculated half life of flonicamid was found to be 3.0, 2.0, 1.7, 1.9, 1.2 and 1.6 days in sterilized soil, black soil, red wine waste 1%, red wine waste 5%, white wine waste 1% and white wine waste 5% respectively. From above observation it was concluded that, the rate of degradation in soil and amended soil was in the order of sterilized black soil < black soil < red waste 1% < red waste 5% < white waste1% < white waste 5% with half-life ranging between 1-2 days for flonicamid and 20-30 days for dinotefuran. The best fit of the residue data to a two-compartment 1st + 1st order kinetics model indicates partitioning of the residues into two phases where one fraction of the applied pesticide, which was immediately available in one of the phases (initial phase), degraded rapidly, leaving the other part possibly remaining in dynamic equilibrium as an adsorbed fraction on cellular components.

4. CONCLUSION

The extraction method was suitable for analysis of dinotefuran and flonicamid with satisfactory precession and accuracy. The dissipation of residues best follows 1^{st} order for flonicamid and $1^{st}+1^{st}$ order for dinotefuran. In the present study the effect of pesticide in soil was studied by addition of wine industry waste. Overall it was observed that soil without addition of amendment show least dissipation, while soil with addition of wine waste shows enhanced dissipation. Present study clearly reveals that, wine waste material has good potential as a cost effective tool for dinotefuran and flonicamid dissipation in soil. Further R&D work on integration of cropping pattern and wine waste amendments under field conditions is warranted to recommend a technology package for the farmers.

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SUPPLEMENTARY FILES

Table 1.1. Physico- chemical properties of black and amended soils

Types of soil	**Black soil**					
Soil properties	Clay (Texture)	pH	Cation exchange capacity (meq/100g soil)	Water holding capacity%	Density(gm/ml)	Organic carbon%
	58.98%	7.7	55.40	58%	1.27	1.03

Wine waste	**Organic carbon (%)**	**Cation exchange capacity**
Red wine waste 1%	2.21	67
Red wine waste 5%	6.11	63
White wine waste 1%	3.15	70
White wine waste 5%	6.06	75

Table 1.2. Degradation parameters for the analyzed dinotefuran in studied soil

Soil	Parameters	Unit	1st order		1st + 1st order	
			SD	DD	SD	DD
Black soil	[*A*]1	mg/kg	852.36	4055.84	180.03	1386.32
	*k*1	days−1	0.018	0.020	0.168	0.315
	[*A*]2	mg/kg	NA	NA	409.64	3312.8
	*k*2	Days−1	NA	NA	0.0087	0.013
	R^2	NA	0.91	0.87	0.98	0.98
	DT50	days	37.57	33.33	27	25.45
Sterilized black soil	[*A*]1	mg/kg	720.18	3928.1	363.86	1101.43
	*k*1	days−1	0.014	0.019	0.322	0.6331
	[*A*]2	mg/kg	NA	NA	540.07	3464.75
	*k*2	days−1	NA	NA	0.0058	3464.75
	R^2	NA	0.67	0.86	0.99	0.95
Red wine waste (1%)	DT50	days	47.27	35.75	30.9	27.87
	[*A*]1	mg/kg	889.21	4037.42	828.7	1350.6
	*k*1	days−1	0.017	0.022	0.032	0.50
	[*A*]2	mg/kg	NA	NA	682.07	3442.88
	*k*2	days−1	NA	NA	0.00002	0.016
	R^2	NA	0.96	0.86	0.99	0.97
	DT50	days	40	32.72	26	23.2
Red wine waste (5%)	[*A*]1	mg/kg	853.30	3918.9	580.41	2026.5
	*k*1	days−1	0.019	0.02	6.10E-02	0.223
	[*A*]2	mg/kg	NA	NA	411.53	2643.0
	*k*2	days−1	NA	NA	7.08	0.0105
	R^2	NA	0.92	0.82	0.99	0.98

	DT50	days	35.75	29.09	25	14.54
White wine waste 1%	[*A*]1	mg /kg	705.27	4165.9	294.17	2489.84
	*k*1	days−1	0.018	0.0369	0.615	0.138
	[*A*]2	mg kg	NA	NA	604.97	2141.82
	*k*2	days−1	NA	NA	0.012	0.013
	R^2	NA	0.80	0.92	0.99	0.99
	DT50	days	38.78	18.78	24	11.51
White wine waste (5%)	[*A*]1	mg /kg	691.79	3192.4	286.17	1789.14
	*k*1	days−1	0.018	0.021	0.796	0.129
	[*A*]2	mg kg	NA	NA	601.01	1848.6
	*k*2	days−1	NA	NA	2.80E-05	0.0061
	R^2	NA	0.763	0.85	0.99	0.99
	DT50	days	38.78	32.12	21	18.18

Table1.3. Degradation parameters for the analyzed flonicamid in studied soil

Soil	Parameters	Unit	1st order		1st + 1st order	
			SD	DD	SD	DD
Black soil	$[A]1$	mg/kg	868.83	7851.18	350.83	3930.8
	$k1$	days−1	0.340	0.188	1.573	0.188
	$[A]2$	mg/kg	NA	NA	569.23	3920.37
	$k2$	Days−1	NA	NA	0.211	0.188
	R^2	NA	0.96	0.91	0.99	0.91
	DT50	days	2.0	3.6	1.4	3.6
Sterilized black soil	$[A]1$	mg/kg	867.06	8997.11	442.24	4666.58
	$k1$	days−1	0.286	0.22	0.228	0.230
	$[A]2$	mg/kg	NA	NA	408.10	4343.0
	$k2$	days−1	NA	NA	0.228	0.2316
	R^2	NA	0.67	0.86	0.99	0.95
	DT50	days	3.0	9.7	3.0	3.0
Red wine waste (1%)	$[A]1$	mg/kg	904.71	6051.72	NA	NA
	$k1$	days−1	0.40	6051.72	NA	NA
	$[A]2$	mg/kg	NA	NA	NA	NA
	$k2$	days−1	NA	NA	NA	NA
	R^2	NA	0.99	0.95	NA	NA
	DT50	days	1.7	1.3	NA	NA
Red wine waste (5%)	$[A]1$	mg/kg	835.69	8060.5	513.09	3832.62
	$k1$	days−1	0.359	0.352	0.360	0.35
	$[A]2$	mg/kg	NA	NA	322.58	4227.8
	$k2$	days−1	NA	NA	0.359	0.3515
	R^2	NA	0.95	0.90	0.95	0.90
	DT50	days	1.9	1.9	1.9	1.9
White wine waste (1%)	$[A]1$	mg /kg	843.77	8060.70	NA	4142.62
	$k1$	days−1	0.56	0.375	NA	0.376
	$[A]2$	mg kg	NA	NA	NA	3918.124
	$k2$	days−1	NA	NA	NA	0.3749

	R^2	NA	0.99	0.95	NA	0.95
	DT50	days	1.2	1.8	NA	1.8
White wine waste (5%)	$[A]1$	mg /kg	852.53	7404.41	NA	3579.69
	$k1$	days−1	0.433	0.349	NA	0.3502
	$[A]2$	mg kg	NA	NA	NA	3824.65
	$k2$	days−1	NA	NA	NA	0.348
	R^2	NA	0.98	0.90	NA	0.90
	DT50	days	1.6	1.9	NA	1.9

SD= Single Dose, DD= Double Dose, NA= Not Applicable

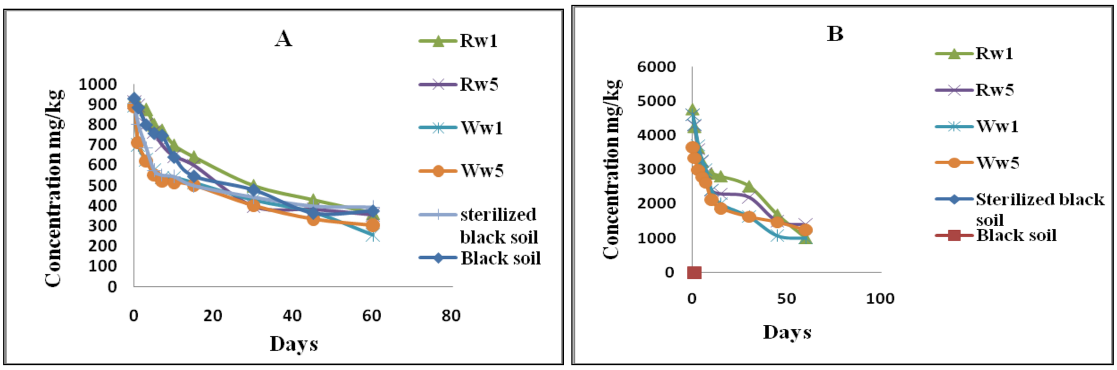

Figure 1.1[a] Degradation pattern of dinotefuran

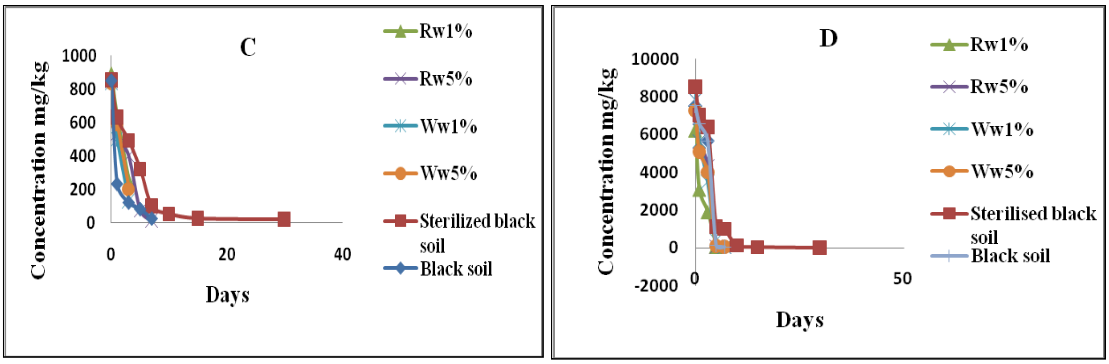

Figure 1.1[b] Degradation pattern of flonicamid

A=Dinotefuran single dose, B= Dinotefuran double dose, C=flonicamid single dose, D= flonicamid double dose.

Rw1%= Red wine waste1%, Rw5%= Red wine waste5%, Ww1%= White wine waste1%, Ww5%= White wine waste5%