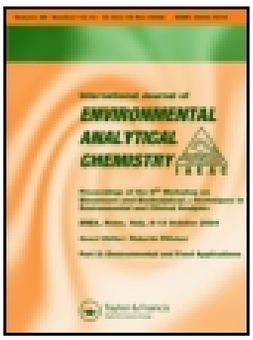

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Fate of cymoxanil, difenconazole and acetamiprid residues on grape varieties during modified atmospheric storage

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ABSTRACT

Grapes are sprayed with an array of agro-chemicals to eliminate the danger of damaging pests that demands a strategic post-harvest storage. Modified atmospheric storage (MAS) using treatments T_0 at 10 °C and `T_0 at 20 °C, both with 0 % carbon dioxide while T_1 at 10 °C and T_2 at 20 °C, both with 10% carbon dioxide, were applied for 3 doses (recommended dose, double than recommended and triple dose) of pesticides on two varieties of grapes under field conditions. Samples were taken at 0^{th} day, 3^{rd} day, 7^{th} day, 15^{th} day, 20^{th} day, 25^{th}day, 30^{th} day and 33^{rd} day intervals from MAS and were extracted using acetonitrile (ACN) and cleaned up by florisil adsorbent column. High performance liquid chromatography (HPLC), equipped with diode array detector, ODS-Hypersil C-18 column was used to separate and quantify the pesticides by employing ACN-MeOH mobile phase with a flow rate of 1 mL min^{-1} in gradient mode. Mathematical model ($Y_t = Y_0e^{-kt}$) was applied on average of all doses, which fitted best to the first order kinetics. Half-lives (HLs-50% of residues decayed) and DT_{90} (90% of residues decayed) values were also calculated. Regarding HLs of acetamiprid, best treatments were T_1 and T_2 where T_1 (7.51) and T_2 (4.02) presented good decay at low temperature when CO_2 was used in combination and also reported good shelf stability of grapes. Likewise, the trend was witnessed from cymoxanil and difenconazole pesticides and grape varieties. Moreover, black grape variety indicated more degradation of residues as compared to perlette, which could be attributed to its acidity, composition and anatomical structure. Hence, MAS is a practicable approach not only to enhance the shelf life of produce but also for dissipation of field applied agro-chemicals.

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Grapes; post-harvest; modified atmospheric storage; mathematical models; supervised pesticides dissipation; MRLs

1. Introduction

Grapes are getting more attention of the researchers as they are consumed around the globe and their annual global production is around 90 million tones [1]. In Pakistan grape fruits constitute 2.48% to agricultural gross domestic product (GDP) and grapes

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cultivation is increasing day by day in the country owing to improved production technology including hoeing, regulated irrigation, pruning scheduling, weeding, spraying and soil management etc [2,3]. Grape berries are attacked by pests like fungi and insects not only in field but also during improper post-harvest storage, which deteriorates the berry as well as causes huge economic losses to farmers. In order to cope up with the pests on grapes, various fungicides and insecticides are applied as per manufacturer's recommendations to protect the produce from different pests to ensure farmer's revenue and consumer health.

The pesticides applied on grapes included acetamiprid which is a systemic insect killer in nature having ability to penetrate in grapes skin. Difenconazole is also systemic in nature and belongs to fungicide category which kills wide range of fungi [4,5]. Cymoxanil is another locally systemic means in particular organ of plant like leaves, stems, twigs and roots it penetrates but remains confined to particular tissue or organ and disappears as function of its half-life, it is effective in controlling downy mildews and powdery mildews including other vine attacking fungi [6]. If these chemical residues applied during field surpass MRLs (maximum permissible limit of chemical set by regulatory body for particular food commodity), then they pose an array of health threats including cancer, respiratory distress, gastrointestinal and dermal issues, etc [7]. Hence, there is dire need for a post-harvest storage to be optimised for dissipating field sprayed pesticides and to enhance the shelf life of grapes. Amongst various storage techniques, controlled atmospheric storage, modified atmospheric (MA) storage and different simulated storage conditions are playing key role i.e. shelf-life extension and chemical residue decay [8]. Henceforth, MA and controlled atmospheric (CA) terms are used interchangeably but MA storage is different from CA storage since in MA gas composition is originally modified and changes as the function of produce respiration rate, permeability of storage structure, diffusivity of film surrounding the fruits or vegetables. Besides, in CA gaseous composition is continuously under control over the entire period of storage [9]. Earlier, a group of researchers [10] determined the triflumuron (TFM) and teflubenzuron (TFB) on pears stored under cold conditions, they observed TFB as persistent during entire storage whereas TFM disappeared by 7% at completion of study following first order kinetic model. The storage not only declines pesticide but also saves produce, where pesticide decay depends upon nature of pesticides, commodity type, field condition and environmental factors [11].

Very little data are available for modified atmospheric storage impact on dissipation of pesticides and shelf stability on grape cultivars. However, different storage types (controlled storage, cold storage, ambient storage, incubation storage etc) have been studied by various researchers with typical results as [12], studied effect of modified atmospheric packaging during 4 weeks duration on carbendazim residues on mandarin fruits and found 8.7–29.2% decline in carbendazim residues in mandarin peel while 6.7–11.8% in mandarin pulp. CA storage was applied on apples for inspection of parathion methyl residues degradation and results of study reported half-life of 68 days as compared to field conditions having 8 days meaning chemical residue persisted longer in CA and needed some new type storage with some parameters to augment dissipation which could be carbon dioxide, relative humidity and temperature variants as in MAS of current study. They hypothesised that CA

degraded parathion methyl less than refrigerated storage owing to oxidative mechanism that prevails more in refrigerated storage than in CA storage [13]. Another study indicated similar findings that include Mueller and Senseman [14] who explained the storage conditions using incubators for soil samples fortified with herbicides to access their dissipation with objective of comparing the field and laboratory conditions. The loss of procymidone (20 days half-life), vinclozoline (11 days half-life), fludioxonil (33 days half-life) and cyprodinil (44 days half -life) was studied in grape juice stored at 40 °C for period of two months where HLs indicated satisfactory dissipation [15]. Moreover, Cold storage (1–3°C) for 5 months was also explored by Ticha et al. [16] for reducing pesticides in Melrose cultivar of apple showing dissipation where phosalone and dodin dissipated to very low concentration after 5 months. Hence, by considering the prospect in review, current study was designed to evaluate modified storage using four treatments, where two without carbon dioxide like (T_0)10 °C and (`T_0) 20 °C and two with 10% carbon dioxide i.e. (T_1) 10 °C and (T_2) 20 °C, were applied to simulate commercial storage to access the fate of pesticides on two varieties (perlette and black grapes). Hence, hypothesis of current research was to probe either MAS storage degrades pesticides and enhances grapes shelf life or not.

2. Materials and protocols

2.1. Chemicals and adsorbents

All solvents (Acetonitrile, Methanol, Ultra-pure water) used were of HPLC grade. Anhydrous magnesium sulphate ($MgSO_4$), sodium chloride (NaCl) and pesticide (acetamiprid, difenconazole and cymoxanil) reference standards having 99% purity were secured from Merck Limited. Activation of $MgSO_4$ and NaCl was carried out in hot air convicted oven at 250°C for 4–5 hours and placed in desiccator to avoid pick up of moisture. Stock solutions of standards were prepared using ACN where dilutions were kept at −40 °C before analysis.

2.2. Treatment and sampling plan for MAS

As per specifications given by manufacturer three doses i.e. 150, 300 and 450 g dose per acre for difenconazole, 250, 500 and 750 g dose per acre for acetamiprid and 600, 1200 and 1800 g dose per acre for cymoxanil were applied on selected plants of perlette and black grapes. Grapes were harvested 24 hours after sprays and then placed inside zipper polyethylene bags imprinted with variety names and sampling interval. Samples were taken out from MAS storage for residue analysis at 0^{th} day, 3^{rd} day, 7^{th} day, 15^{th} day, 20^{th} day, 25^{th} day, 30^{th} day and 33^{rd} day intervals or till they remained acceptable.

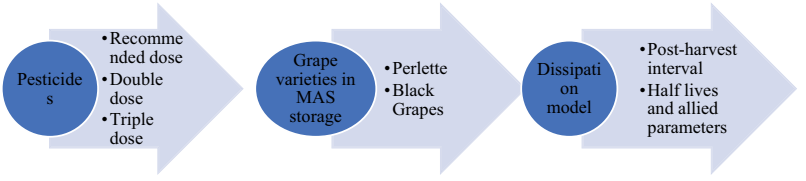

Figure 1. Graphical depiction of pesticides, grape varieties and storage.

2.3. Modified atmospheric storage (MAS)

Memmert Chambers (ICH-260-C & ICH-110-C, Germany) at NIFSAT (National Institute of Food Science and Technology), Food Safety Laboratory, were used for Modified Atmospheric Storage (Figure 1). Sampling and analyses were done as implemented by Burcak et al. [17] with slight modifications in sampling interval, placing in perforated polyethylene bags and using two grape varieties. Following parameters were applied on stored grapes.

2.4. MAS parameters

Relative humidity of chambers was maintained at 75–80% with temperature variants (10 °C, 20 °C) and CO_2 (0% and 10%) according to treatment plan. Four treatments (T_0,`$T_0$,$T_1$ and $T_2$) were applied. Where $T_0$ was at 10 °C and `T_0 at 20 °C, both with 0% carbon dioxide while T_1 at 10 °C and T_2 at 20 °C, both with 10% carbon dioxide, were applied for 3 doses of pesticides on both varieties of grapes.

2.5. Extraction of pesticide residues

Samples of both grape cultivars, secured according to sampling plans were extracted using standard protocol adopted by Nadeem *et al*. [11]. Grape berries after crushing were extracted using (1:2) ratio of acetonitrile to sample and cleaned up using florisil column which was prepared using anhydrous sodium sulphate sandwiched between glass wool to avoid interferences from co-extractives accumulated during extraction. Following clean-up, samples were distillated in rotary vacuum evaporated till 2–3 mL obtained. The samples were flushed with gentle stream of nitrogen to near dryness. Finally, residues obtained were reconstituted in extracting solvent and micro filtrated and kept in vials at −40°C till HPLC analysis.

2.6. Instrumental analysis by HPLC-DAD

HPLC (Agilent, Series-1200) equipped with diode array detector (DAD) was applied for residue analysis. Chromatographic analysis was carried out using C18 column (ODS-2-Hypersil). Mobile phases (acetonitrile and methanol) were run at flow rate of 1 mL min^{-1} as final protocols with gradient run as follows with step-1; ACN for 0.5 min as 0% and MeOH 100%, step-2; ACN for 8 min as 50% and MeOH 50%, step-3; ACN for 6 minutes as 70% and MeOH 30% and finally ACN for 10 min as 100% and MeOH 0% for

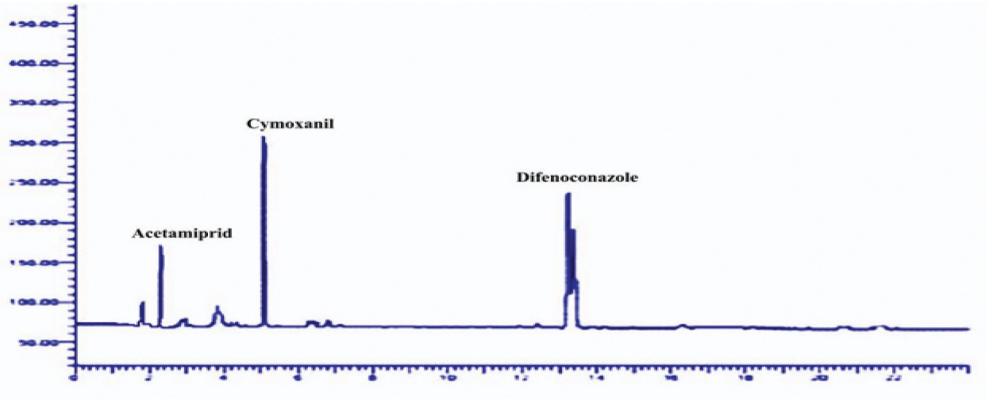

Figure 2. Standard of acetamiprid (2.13 minutes), cymoxanil (5.07 minutes) and difenconazole (13.25 minutes) using HPLC-DAD.

vivid peaks of pesticide standards. Wavelength was set 235 nm and volume of sample injection applied was 10–15 µL. Standard chromatogram (Figure 2) depicted 2.13 min retention time for acetamiprid but 5.07 and 13.25 min for cymoxanil and difenconazole, respectively using final method.

2.7. Dissipation kinetic analysis

Mathematical models like first phase decay ($Y_t = Y_0 e^{-kt}$), two phase decay ($Y = Z + T_f \times e\ (K_f \times X) + T_s \times e(-K_s \times X)$) and three phase decay ($Y = Z + (Y_0 - Z) \times T_{Pf} \times 01 \times exp(-K_f \times X) + (Y_0 - Z) \times (100 - T_{Pf} - T_{ps}) \times 01 \times exp(K_{med} \times X) + (Y_0 - Z) \times T_{ps} \times 01 \times \exp(-K_s \times X)$), were applied on the data using (Graph Pad Prism Version-8.0.2) where 2nd and 3rd phase models reported ambiguous and too few parameters as compared to first decay so were omitted. Allied statistical indices were calculated including half-lives and DT_{90} for pesticides using following 1st order model (Tables 1–3). Parameters in models include Y_t = residue at interval, Y_0 = residue at zero-day, t = half-life, Z = graph plateau, K_s = constant for slow decay, K_f = constant for fast decay, Kmed= constant for medium decay, T_s = Time for slow dissipation, T_f = Time for fast decay, T_{Pf} = Time for percent fast, T_{ps} = Time for percent slow, e = exponential.

3. Results

3.1. Acetamiprid dissipation in MAS of perlette and black

In MAS four treatments were planned to check whether the acetamiprid dissipated to MRL (0.5 mg Kg^{-1}) or not (Figure 3). Perlette variety was placed in MAS by clearly mentioning treatments. So, RD dissipated under T_0 varying from 6.94 ± 0.57 to 3.15 ± 0.2 (mg Kg^{-1}) during 15 days but under `T_0 varied from 7.25 ± 0.16 to 2.83 ± 0.23 (mg Kg^{-1}) and grapes spoilt at 7th day with speedy degradation of residue. Nonetheless under T_1 residues varied from 6.78 ± 0.28 to 0.15 ± 0.01(mg Kg^{-1}) going below MRLs but with low dissipation rate than T_0 and spoilt at 25th day whereas under T_2 residues varied from 6.88 ± 0.46 to

Table 1. Model summary for acetamiprid.

Mathematical Modelling and Statistical Inferences				
	Acetamiprid in Perlette			
Treatments	T_0	$`T_0$	T_1	T_2
Half-life(days)	14.55	5.99	7.51	4.02
R^2	0.99	0.99	0.98	0.97
K_{diss}	0.04	0.10	0.09	0.17
DT_{90}(days)	48.33	19.92	24.94	13.34
Treatments	**Acetamiprid in Black Grapes**			
	T_0	**$`T_0$**	**T_1**	**T_2**
Half-life(days)	9.21	6.61	5.90	4.65
R^2	0.98	0.96	0.99	0.99
K_{diss}	0.07	0.10	0.11	0.15
DT_{90}(days)	30.60	21.97	19.59	15.45

Table 2. Model summary for cymoxanil.

Mathematical Modelling and Statistical Inferences				
	Cymoxanil in Perlette			
Treatments	T_0	$`T_0$	T_1	T_2
Half-life (days)	25.13	9.66	12.30	8.93
R^2	0.99	0.85	0.98	0.94
K_{diss}	0.03	0.07	0.06	0.08
DT_{90} (days)	83.46	32.11	40.85	29.68
Treatments	**Cymoxanil in Black Grapes**			
	T_0	**$`T_0$**	**T_1**	**T_2**
Half-life (days)	20.93	13.69	12.20	9.21
R^2	1.00	0.95	0.97	0.97
K_{diss}	0.03	0.05	0.06	0.08
DT_{90} (days)	69.54	45.48	40.53	30.58

Table 3. Model summary for difenconazole.

Mathematical Modelling and Statistical Inferences				
	Difenconazole in Perlette			
Treatments	T_0	$`T_0$	T_1	T_2
Half-life (days)	16.11	9.44	13.00	10.17
R^2	1.00	0.99	0.99	0.98
K_{diss}	0.04	0.07	0.05	0.07
DT_{90} (days)	53.52	31.34	43.18	33.78
Difenconazole in Black Grapes				
	T_0	**$`T_0$**	**T_1**	**T_2**
Half-life (days)	14.09	10.82	11.25	9.55
R^2	0.99	0.97	1.00	0.99
K_{diss}	0.05	0.06	0.06	0.07
DT_{90} (days)	46.79	35.95	37.37	31.73

T_0 = 0% CO_2 + R.H. 80%+10 °C.
$`T_0$ = 0% CO_2 + R.H. 80%+20 °C.
T_1 = 10% CO_2 + R.H. 80%+10 °C.
T_2 = 10% CO_2 + R.H. 80%+20 °C.

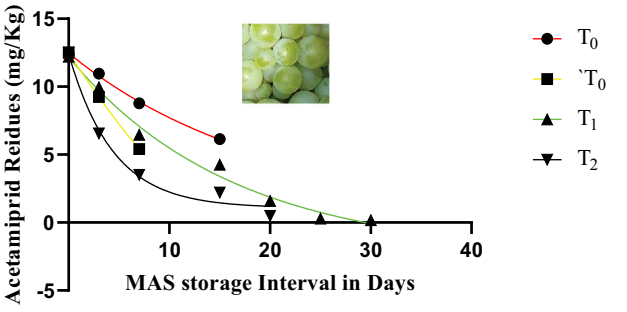

Figure 3. Acetamiprid dissipation in MAS on Perlette.

0.28 ± 0.03 (mg Kg^{-1}) during 20 days with greater dissipation rate going below MRLs but samples were rotten after it. Likewise pattern was represented by DD where residues varied from 11.84 ± 0.37 to 4.85 ± 0.29 (mg Kg^{-1}) during 15 days but were above MRL under T_0 while under `T_0 from 11.72 ± 0.74 to 5.22 ± 0.38 (mg Kg^{-1}) in 7 days and samples spoilt after that. Similarly, DD decomposed under T_1 varying from 11.55 ± 0.65 to 0.29 ± 0.03 (mg Kg^{-1}) during 25 days but reached under MRL whereas under T_2 residues changed from 12.77 ± 0.75 to 0.53 ± 0.04 in 20 days with fast rate going slightly above MRL. Contrarily, TD showed more persistence than RD and DD and residues varied from 18.41 ± 1.13 to 10.42 ± 0.59 under T_0 during 15 days but very above than MRL and under `T_0 acetamiprid decayed from 18.49 ± 1.53 to 8.14 ± 0.18 (mg Kg^{-1}) in 7 days. Nevertheless, T_1 decayed pesticide from 18.29 ± 0.23 to 0.18 ± 0.01 (mg Kg^{-1}) in 30 days going below MRL meaning thereby more life of grapes and exceptional degradation of chemical however T_2 depicted fast dissipation from 17.93 ± 1.01 to 0.68 ± 0.06 (mg Kg^{-1}) in 20 days but portrayed more and early spoilage than T_1. Furthermore, by taking average from three doses HLs regarding T_0, `T_0, T_1 and T_2 were 14.55, 5.99, 7.51 and 4.02 days but DT_{90} (period when 90% of residues degrades) values as 48.33, 19.92, 24.94 and 13.34 days, calculated for acetamiprid from Perlette grapes, respectively (Table 1).

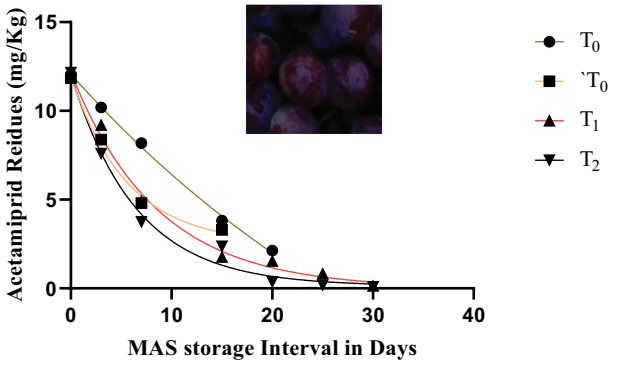

Figure 4. Acetamiprid dissipation in MAS on black grapes.

Similar conclusions (Figure 4) were also reported by Black grapes regarding acetamiprid where RD dissipated under T_0 varying from 6.52 ± 0.39 to 1.20 ± 0.1 (mg Kg^{-1}) during 20 days although under `T_0 varied from 6.46 ± 0.17 to 1.73 ± 0.04 (mg Kg^{-1}) but Black grapes spoilt at 15th day with fast degradation of residues. Parallel trend was observed under T_1 where residues varied from 6.48 ± 0.22 to 0.07 ± 0.005 (mg Kg^{-1}) going below MRL earlier than Perlette but with low dissipation rate than T_0 and were acceptable till 30th day. Whereas under T_2 residues changed from 6.78 ± 0.37 to 0.04 ± 0.002 (mg Kg^{-1}) during 30 days but at greater dissipation rate and went below MRL earlier than T_1 having small shelf life and samples were tainted. The same pattern was represented by DD where residues varied from 12.13 ± 0.63 to 2.08 ± 0.14 (mg Kg^{-1}) during 20 days after which sample became spoilt but residues were above MRL under T_0 while under `T_0 acetamiprid varied from 12.22 ± 0.74 to 3.16 ± 0.14 (mg Kg^{-1}) in 15 days after which sample spoilt. Similarly, DD decayed under T_1 changing from 12.12 ± 0.27 to 0.14 ± 0.01 (mg Kg^{-1}) during 30 days but reached under MRL whereas under T_2 residues altered from 12.38 ± 0.86 to 0.07 ± 0.004 (mg Kg^{-1}) in 30 days with fast speed but went quite below MRL. No doubt T_1 and T_2 described similar behaviour but former conferred more shelf life and sample freshness. Oppositely, TD showed more persistence than RD and DD and residues varied from 17.45 ± 1.61 to 3.1 ± 0.28 (mg Kg^{-1}) under T_0 during 20 days but very above than MRL and under `T_0 agrochemical lost from 16.84 ± 1.14 to 4.98 ± 0.36 (mg Kg^{-1}) in only 15 days. Nevertheless, T_1 decayed acetamiprid from 17.18 ± 0.73 to 0.21 ± 0.02 (mg Kg^{-1}) in 30 days but went below MRL meaning thereby more life of grapes and good decay of chemical though T_2 depicted fast decadence from 17.32 ± 1.07 to 0.13 ± 0.003 (mg Kg^{-1}) in 30 days but less life than T_1. Additionally, by taking average from three doses HLs regarding T_0, `T_0,T_1 and T_2 were 9.21, 6.61, 5.9 and 4.65 days but DT_{90} values as 30.59, 21.97, 19.59 and 15.45 days, calculated for acetamiprid from Black grapes (Table 1).

3.2. Cymoxanil dissipation in MAS of perlette and black

In MAS four treatments were compiled to check whether the cymoxanil disintegrated to MRL (0.3 mg Kg-1) or not. The results related to cymoxanil degradation have been elucidated in Table 2. Perlette grapes were placed by using proper coding under four

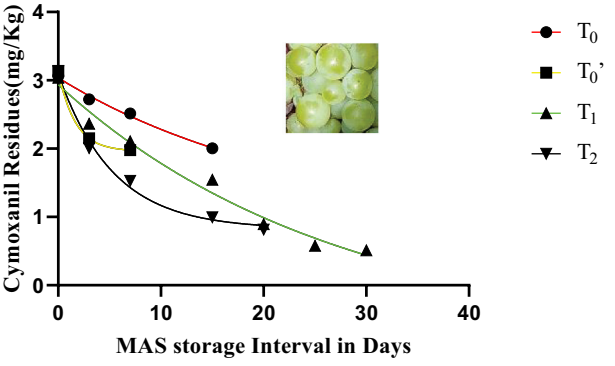

Figure 5. Cymoxanil dissipation in MAS on perlette grapes.

treatments for checking fate of cymoxanil (Figure 5). So, RD from Perlette degenerated under T_0 varying from 1.66 ± 0.09 to 1.11 ± 0.06 (mg Kg^{-1}) during 15 days but under `T_0 changed from 1.69 ± 0.1 to 1.07 ± 0.13 (mg Kg^{-1}) but grapes spoilt at 7th day with fast decay of cymoxanil. But under T_1 residues lessened from 1.61 ± 0.09 to 0.29 ± 0.03 (mg Kg^{-1}) going near MRLs but having low dissipation rate than T_0 and rotted at 25th day. Moreover, under T_2 residues reduced from 1.7 ± 0.07 to 0.49 ± 0.04 (mg Kg^{-1}) during 20 days but at greater dissipation rate and did not go below MRL and samples were rotten after it. Similar outline was signified by DD where residues varied from 3.09 ± 0.16 to 1.97 ± 0.18 (mg Kg^{-1}) in 15 days but were very above MRL under T_0, nevertheless under `T_0 from cymoxanil changed 3.34 ± 0.17 to 1.95 ± 0.13 (mg Kg^{-1}) in 7 days and samples were unfit for use afterwards. Harmoniously, DD decayed under T_1 varying from 3.07 ± 0.15to 0.66 ± 0.06 (mg Kg^{-1}) during 25 days but did not reach to MRL whereas under T_2 residues changed from 3.27 ± 0.18 to 0.85 ± 0.07 (mg Kg^{-1}) in 20 days with fast decay and residues were above MRL. TD performed contrarily and showed more persistence than RD and DD with residues varied from 4.43 ± 0.28 to 2.94 ± 0.21 (mg Kg^{-1}) under T_0 during 15 days but were very above the MRL and under `T_0 cymoxanil decayed 4.39 ± 0.23 to 2.92 ± 0.13 (mg Kg^{-1}) in 7 days. Nevertheless, T_1 disintegrated pesticide from 4.43 ± 0.19 to 0.51 ± 0.04 (mg Kg^{-1}) in 30 days but residues were above MRL meaning thereby more life of grapes and good decline of chemical but T_2 portrayed fast dissipation from 4.43 ± 0.22 to 1.11 ± 0.08 (mg Kg^{-1}) in 20 days but more and early spoilage than T_1. In the same way, taking average of three doses portrayed HLs (days) as 25.13, 9.66, 12.3 and 8.93 but DT_{90} values (days) as 83.46, 32.11, 40.85 and 29.68 related to T_0, `T_0, T_1 and T_2, respectively, for cymoxanil from Perlette grapes (Table 2).

Alike outputs were also designated by Black grapes which illustrated (Figure 6) more shelf life and more dissipation than Perlette where RD dissipated under T_0 varying from 1.41 ± 0.07 to 0.83 ± 0.06 (mg Kg^{-1}) in 20 days with residues above MRL even though under `T_0 cymoxanil varied from 1.52 ± 0.13 to 0.76 ± 0.05 (mg Kg^{-1}) where Black grapes spoilt at 15th day with fast degradation of residues. Equivalent fate was observed under T_1 where residues varied from 1.46 ± 0.05 to 0.21 ± 0.02 (mg Kg^{-1}) going well below MRL earlier than Perlette but with low dissipation rate as compared to T_0 and grapes were acceptable till 30th day. Besides, under T_2 residues changed from 1.4 ± 0.08 to 0.18 ± 0.02 (mg Kg^{-1}) during 30 days but at greater dissipation rate and went below MRL earlier than

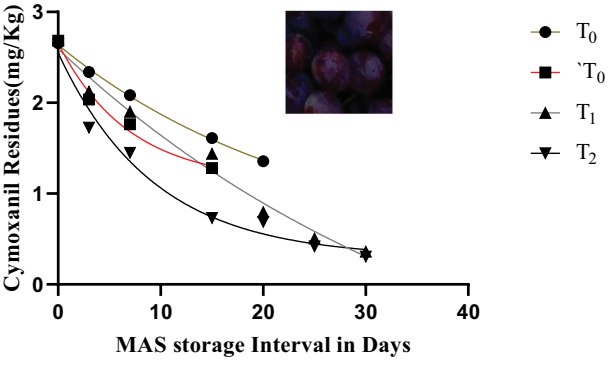

Figure 6. Cymoxanil dissipation in MAS on black grapes.

T_1 but samples were decayed. The corresponding pattern was described by DD where residues varied from 2.40 ± 0.1 to 1.14 ± 0.07 (mg Kg^{-1}) during 20 days after which samples rotted but residues were very above than MRL under T_0 although under `T_0 lessened from 2.41 ± 0.17 to 1.20 ± 0.1 (mg Kg^{-1}) in 15 days after which grapes spoilt but were above MRL. In the same way, DD decomposed under T_1 changing from 2.42 ± 0.06 to 0.40 ± 0.02 (mg Kg^{-1}) during 30 days and were above MRL whereas under T_2 residues altered from 2.36 ± 0.1 to 0.310 ± 0.03 (mg Kg^{-1}) in 30 days with fast speed but went very near to MRL. Surely, T_1 and T_2 defined similar behaviour but former recommended more shelf life and sample acceptability. On the other hand, TD displayed more severity than RD and DD and residues varied from 4.16 ± 0.14 to 2.10 ± 0.16 (mg Kg^{-1}) under T_0 during 20 days but were very above the MRL and under `T_0 cymoxanil lost from 4.12 ± 0.21 to 1.87 ± 0.26 (mg Kg^{-1}) in only 15 days with again residues above MRL. However, T_1 decayed residues from 4.2 ± 0.34 to 0.48 ± 0.01 (mg Kg^{-1}) in 30 days reaching above MRL meaning thereby more life of grapes and degeneration of cymoxanil but then again T_2 represented fast decay from 4.18 ± 0.34 to 0.430 ± 0.1 (mg Kg^{-1}) in 30 days nevertheless less shelf-life than T_1 and never reached MRL. Likewise, taking average of three doses represented HLs (days) as 20.93, 13.69, 12.2 and 9.21 but DT_{90} values (days) as 69.54, 45.48, 40.53 and 30.58 related to T_0, `T_0, T_1 and T_2, respectively for cymoxanil from Black grapes (Table 2).

3.3. Difenconazole dissipation in MAS of perlette and black

Four treatments were applied during MAS to check whether the difenconazole degraded to MRL(3 mg Kg^{-1}) or not. Perlette grapes were placed by using coding under four treatments for checking fate of difenconazole (Figure 7). The findings are presented in Table 3. Consequently, RD from Perlette degraded under T_0 varying from 8.9 ± 0.46 to 4.20 ± 0.10 (mg Kg^{-1}) during 15 days but under `T_0 changed from 9.35 ± 0.43 to 4.84 ± 0.38 (mg Kg^{-1}) where samples spoilt at 7^{th} day with fast decay of difenconazole. Nevertheless, under T_1 residues diminished from 9.19 ± 0.6 to 1.73 ± 0.08 (mg Kg^{-1}) going below MRL but having low dissipation rate than T_0 and rotted at 25^{th} day. In addition, under T_2 residues declined from 8.62 ± 0.39 to 2.3 ± 0.13 (mg Kg^{-1}) during 20 days but at greater dissipation rate and went below MRL but samples were rotten after it. Similar trend was outlined by DD where residues varied from 14.3 ± 0.73 to 8.68 ± 0.76 (mg Kg^{-1})

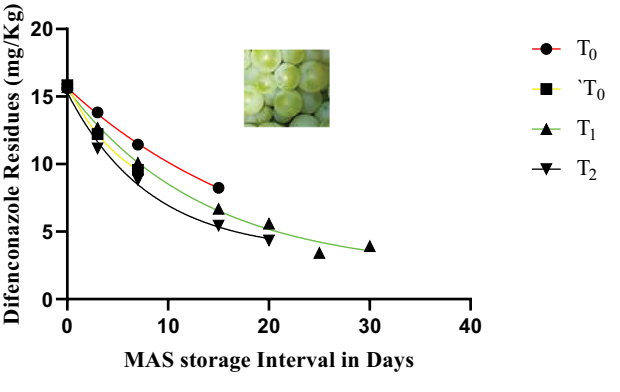

Figure 7. Difenconazole dissipation in MAS on perlette.

in 15 days but above MRL under T_0, yet under `T_0 from 14.4 ± 0.66 to 8.29 ± 0.55 (mg Kg^{-1}) in 7 days and samples were unfit for use after it. Similarly, DD decayed under T_1 varying from 14.44 ± 0.86 to 3.5 ± 0.14 (mg Kg^{-1}) during 25 days reaching MRL whereas under T_2 residues varied from 14.35 ± 0.77 to 3.87 ± 0.16 (mg Kg^{-1}) in 20 days with fast decay and still residues were above MRL. TD performed differently and exhibited more persistence than RD and DD with residues varied from 23.63 ± 0.55 to 11.85 ± 0.61 (mg Kg^{-1}) under T_0 during 15 days but very above the MRLs and under `T_0 difenconazole decayed from 23.77 ± 0.66 to 15.6 ± 0.54 (mg Kg^{-1}) in 7 days. Though, T_1 degenerated pesticide from 23.43 ± 0.96 to 3.92 ± 0.24 (mg Kg^{-1}) in 30 days but above MRL meaning thereby more life of grapes and decline of residues but T_2 described fast dissipation from 23.54 ± 0.81 to 6.84 ± 0.14 (mg Kg^{-1}) in 20 days but more and early spoilage than T_1 and did go below MRL. In the same way, the average of three doses designated HLs (days) as 16.11, 9.44, 13.00 and 10.17 but DT_{90} values (days) as 53.52, 31.34, 43.18 and 33.78 related to T_0, `T_0, T_1 and T_2 for difenconazole from Perlette grapes, respectively (Table 3).

Analogous results (Figure 8) were also presented by Black grapes which demonstrated more shelf life and more dissipation than Perlette where RD dissipated under T_0 varying from 8.24 ± 0.42 to 2.69 ± 0.15 (mg Kg^{-1}) in 20 days with residues below MRL even though under `T_0 varied from 8.26 ± 0.3 to 3.02 ± 0.2 (mg Kg^{-1}) where Black grapes spoilt at 15th day with fast degradation of residues (near MRL). Parallel fate trend was observed under T_1 where residues varied from 8.32 ± 0.45 to 1.25 ± 0.06 (mg Kg^{-1}) going well below MRL earlier than Perlette but with low dissipation rate than T_0 and remained acceptable longer till 30th day whereas under T_2 residues changed from 8.4 ± 0.46 to 1.07 ± 0.1 (mg Kg^{-1}) during 30 days but with greater dissipation rate and went well below MRL earlier than T_1 but samples were spoilt after it. The consistent pattern was described from DD where residues varied from 13.33 ± 0.8 to 3.88 ± 0.1 (mg Kg^{-1}) during 20 days after which samples became rotten but residues were very above MRL under T_0, and under `T_0 residues changed from 13.39 ± 0.31 to 5.83 ± 0.38 (mg Kg^{-1}) in 15 days after which sample spoilt but were above MRL. In the same way, DD disintegrated under T_1 changing from 13.3 ± 0.52 to 2.15 ± 0.11 (mg Kg^{-1}) during 30 days going below MRL whereas under T_2 residues varied from 13.13 ± 0.66 to 1.75 ± 0.09 (mg Kg^{-1}) in 30 days with fast speed and residues were below MRL. Surely, T_1 and T_2 reported similar behaviour but former

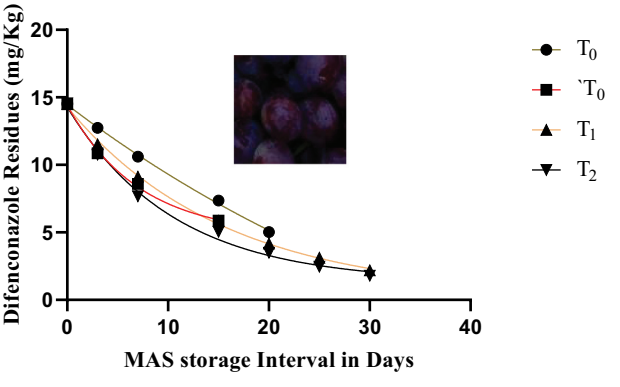

Figure 8. Difenconazole dissipation in MAS on black grapes.

recommended more shelf life and sample freshness. Oppositely, TD displayed more stanch behaviour than RD and DD and residues varied from 22.02 ± 1.15 to 8.53 ± 0.35 (mg Kg^{-1}) under T_0 during 20 days but very above the MRL and under `T_0 difenconazole lost from 21.83 ± 1.12 to 8.76 ± 0.43 (mg Kg^{-1}) in only 15 days and was again above MRL. However, T_1 disintegrated residues from 21.9 ± 1.19 to 3.17 ± 0.19 (mg Kg^{-1}) in 30 days reaching near MRL but T_2 represented fast decay from 22.15 ± 1.13 to 2.53 ± 0.18 (mg Kg^{-1}) in 30 days but less shelf-life than T_1 and reached in close proximity of MRL. On similar grounds, the average of three doses nominated HLs (days) as 14.09, 10.82, 11.25 and 9.55 but DT_{90} values (days) as 46.79, 35.95, 37.37 and 31.73 related to T_0, `T_0, T_1 and T_2 for difenconazole from Black grapes, respectively (Table 3). Novelty of current research includes MAS effect on exponential decay of pesticides on grape varieties upon which very little data have been reported.

4. Discussion

Modified storage conditions are applied to mature fruit storage to save produce before final processing or for export purposes. The supervised pesticides dissipated in present study during MAS storage but rate of dissipation was individual in nature for each pesticide. The systemic pesticides dissipated later than non-systemic as latter were directly influenced by storage. Moreover, grape varieties also played profound role for pesticide degradation i.e. acidic hydrolysis was more influential in case of Black as compared to Perlette variety. Matrix effect like pH, total solids, pulpy portion and chemical composition of black grape variety is different than perlette which can be perceived as key player for pesticide decay at different rates in both cultivars. Among the four treatments of MAS. T_1 was found best because low temperature lengthened the half-life and CO_2 concentration played greater role for pesticide decay. Nonetheless, treatment (T_2) having combination of high temperature and CO_2 degraded residues with greater speed i.e. with less shelf life. Hence temperature affects the dissipation because of volatility and mobility of pesticide between produce and storage structure but CO_2 creates hypoxic conditions which stops microbial decay [18].

Additionally, fan speed of MAS storage plays important role for air circulation and removing of volatile residues from grape surface. Currently, azoxystrobin behaviour was studied by a group of researchers during cold storage with 29 ± 1% decline in residues on grapes while 53 ± 2% reduction in model systems [19]. Moreover, cabbage was stored at 5°C for two weeks and organochlorine pesticides were reduced significantly in cabbage heads [20] indicating refrigeration an opportunity to get rid of chemical residues prior to consumption. Later, table grape berries were treated with mixture of fungicide solution and stored at 2°C and 95% R.H by Karaca et al. [21] who found ozone in combination with storage an effective strategy to diminish residue with pyrimethanil 3.6, cyprodinil 2.8 and fenhexamid 1.6 fold. Further, table grapes and lettuce were examined for fludioxonil and cyprodinil during cold storage and in field conditions. A group of researchers depicted that dissipation occurs in cold storage but half-lives were 3 to 6 times higher in refrigeration [22].

In present results, Half-lives of residues were calculated under different treatments and it was concluded that HL was low (means more dissipation) at high temperature but high (persistence of residues) at low temperature and HL was even lower when CO_2 was used

synergistically with low temperature which could be attributed to carbon dioxide. However, no doubt high temperature and CO_2 revealed more pesticide decay but grapes spoilt earlier than where low temperature and CO_2 were applied in combination. The results of Adak et al. [23] are in agreement with current study regarding CO_2 who studied its elevated levels influence on Chlorpyrifos in soil samples secured from rice field and found 88.4% disappearance of residues at 700 ppm of CO_2 within 5 days presenting good opportunity for produce stored in MAS. Each chemical residue has its response to MAS condition and elevated CO_2 concentrations where Manna et al. [24] reported non-significant reduction of azoxystrobin in rice soils with HL (days) as 19.3 in experimental conditions but 20.3 in outdoor experiments. Conclusively, MAS which contains combination of low temperature, carbon dioxide, nitrogen plays crucial role for decay of residues as in present results residues followed the first order kinetics and disappeared almost when sprayed at RD while for some residues even DD could not be degraded under MAS.

5. Conclusion

Conclusively, among the applied MAS treatments, T_1 was found best in terms of saving the grapes as well as for dissipating the residues to MRLs. Recommended doses are decayed to MRLs with greater ease rather than DD and TD. Hence, 10% CO_2, 10°C temperature and 80% R.H is best choice for MAS storage of field sprayed grapes which not only degraded pesticides but also enhanced shelf life of grapes. Low temperature and CO_2 combination performs in better way to reduce residues of pesticides than alone where low temperature slows the half-life and opposite occurs in high temperature. Acetamiprid reported DT_{90} (days) values as 48.33, 19.92, 24.94, 13.34 relevant to T_0, `T_0, T_1 and T_2 and almost similar trend was witnessed from cymoxanil and difenconazole. Black grapes reported less DT_{90} as compared to perlette i.e. 19.59(T_1) and 24.94 (T_1), respectively showing greater pesticide disappearance in black grapes. Moreover, MAS, nature of sprayed residues and varieties of grapes are among the contributory factors to degrade the residues, so, grape exporters and traders can use it for better export to far off places with security and processors can optimise processing to achieve safe MRLs.

Disclosure statement

Authors have not reported any conflict of interest.

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