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PROBING THE DECAY MODELLING OF FUNGICIDES ON GRAPE VARIETIES

Muhammad Nadeem[1,*], Muhammad Atif Randhawa[1], Masood Sadiq Butt[1] and Muhammad Asgher[2]

[1]National Institute of Food Science and Technology, University of Agriculture, Faisalabad- 38040, Pakistan;
[2]Department of Biochemistry, University of Agriculture, Faisalabad 38040, Pakistan
***Corresponding author's e-mail: Nadeem.foodscience@gmail.com**

Pesticides are applied on grapevines to combat various pests which are catastrophic for grapes and cause menace for farmers. Hence, to investigate the fate of difenconazole and cymoxanil their supervised trial was conducted on 2 grape varieties with 3 doses of each. Perlette variety is elliptical and sweet in taste with greenish color whereas black grapes are round and have blackish appearance with sweet and sour taste. Moreover, black grape has thick skin as compared to perlette. The residues (mg Kg^{-1}) of cymoxanil dissipated from 2.44±0.11 to 0.18±0.02 at recommended dose (RD), 3.08±0.25 to 0.21±0.02 at double dose (DD) and 5.70±0.29 to 0.26±0.02 at triple dose (TD) on perlette while 2.42±0.14 to 0.078±0.007 at RD, 3.45±0.28 to 0.003±0.001 at DD and 5.71±0.28 to 0.083±0.008 at TD on black grape, correspondingly showing greater dissipation. Similar trend was witnessed from perlette where difenconazole residues (mg Kg^{-1}) dissipated from 9.41±0.24 to 0.45±0.03 at RD, 15.98±1.42 to 0.66±0.023 at DD while 23.93±0.31 to 0.74±0.040 at TD. Nonetheless, on black grapes difenconazole disappeared more as compared to perlette from initial to final residues (mg Kg^{-1}) *i.e.*9.64±0.21 to 0.26±0.015 at RD, 16.13±0.42 to 0.53±0.048 at DD but 24.15±1.57 to 0.026±0.002 at TD, respectively. Mathematical first order model having exponential decay was best fitted to forestated residues where allied parameters (half-life, end point identifier *i.e.* DT90) were calculated for both varieties and pesticides. Cymoxanil dissipated earlier than difenconazole and black grapes represented excellent pesticide loss than perlette.

Keywords: Grape varieties; Vineyard; Supervised Fungicides; Mathematical model; Fungicides decay; Maximum residual limit.

INTRODUCTION

Grape berries are delicious and gift of nature with health promoting capabilities. Grape history dates back 3500 BC-2900BC, when grapevines were grown for different products of human use (Ali *et al.*, 2010). There are 3 types of grapes depending upon end product *i.e.* table grapes for fresh use, raisin for drying and wine grapes for wine production (Chervin *et al.*, 2012). Pesticides are applied on food crops to augment their yield and to eliminate a huge array of pests. These chemicals are either synthetic or natural with 800 active ingredients being utilized in more than 3000 commercial products and marketed around the globe (Chang *et al.*, 2016). So, knowledge of dissipation is very crucial to know residual effect of pesticides in plants, animals and aquaculture along various steps of processing in food chain. As pesticides are notorious for adverse health effects *i.e.* reproductive, carcinogenic, dermatological, endocrinal, gastrointestinal and neurological anomalies in animals and humans. Pesticides pose health effects either by respiratory, dermal or digestive tract where pesticide type, exposure and health status of a person matters for health dysfunctions. Likewise, accidental intake, occupational exposure and intentional ingestion may cause hospitalization or even death in severe cases (Nicolopoulou-Stamati *et al.*, 2016).

So, fate of various chemicals has been studied comprehensively but dissipation kinetics requires more rigorous studies to explore the underlying mechanisms as certain processes and aspects are still not fully understood (Fantke and Juraske, 2013). Recently, a team of researchers explicated that pesticides can be dissipated to avoid health threat and reported triazoles and diverse class residues on grapes by compiling various doses and observed accelerated decay to safety limits by adjunct use of *Bacillus* strains. They reported >99% (tetraconazole), 87.38 % (myclobutanil) and 90.82% (flusilazole) degradation of residues (Salunkhe *et al.*, 2015). Previously, Navarro *et al.* (2001) reported dissipation half-life of six pesticides after field application and reported following outcomes like fenarimol (7.8 days), metalaxyl (12 days), chlorpyrifos (4.4 days), penconazole (6.6 days), mancozeb (13.5 days) and vinclozoline (8.3 days).

Although, there is a quest to develop the agro-chemicals which are less persistent but have excellent performance according to requirement. Hence, more degradable compounds are being synthesized and replaced with previous persistent ones, because according to an estimate 0.1 to 10 %

pesticides reach the target and remaining are environmental pollutants. Therefore, to get rid of allied danger, degradation techniques are being sought and applied accordingly (Gill and Garg, 2014; Carvalho, 2017; Parte *et al.*, 2017).

Various factors of dissipation include plant factors (foliage, canopy, growth rate, species), soil factors (acidic or alkaline nature, composition, leaching, percolation, adsorption, erosion, surface run off), climatic factors (humidity, temperature, wind speed, precipitation), physico-chemical factors (solubility, volatility, oxidation, hydrolysis, photolysis, dissolution, thermal degradation) and microbial factors (bacteria, actinomycetes, virus and fungi, fermentation) (Edwards, 1975; Gavrilescu, 2005; Kah *et al.,* 2007; Amvrazi, 2011; Porto *et al.*, 2011; Hassan, 2015; Lewis and Tzilivakis, 2017).

Purposely, after current findings difenconazole and cymoxanil can be applied commercially on grapes with prior estimate of residual limit, safe waiting period, dose effect and formulation nature, particularly in Pakistani climate where farmers are expanding the grapevines. Consequently, present research was conducted on perlette and black grape varieties using 3 doses of each from 2 fungicides applied during open field trial where current research was performed with hypothesis that either supervised doses of pesticides decay to MRLs (maximum residual limits) or not during pre-harvest interval and which variety responds earlier.

MATERIAL AND METHODS

***Selection of field location*:** Cymoxanil and difenconazole are systemic (which penetrate to commodity) fungicides as grapes are susceptible to fungus attack so these are frequently applied. Hence, supervised trial was carried out using difenconazole and cymoxanil pesticides on 3 years old Vineyard at Chak-60 J.B. (Shahbazpur) near Faisalabad where farmer was using normal agronomic practices.

***Conduction of Experiment*:** Henceforward, 12 plants of each selected cultivar were properly tagged with pesticides names, doses and date of application. Trial was conducted in the months of May and June, 2017. Among the supervised fungicides *viz.* difenconazole and cymoxanil were selected. According to manufacturer specification three doses *i.e.* @ 1605, 3210 and 4815 mL a.i. ha^{-1} of cymoxanil and 370, 740 and 1110 mL a.i. ha^{-1} of difenconazole were prepared by adding water and sprayed with sprayer (Knapsack; 20 Ltr. capacity) equipped with hollow cone type nozzle and hand operated pump in form of fine droplets early in the morning. The vines were sprayed with aforementioned residues 35-40 days before of routine harvest which was usually accomplished in selected garden and this period is designated as pre-harvest interval.

***Layout and Design of Vineyard*:** The selected garden had typical layout where different varieties had been planted in rows but in distinct pattern. Amongst different varieties, perlette with green color and oval shape while black grapes with dark blackish color and ovoid configuration, were selected for supervised trial of pesticides.

***Meteorological observations*:** During trial, average, maximum, minimum temperature, relative humidity and rain fall data were secured from local weather station located at University of Agriculture Faisalabad. Meteorological observation data were interpreted by acting upon guidelines of Mohapatra and Lekha (2016) with some changes.

***Grape sampling from Field Trial*:** Two grape varieties (perlette and black) were secured from supervised trial using random sampling at intervals 0^{th} day (2hr after spray), 3^{rd} day, 7^{th} day, 15^{th} day, 20^{th} day, 25^{th} day, 30^{th} day, 33^{rd} day and 35^{th} day while fruit on vine. Moreover, berries hidden under leaf canopy or having visual disease symptoms were not included while sound fruits with direct contact of spray doses were harvested at each sampling interval by following prescriptions of Mohapatra and Lekha (2016) with some changes.

***Extraction and Clean-up procedure*:** Supervised pesticides were extracted from both varieties at sampling intervals, afterwards, clean-up was carried out by acting upon the guide lines and standard procedure adopted by Randhawa *et al.* (2007a, 2007b). Grape berries were extracted with solvent acetonitrile using orbital shaker and debris was removed after filtration. The filtrate having co-extractives was passed through florisil clean-up along with anhydrous sodium sulphate using glass column. The column was prepared with adsorbent, activated Na_2SO_4 and rested over cotton wool plug. The cleaned-up residues were concentrated using rotary vacuum evaporator following nitrogen flushing till 1 to 2 mL residue obtained. The final residue was then reconstituted and micro filtered for high performance liquid chromatography (HPLC) equipped with UV-visible detector for analysis.

***HPLC analysis*:** Standard and finalized protocol was applied after setting detector wavelength at 220 nm while flow rate to 1 mL per minute. ODS-2-Hpersil thermo-scientific (USA) separating stainless steel C-18 column was used. Mobile phases comprising of 100% acetonitrile+0.1% TFA (trifluroacetic acid)=(A) and 100% methanol=(B),were degassed in sonicator (D-78224, Singen-HTW, Germany) after filtration. Finalized pump program comprised A=100% and B=0% for 0.5 minutes, A=50% and B=50% for 8 minutes, A=70% and B=30% for 6 minutes, A=100% and B=0% for 10 minutes to elucidate standard chromatogram and distinct peaks (Fig.1).

***Dissipation order*:** Mathematical model *i.e.,* first order dissipation kinetics was applied to determine various dissipation parameters as data fitted best to this model where half-lives and related parameters (half-life, end-point identifier, co-efficient of determination and dissipation constants) were the outcomes of best fitted model (Mai *et al.,* 2018).

$$P_t = P_{0*}e^{(-kx)}$$

Where, P_{t}=pesticide residues at time t; P_{0}= initial pesticide residues; K_{diss} = dissipation constant X = denotes the time series or interval.

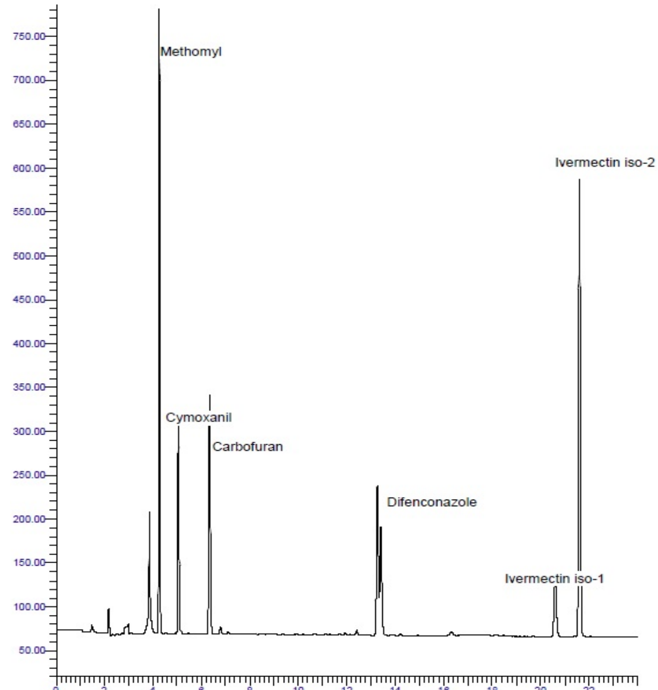

Figure 1. Standard chromatogram of cymoxanil and difenconazole

***Recovery and validation studies*:** Spiking of supervised fungicides was done at 2, 3 and 5 (mg Kg^{-1}) levels and 96.07±2.87, 95.76±3.85 and 94.66±4.81 % recoveries were calculated for cymoxanil while 91.99±3.13, 101.61±5.71 and 101.74±5.13 for difenconazole in perlette. Likewise, percent recoveries with numerical values of 96.13±4.18, 95.42±3.8 and 95.46±3.42% were reported in black grapes for cymoxanil but 96.21±5.23, 95.76±4.38 and 95.73±3.54 for difenconazole, respectively at stated spikings. Moreover, limits of detections (LODs) and limits of quantifications (LOQs) explicated were 19.32 and 58.56 (µg Kg^{-1}) for cymoxanil but 6.76 and 20.49 (µg Kg^{-1}) for difenconazole correspondingly.

RESULTS

As results related terms are considered, DT90 is duration needed to disappear the residue by 90% while Half-life states 50% residue dissipation under specific period of time dictated by numerous factors (Fig.2) of extrinsic and intrinsic nature. Hence for both varieties these parameters were meaningful to comprehend fate of fungicide residues. Moreover, safety limits of both systemic fungicides were (3 mg Kg^{-1}) and (0.30 mg Kg^{-1}) corresponding to difenconazole and cymoxanil. Results of below given residues have been represented at each sampling interval with percent decline compared to 0th day (0% dissipation) and until 35th day (maximum % loss) to access fungicide fate with passage of time.

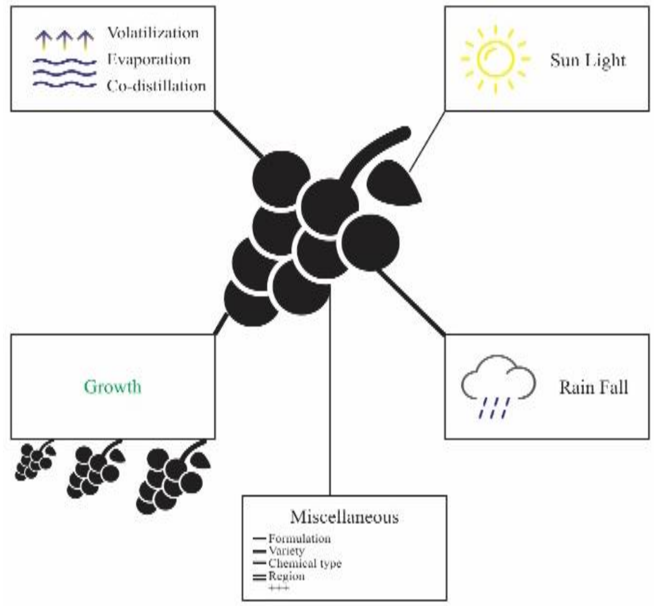

Figure 2. Multifaceted factors dictating fungicide dissipation on Grapes

***Fate of Cymoxanil in Perlette*:** Initial deposits (mg Kg^{-1}) of cymoxanil at 0th day were determined as 2.44±0.11, 3.08±0.25 and 5.70±0.292 for RD, DD and TD in perlette, respectively. The initial deposits of RD disintegrated with the passage of time interval with mean values 2.44±0.11, 1.90±0.076, 1.11±0.068, 0.36±0.032 and 0.18±0.017 at 0th day, 3rd day, 7th day, 15th day and 20th day, respectively but became below detection limit (BDL) at 25th day. The percent reductions of aforementioned RD were 0.00, 22.38, 54.51, 85.14 and 92.46 at 0th day, 3rd day, 7th day, 15th day and 20th day, respectively while 100% reduction was considered at BDL related to 25th day. Similarly, the initial deposits (mg Kg^{-1}) of double dose in perlette dissipated with the advancement of time with mean values 3.082±0.25, 2.49±0.22, 1.653±0.16, 0.718±0.032, 0.36±0.024 and 0.21±0.02 alongwith percent decrease 0.00, 19.18, 46.37, 76.71, 88.32 and 93.14 at 0th day, 3rd day, 7th day, 15th day, 20th day and 25th day, respectively and reduced below detection limits at 30th day where 100% reduction was considered. Moreover, triple dose of cymoxanil in perlette demonstrated dissipation with passage of time but reduction was low as compared to RD and DD indicating greater dose has more stability towards degradation. The residues (mg Kg^{-1}) decomposed with mean values of 5.70±0.29, 4.73±0.31, 3.30±0.30, 1.83±0.083, 0.97±0.06, 0.96±0.079, 0.33±0.011 and 0.26±0.021 alongwith percent dissipation 0.00, 17.01, 42.05, 67.85, 82.90, 83.09, 94.18 and 95.52 at 0th day, 3rd day, 7th day, 15th day, 20th day, 25th day,

Table1. Model depiction of fate summary of Cymoxanil and Difenconazole.

Statistical Indices of Model	Perlette Cymoxanil			Perlette Difenconazole		
	RD	**DD**	**TD**	**RD**	**DD**	**TD**
			Best Fitted Values			
K dissipation	0.12	0.098	0.081	0.087	0.066	0.065
Half-life (days)	5.89	7.094	8.550	7.98	10.46	10.67
			Goodness of fit			
R^2	0.99	0.99	0.99	0.97	0.97	0.97
			End point identifier			
DT_{90} (ln10/K dissipation)	19.60	23.57	28.40	26.50	34.74	35.44
			Safe waiting periods			
Pre-harvest interval	20days	25days	33days	20days	25days	<33days
Statistical Indices of Model	**Black grape Cymoxanil**			**Black grape Difenconazole**		
	RD	**DD**	**TD**	**RD**	**DD**	**TD**
			Best Fitted Values			
K dissipation	0.14	0.11	0.098	0.096	0.078	0.075
Half-life (days)	4.95	6.11	7.056	7.25	8.88	9.30
			Goodness of fit			
R^2	0.99	0.99	0.99	0.98	0.99	0.98
			End point identifiers			
DT_{90} (ln10/K dissipation)	16.42	20.31	23.44	24.09	29.50	30.90
			Safe waiting periods			
Pre-harvest interval	15days	<25days	30days	>15days	<25days	30days

RD=Recommended dose, DD=Double dose, TD=Triple dose, Residues= (mg Kg^{-1}), DT-90 and Half-life=days

30th day and 33rd day, respectively but became BDL at 35th day. Inferring there upon, RD dissipated and reached to MRL (0.3 mg/Kg) before 20th day, DD till 25th day and TD took longer than RD and DD *i.e.* 33 days to reach MRL. Moreover, three doses exposed (Table 1) half-lives (days) 5.90 ,7.09 and 8.60 days related to RD, DD and TD while 19.60, 23.57 and 28.40 as DT_{90} values, respectively. First order curve (Fig.3) clearly depicted the decay of cymoxanil at three doses with passage of time in perlette grapes.

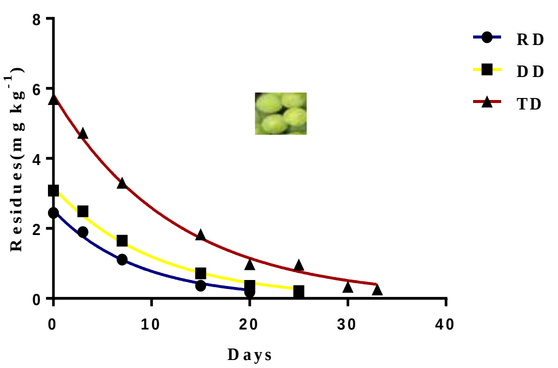

Figure 3. Cymoxanil residues dissipation in Perlette

Fate of Cymoxanil in Black Grapes**:** Initial deposits (mg Kg^{-1}) of cymoxanil at 0th day were found as 2.42±0.14, 3.50±0.28 and 5.71±0.28 for RD, DD and TD in black grapes, respectively. The initial deposits of RD decayed with the succession of time having mean values 2.42±0.14, 1.72±0.11, 0.91±0.045, 0.26±0.016 and 0.078±0.007 at 0th day, 3rd day, 7th day, 15th day, and 20th day, respectively but reduced below detection limits at 25th day. The percent reductions of above mentioned RD were 0.00, 28.98, 62.26, 89.15 and 95.44 at 0th day, 3rd day, 7th day, 15th day and 20th day, respectively. Likewise, the initial residues of cymoxanil at double dose in black grapes degenerated with the succession of time having mean values (mg Kg^{-1}) 3.45±0.28, 2.54±0.11, 1.55±0.052, 0.71±0.068, 0.35±0.031, 0.11±0.011 and 0.003±0.001 along with percent decrease 0.00, 26.33, 54.91, 79.30, 89.87, 95.67 and 99.78 at 0th day, 3rd day, 7th day, 15th day, 20th day, 25th day and 30th day, respectively and decomposed below detection limits at 30th day where 100% reduction was observed. Moreover, TD of cymoxanil in black grapes revealed dissipation with passage of time but reduction was as low as compared to recommended and double dose indicating dosage had more impact on residue stability. The TD residues dissipated with mean values (mg Kg^{-1}) 5.71±0.28, 4.34±0.18, 2.79±0.11, 1.40±0.13, 0.92±0.076, 0.43±0.036, 0.21±0.014 and 0.083±0.008 along with percent dissipation 0.00, 23.99, 51.12, 75.52, 83.87, 92.40, 96.26 and 98.09 at 0th day, 3rd day, 7th day, 15th day, 20th day, 25th day, 30th day and 33rd day, respectively but became BDL at 35th day. In conclusion, RD dissipated and reached below MRL (0.3 mg/Kg) at 15th day, DD just after 20th day and TD took

30 days but more time than RD and DD to reach MRL. There was more dissipation observed in black grape as compared to perlette while the three doses degraded with same trend *i.e.* RD>DD>TD in both cultivars. Model fate summery of cymoxanil indicated half-lives (days) (Table 1) 4.95, 6.11 and 7.06 at RD, DD and TD yet DT_{90} values at three doses were 16.42, 20.31 and 23.44 days, respectively.Fig.4 represents first order curves for decay of cymoxanil at three doses with passage of time in black grapes.

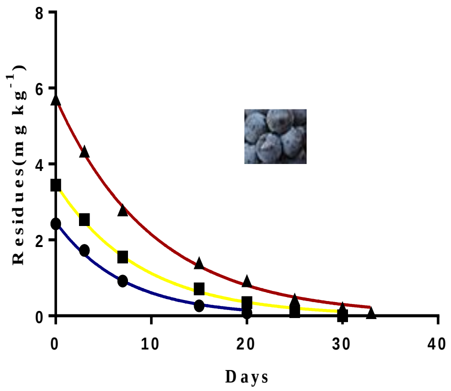

Figure 4. Cymoxanil residues dissipation in Black cultivar.

***Fate of Difenconazole in Perlette*:** Initial deposits (mg Kg^{-1}) of difenconazole at 0th day were measured as 9.41±0.24, 15.98±1.42 and 23.93±0.31 for RD, DD and TD in perlette, respectively. The initial deposits of recommended dose dissipated with the passage of time interval with means 9.41±0.24, 7.97±0.15, 4.91±0.096, 3.64±0.22, 1.15±0.068 and 0.45±0.025 at 0th day, 3rd day, 7th day, 15th day, 20th day and 25th day, respectively but became BDL at 30th day. The percent reduction of aforementioned RD were 0.00, 15.36, 47.80, 61.38, 87.80 and 95.27 at 0th day, 3rd day, 7th day, 15th day, 20th day and 25th day, respectively. Similarly, the initial deposits of DD in perlette dissipated with the advancement of time having mean (mg Kg^{-1}) values 15.98±1.42, 12.02±0.42, 10.60±0.60, 7.41±0.42, 3.28±0.19, 2.85±0.28, 2.30±0.21 and 0.66±0.023 along with percent decrease 0.00, 24.85, 33.33, 53.66, 79.52, 82.19, 85.61 and 94.55 at 0th day, 3rd day, 7th day, 15th day, 20th day, 25th day, 30th day and 33rdrespectively and sampling interval completed at 35th day. Moreover, TD of difenconazole in perlette exposed dissipation with passage of time but reduction was low as compared to RD and DD indicating that high initial deposits of pesticides tended to stay longer on sprayed produce. The residues decayed with mean (mg Kg^{-1}) values 23.93±0.31, 18.53±0.66, 16.52±0.66, 11.46±0.51, 5.16±0.37, 4.62±0.41, 3.93±0.13, 1.77±0.051 and 0.74±0.04 along with percent dissipation 0.00, 22.58, 30.99, 52.13, 78.44, 80.72, 83.59, 92.61 and 95.99 at 0th day, 3rd day, 7th day, 15th day, 20th day, 25th day, 30th day, 33rd day and 35th day, respectively. Difenconazole dissipated rapidly in black grape as compared to perlette and dissipated to MRL (3 mg Kg^{-1}) in perlette at 20th day regarding RD, after 30th day at DD while TD approached at 33rd day to safety limit. Model summary in (Table 1) represented half-lives (days) as 7.98, 10.46 and 10.67 at RD, DD and TD while DT_{90} values were 26.50, 34.74 and 35.44 at said doses, correspondingly. Moreover, decay curves of difenconazole on perlette cultivar as function of dose and time have been elucidated in Fig.5.

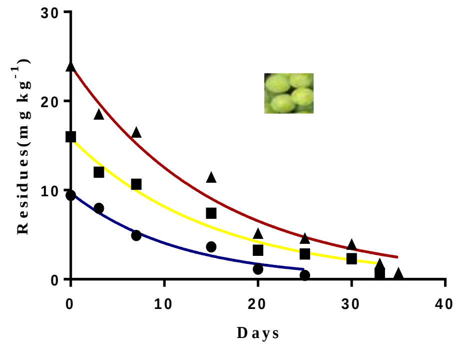

Figure 5. Difenconazole residues dissipation in Perlette.

***Fate of Difenconazole in Black Grape*:** Initial deposits (mg Kg^{-1}) of difenconazole at 0th day were calculated as 9.64±0.21, 16.13±0.42 and 24.15±1.57 for RD, DD and TD in black grape, respectively. The initial residues regarding RD decayed with the succession of time having mean values 9.64±0.21, 7.18±0.092, 4.99±0.17, 3.094±0.30, 0.97±0.044 and 0.26±0.015 at 0th day, 3rd day, 7th day, 15th day, 20th day and 25th day, respectively but reduced below detection limits at 30th day. The percent reductions of aforesaid RD were 0.00, 25.51, 48.26, 67.88, 89.91 and 97.31 at 0th day, 3rd day, 7th day, 15th day, 20th day and 25th day, respectively. Correspondingly, the initial deposits (mg Kg^{-1}) of difenconazole DD in black grape declined with the succession of time having mean values 16.13±0.42, 12.39±0.67, 10.66±0.93, 5.39±0.48, 3.12±0.11, 1.90±0.066, 1.35±0.031 and 0.53±0.048 along with percent decrease 0.00, 23.18, 33.92, 66.58, 80.65, 88.24, 91.63 and 95.75 at 0th day, 3rd day, 7th day, 15th day, 20th day, 25th day, 30th day and 33rd day, respectively and decomposed below detection limits at 35th day where 100% reduction was perceived. Additionally, TD of difenconazole in black grape showed dissipation with passage of time but degradation was low as compared to RD and DD indicating dosage has considerable effect on residue stability.

The TD residues dissipated portraying mean values (mg Kg^{-1}) 24.15±1.57, 19.26±0.98, 16.77±1.63, 8.87±0.11, 5.67±0.25, 3.20±0.28, 2.99±0.097, 0.33±0.015 and 0.026±0.002 along with percent dissipation 0.00, 20.24, 30.56, 63.28, 76.51, 86.75, 87.62, 98.62 and 99.89 at 0th day, 3rd day, 7th day, 15th day, 20th day, 25th day, 30th day, 33rd day and 35th day, respectively. At end, RD dissipated and reached to MRL (3 mg Kg^{-1}) at 15th day, DD up to 20th day and TD took 30 days to reach MRL. Results (Table 1) of half-lives (days) related to RD, DD and TD were 7.25, 8.88 and 9.30 but DT_{90} values were 24.10, 29.50 and 30.90 at aforementioned doses, respectively. Furthermore, decay curves of difenconazole on black grape cultivar as function of fungicide dose and time have been revealed in Fig.6.

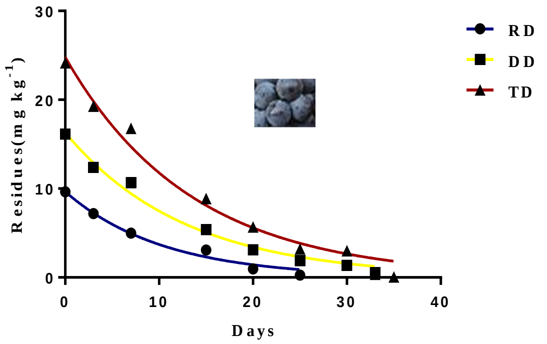

Figure 6. Difenconazole residues dissipation in Black variety.

DISCUSSION

Present findings indicated more degradation of fungicide residues in black grapes as compared to perlette which could be attributed to acidity of black grape causing acidic hydrolysis which also occurs in low acidity having variety (perlette) but at lower rate. Structurally, thick skin of black variety picks more residues than pulp while in perlette thin skin permits percolation to pulp and stability of systemic pesticides enhances causing delayed decay. Moreover, pesticide systemic and contact nature defines the fate as systemic residues are more penetrated and less prone to environmental factors than contact which mostly stay on fruit commodity surface (Besil *et al.,* 2018). Further, growth changes could be functional in both varieties during entire field trial as well as rain falls which also mitigated the residues. Henceforth, farmers should take it serious and avoid excessive doses in order to alleviate danger of surpassing maximum residual limits. Hereafter, mobility of pesticides relies on multifaceted phenomena where one factor volatility indicated the tendency of chemical to be converted into vapors or gas. Therefore, more volatile pesticides tend to volatilize from surface to atmosphere under influence of wind and temperature. Solubility indicates the chemical dissolving in solvents particularly water so are more inclined to run off or leach into soil. Moreover, ionic and neutral nature of agrochemical also dictates the adsorption or adherence to soil particles or commodity surface (cuticle) and translocation (Trapp, 2004; Chu, 2005; Freed, 2013; Whithaus and Blecker, 2016).

Pesticide systemic and non-systemic nature also determines it's kinetics in food and environment. Systemic chemicals act within the produce, with soil drench application conferring curative effect and are not liable to environmental factors as in case of contact agrochemicals. Contact pesticides are mostly preventive and affected by environmental features. These reside on surface of food commodities usually skin or outer protective coverings, thereby killing pests feeding on fruits and vegetables (Terrazas *et al.,* 1998; Huo *et al.,* 2007; Moulas *et al.,* 2013; Paranjape *et al.*, 2014).

Pesticides formulation is an important aspect governing the destiny of chemical residues during application on crops. Innovations in technology are in practice regarding development and delivery of active ingredients so that it is easy to measure, apply, develop, transport and reconstitute. Formulation generally refers to the combination of active ingredient and inert substances. Moreover, new formulations; suspension concentrates (SC), capsule suspensions (CS), oil-in water emulsions (EW), water-soluble packs (WS), are replacing the old ones; water-miscible solvent (SL), dusts (DP), wettable powders (WP),soluble powder (SP), emulsifiable concentrates(EC) due to ease in use, to remove limitation in solubility, constitution, etc., owing to diversity of active ingredients and achievement of the targets (Knowles, 2012; Hazra, 2015; Sarwar, 2015).Comparable pick up of residues of in perlette and black variety after supervised trial was due to harvest 2hr after application.

Scientists classify pesticides on half-life basis as non-persistent (less than 30 days), moderately persistent (HL between 30 and 100 days) and persistent nature (HL above 100 days) (Geyikci, 2011). Current study revealed HL less than 30, showing non-persistent nature but DD and TD affected the persistence. The two residues had different initial deposits which indicated that more initial there will be more half-life and vice versa until a chemical having exception. Half-life and DT-90 values are basically indicators of residue disappearance by 50% and 90%, respectively depending upon duration and outline the specific time interval for specific residue concentration indicating either it is below permissible limit or not. Pre-harvest interval (PHI) is a time before harvest or till produce matures and ready to be picked while safe waiting period is a time after pesticide application till picking indicating residue is surely below MRL. Chandra *et al*. (2014) studied dissipation of chlorpyrifos, monocrotophos and cypermethrin on okra using dosage effect and reported 15, 19 and 17 days to become undetected, respectively. Moreover, various contributory dissipation factors indicated the behavior of each of the residues on both varieties as function of first order model.

***Conclusion*:** Consequently, cymoxanil had half-lives as 5.89, 7.094 and 8.55 at RD, DD and TD while DT_{90} values were 19.60, 23.57 and 28.40 days, respectively on perlette. Furthermore, difenconazole exhibited half-lives (HLs) as 7.98, 10.46 and 10.67 at RD, DD and TD whereas DT_{90} values as 26.50, 34.74 and 35.44 day on perlette, correspondingly. The similar pattern was outlined by black grapes for both residues but dissipated at greater rate in black as compared to perlette. Cymoxanil explicated numerical values of HLs as 4.95, 6.11 and 7.056 days at RD, DD and TD on black grapes while 16.42, 20.31 and 23.44 as DT_{90} values corresponding to said doses. Also, the difenconazole elucidated the HLs as 7.25, 8.88 and 9.30 days at foresaid doses on black grapes while depicted DT_{90} values as 24.096, 29.50 and 30.90, respectively. The first order model explained the data with excellent co-efficient of determination and PHIs were also calculated indicating attitude of residues to help farmers to avoid risky reaping of grapes. The safe waiting periods till harvest for perlette corresponding to RD, DD and TD of cymoxanil, were as 20, 25 and 33days while black grapes represented 15, <25, 30days. Further difenconazole represented uniqueness regarding safe waiting periods at RD, DD and TD with 20, 25 and <33days in perlette but >15, <25days and 30 days were elucidated by black grapes, respectively. Cymoxanil dissipated earlier as compared to difenconazole as its half-life is less than latter one and former is more vulnerable to climatic (rain, temperature, sunlight, air speed) and commodity factors (grape variety, growth, acidity, structure, anatomical difference) for stability as compared to difenconazole. However, both being systemic pesticides are greatly influenced by commodity factors rather than environmental factors.

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