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The effect of processing on degradation of pesticides sprayed on Perlette and Black grapes

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Abstract

Grapes, owing to natural delicacy and good nutritional profile, are consumed around the globe. Farmers apply various pesticides to combat danger of pest attack which in turn may endanger the health of consumers. In the present work, pesticides were sprayed on mature grapes (Perlette and Black varieties), and after 24 h, these grapes were processed into various products in order to investigate the impact of different processings on pesticide residues. Five grape products (juice, jam, nectar, squash, raisins) were developed each using two processing methods; processing-1 (P1) and processing-2 (P2). The products depicted residue trends as follows i.e. juice < nectar < raisin < jam < squash with overall means of 4.38 ± 0.70 < 4.88 ± 0.70 < 5.47 ± 0.72 < 5.81 ± 0.72 < 6.48 ± 0.75 mg kg^{-1} in Perlette variety; and 4.09 ± 0.67 < 4.54 ± 0.66 < 5.03 ± 0.67 < 5.26 ± 0.67 < 5.90 ± 0.69 mg kg^{-1} in Black variety. Before processing, raw produce had residues corresponded to recommended dose (RD), double dose (DD) and triple dose (TD) of 4.89 ± 0.92, 8.31 ± 1.52, and 13.05 ± 2.47 mg kg^{-1}, respectively. Juice showed residues corresponding to P1 and P2 with values of 1.021 ± 0.182 and 0.84 ± 0.15 mg kg^{-1}, respectively, at RD. Nectar had 1.42 ± 0.252 and 1.06 ± 0.19 mg kg^{-1} residues at foresaid processing relevant to RD. Jam had 2.07 ± 0.38 and 1.55 ± 0.27 mg kg^{-1} residues, while squash had 2.43 ± 0.42 and 2.20 ± 0.39 mg kg^{-1} residues, respectively, at RD. Raisins had 1.96 ± 0.35 and 1.28 ± 0.23 mg kg^{-1} residues at two processings at RD, respectively. Similar dissipation trend was also revealed by DD and TD at both processing levels which were different for each product.

Introduction

Grapes are usually processed into value added products to augment their marketing values at national and international levels. During processing, reducing the pesticide residues is important since consumers are more aware nowadays on the effects of agro-chemical residues on their health. Pesticides can enter the body mainly via three routes: inhalation, skin contact, and ingestion. Following entry into blood stream, the chemical is metabolised by the body through two main phases either it is made harmless and excreted; or it exerts its effect symptomatically thereby causing disorders. The disruption of normal bodily function is called toxicity in short, when homeostatic mechanism of the body is disrupted (Kamrin, 1997; Abass *et al*., 2012). Pesticides' scale of toxicity ranges from (1) extremely toxic, (2) highly toxic, (3) moderately toxic, (4) slightly toxic, to (5) non-toxic depending upon acute toxic symptoms to body (Líska and Kolesar, 1982; Singh, 2012). The chemicals, if used non-judiciously can cause serious consequences to human health or even death. Pesticides show different damaging effects such as nervous system distraction, upsetting digestive system, interfering with reproductive system, paralysis, deteriorating ocular health, acting as mutagens, teratogens, and carcinogens, disrupting enzymatic systems, and inflicting serious threats to human beings (Jaga and Dharmani, 2006; Rajendran, 2016).

However, processing impact is calculated by measuring ratio of pesticides in raw products and in

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processed products. Processing factor (residues in processed products / residues in raw products) of < 1 indicates dissipation of chemical residues, while ≥ 1 indicates their stability or even concentration during various processing approaches (Pan *et al*., 2015; Kong *et al*., 2016; Saber *et al*., 2016). Previously, the dissipation of pesticides was determined by Poulsen *et al*. (2007) from table grapes by rinsing with tap water; after which they found 20 - 49% decline in dithiocarbamates, procymidone, copper, and iprodione although pyrethroids and organophosphates dissipated but not to greater extent. Very little data were found regarding grape processed into products such as jam, jelly, juice, squash, and nectar for dissipation of chemical residues. Chen *et al*. (2009) evaluated the impact of pulsed electric field (PEF) on apple juice containing chlorpyrifos and methamidophos with the results that PEF treatment is effective for pesticide degradation.

Similarly, El-Behissy *et al*. (2001) conducted research on date processing into jam, dehydrated product, and syrup production for dichlorvos dissipation, and found significant removal of residues using the mentioned processing methods. The removal of pesticides by processing methods is a function of various properties of active ingredient either systemic or contact nature as well as commodity type (Hendawi *et al*., 2013). A group of researchers explored grape drying by two methods i.e. sun-drying and oven-drying to study the reduction percentage of residues. They revealed degradation by sun drying up to 82% in methidathion, 73% in chlorpyrifos, 92% in diazinon, and 39% in dimethoate, while oven drying was excellent at 70°C and 80°C which caused > 90% reduction in residues at comparatively lesser time (Özbey *et al*., 2017). Many techniques have been applied for accessing pesticide loss during processing but there are varied responses which depend on many factors thus demanding more efforts to explore the phenomena.

The regulatory bodies have established maximum residual limits (MRLs) for pesticide residues in foods to safeguard the consumers. Various techniques are in progress to mitigate the issues, and processing industries can play pivotal role in adherence with consumer's safety laws if processing of commodities is in accordance with attenuation of these dangerous chemicals. Hence, the present work has application for home and industrial processing to reduce pesticides and to have safe foods. The present work was designed in which the fate of pesticides at three doses was assessed when Perlette and Black grape varieties were processed into five products.

Materials and methods

Supervised trial using three doses

Mature produce after 24 h of pesticide application was used for product development. Seven pesticides with MRLs like lufernon (1,000 μg kg^{-1}), mandipropamid (2,000 μg kg^{-1}), bifenthrin (300 μg kg^{-1}), acetamiprid (500 μg kg^{-1}), difenconazole (3000 μg kg^{-1}), chlorpyrifos (10 μg kg^{-1}), and cymoxanil (300 μg kg^{-1}) were sprayed using three doses; recommended dose (RD), double dose (DD) and triple dose (TD). As processing (recipes, conditions, additives, etc.) has an effect on pesticide residues, five products were chosen; nectar, juice, jam, squash, and raisins, in order to know the impact of processing on three supervised doses.

Grape processing into various products

Nectar

Standard recipe was followed for the development of grape nectar where processing-1 (P1) was performed at 96°C for 6 min, while processing-2 (P2) was performed at 96°C for 10 min (Kumar *et al*. 2015) with some modification (grape cultivar, processing method, recipe, and additives).

Juice

Grape berries were processed into juice using standard formula with processing similar to nectar; P_1 = (96°C, 6 min) and P_2 = (96°C, 10 min) (Kumar *et al*. 2015) with some modification (grape cultivar, processing method, recipe, and additives).

Jam

Grape berries were processed into jam using two acidity levels: AL_1 = 0.124% and AL_2 = 0.248% to check the impact of acidity and processing on pesticide dissipation (Poiana *et al*., 2011).

Squash

Squash was prepared by using two acidity levels from citric acid: L_1 = 0.071% and L_2 = 0.142% by using standard recipe formula with no compromise on sensory quality.

Raisins

Perlette and Black grapes were placed into two dryers i.e. hot air dryer (HAD) and solar air dryer (SAD) following the method of Almeida *et al*. (2013) with some modification such as grape types, initial dip solutions, and dryer type. Initial dip containing 1% KMS (potassium metabisulphite) + 0.1 N NaOH (sodium hydroxide) + 0.5% Na_2CO_3 (sodium carbonate) was applied on both varieties to aid drying and preserve quality as per normal practice. Prior to raisin processing, moisture was determined in the two varieties and each lot was subjected to two drying methods separately. Drying was stopped by visually checking the acceptability of grapes based on texture and appearance; and final moisture was determined using hot air oven drying method until constant weight (Doymaz, 2006).

Dissipation or persistence kinetics

The degradation or stability of pesticide residues was checked during processing (dilution or concentration of pesticides) of five products. Processing factors and dose effects were analysed for each developed product. Developed products were analysed for residues using HPLC-UV-VIS following the method of Randhawa *et al*. (2007).

Statistical analysis

Data were subjected to factorial under complete randomised design (CRD), and each parameter was analysed statistically to determine the level of significance. Data were compared by Tukey's HSD test by following methods and principles described by Montgomery (2008).

Results

In the present work, processing levels managed to reduce the residues in five products as indicated in Figure 1; whereas flow lines in Figure 2 indicated the product development steps for each product.

Fate of pesticides during processing of Perlette and Black grapes

Juice

Statistical analysis indicated a highly significant impact of varieties and juice processing on residues with all interactions (pesticide × processing × variety), and significant difference between the three doses of pesticides applied. However, the interaction of processing × variety was non-significant at DD in grape juice. Perlette and Black grape were processed into juice using two processing methods i.e. heating of juice at 6 and 10 min. P2 represented good dissipations as compared to P1; and Black grapes were found better than Perlette which can be attributed to composition (pH, pulp, skin, and seed) and physiological (thick or thin skin) differences of both varieties.

Overall percentage declines indicated that comparable maximum loss was noticed in chlorpyrifos and bifenthrin from Perlette (84.82 and 84.21%) while similar trend was depicted in Black (86.23 and 85.13%). Overall minimum loss occurred in lufenuron showing its stanch behaviour but Black variety lost more than Perlette with 68.12 and 65.53%, respectively. Overall processing showed significant impact with reductions of P1 and P2 of 75.24 and 79.55%, respectively. The mean value of residues regarding varieties showed significant difference between Perlette and Black at 4.38 ± 0.70 and 4.09 ± 0.67 mg kg^{-1}, respectively. Additionally, processing factors for all seven pesticides at applied doses were below 1 but distinct from each other indicating dissipation as depicted in Table 1. Two juice processings showed only RD dissipated lufenuron and mandipropamid below MRLs in Perlette and Black; but difenconazole disappeared to MRL at two processings of RD and DD for both varieties. Cymoxanil loss was very close to MRL in RD processing in Black grapes only.

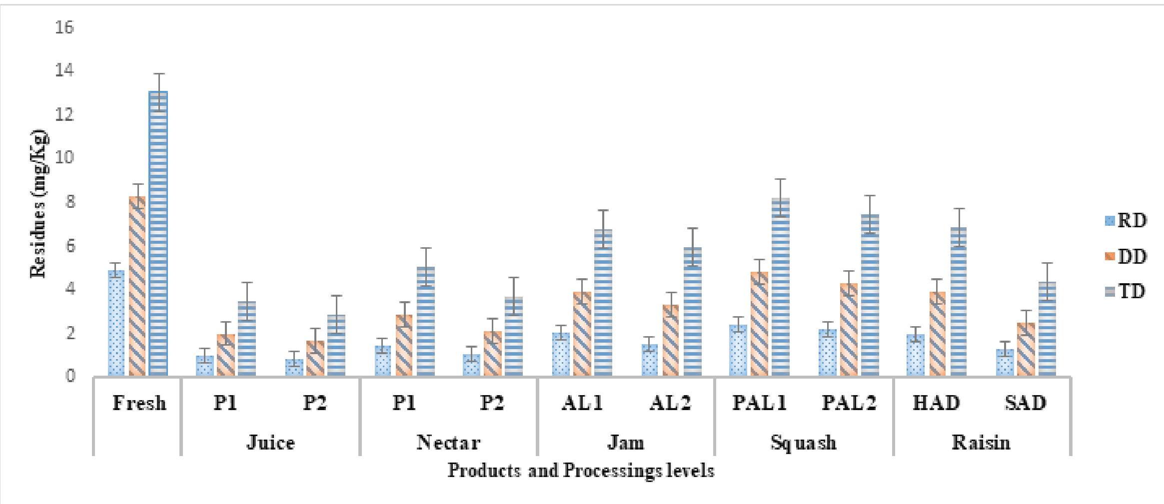

Figure 1. Perlette and Black grape varieties processing with overall pesticides dissipation pattern. RD = recommended dose; DD = double dose; TD = triple dose; P1 = processing level-1; P2 = processing level-2; AL1 = acidity level-1; AL2 = acidity level-2; HAD = hot air dryer; SAD = solar air dryer; PAL1 = pulp level-1; PAL2 = pulp level-2.

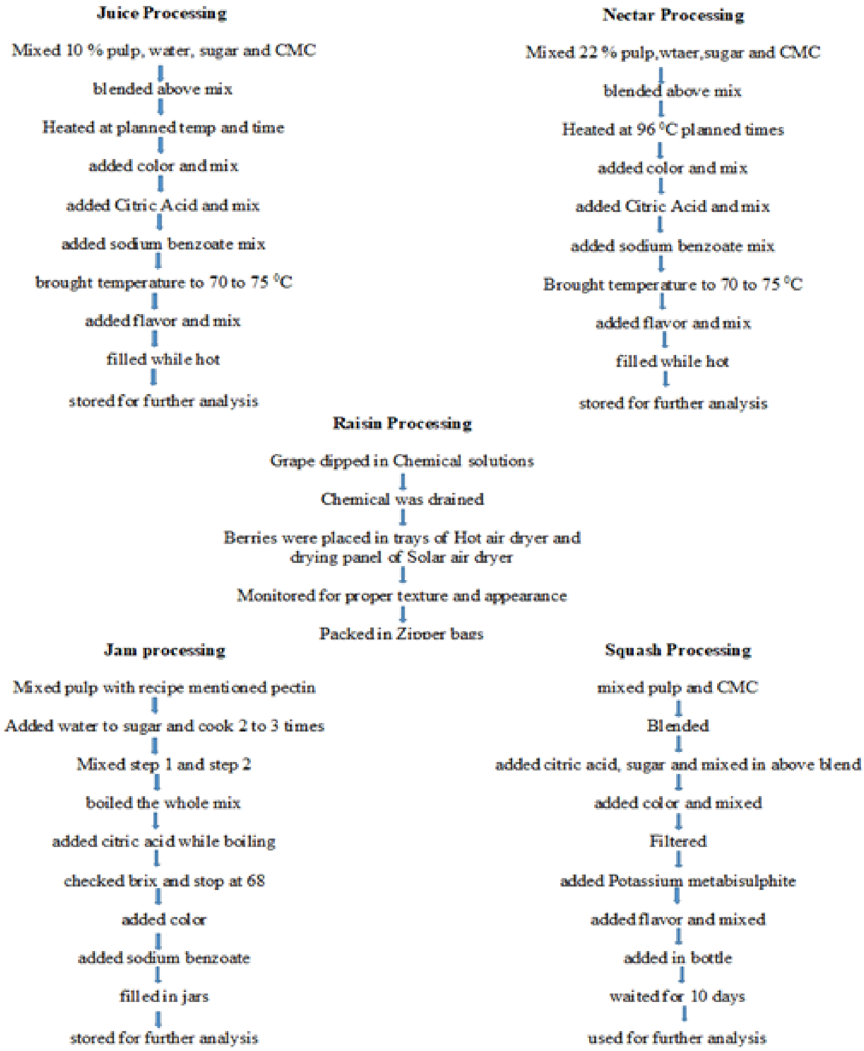

Figure 2. Perlette and Black grape varieties processing into five different products (juice, nectar, raisin, jam, squash).

Nectar

Statistical analysis indicated highly significant impact of varieties and nectar processing on residues with all interactions (pesticide × processing × variety), and significant difference between the three doses of pesticides applied. The interaction of processing × variety was non-significant at DD in grape nectar. Nectar was processed from two grape varieties with each variety being processed at two exposures of 6 and 10 min stay time during pasteurisation (96°C). P2 showed notable dissipations as compared to P1; and Black were found better than Perlette which can be attributed to composition (pH, pulp, skin, and seed) and physiological (thick or thin skin) differences of both varieties. The percentage of reductions again depicted similar behaviour in nectar as in juice as minimum loss occurred in lufenuron (53.75% in Perlette and 54.22% in Black) in both varieties but difenconazole and chlorpyrifos showed comparable loss with 74.12 and 79.75% in Perlette, respectively; although Black displayed maximum dissipation of bifenthrin (80.39%) and chlorpyrifos (79.98%). Overall processing impacted significantly with percent losses of 64.66 and 73.78% in P1 and P2, respectively. Overall residues were 4.88 ± 0.70 and 4.54 ± 0.66 mg kg^{-1} for Perlette and Black, respectively. Processing factors on nectar are displayed in Table 1, where all PFs (processing factors) at three doses were found to be less than 1 indicating effectiveness of processing. P2 of nectar at only RD dissipated lufenuron and mandipropamid near to MRLs in both varieties, but difenconazole went below MRLs in both processing of its RD and only P2 of its DD.

Jam

Jam is a product well relished by consumers during breakfasts and prepared from different fruits. To study whether jam processing alleviates the danger of pesticides in effective manner or not, Perlette and Black grape varieties were processed into jam using two acidity levels as acidic hydrolysis is among

Table 1. Processing factors of pesticides after processing of grapes into five different products (juice, nectar, raisin, jam, squash).

Product	Pesticide	P1			P2			Product	P1			P2		
		pf (RD)	pf (DD)	pf (TD)	pf (RD)	pf (DD)	pf (TD)		pf (RD)	pf (DD)	pf (TD)	pf (RD)	pf (DD)	pf (TD)
Grape Juice	Lufernon	0.33	0.38	0.42	0.27	0.32	0.35	Grape Jam	0.64	0.75	0.87	0.51	0.73	0.84
	Mandipropamid	0.19	0.22	0.25	0.16	0.19	0.21		0.46	0.49	0.53	0.28	0.42	0.47
	Bifenthrin	0.15	0.18	0.19	0.12	0.14	0.16		0.30	0.35	0.37	0.23	0.25	0.33
	Acetamiprid	0.27	0.32	0.35	0.23	0.26	0.29		0.54	0.57	0.69	0.39	0.48	0.52
	Difenconazole	0.19	0.21	0.23	0.16	0.17	0.19		0.38	0.40	0.44	0.30	0.33	0.40
	Chlorpyriphos	0.14	0.17	0.19	0.12	0.14	0.16		0.28	0.32	0.38	0.21	0.25	0.30
	Cymoxanil	0.30	0.34	0.38	0.24	0.28	0.31		0.62	0.68	0.79	0.47	0.56	0.73
	Lufernon	0.30	0.35	0.39	0.25	0.29	0.32		0.59	0.70	0.78	0.47	0.62	0.72
	Mandipropamid	0.18	0.21	0.23	0.15	0.17	0.19		0.34	0.40	0.45	0.27	0.32	0.35
	Bifenthrin	0.14	0.16	0.19	0.12	0.13	0.16		0.28	0.31	0.37	0.21	0.25	0.29
	Acetamiprid	0.25	0.30	0.33	0.21	0.24	0.27		0.50	0.57	0.63	0.39	0.49	0.60
	Difenconazole	0.17	0.19	0.21	0.14	0.16	0.18		0.33	0.38	0.38	0.26	0.30	0.33
	Chlorpyriphos	0.13	0.15	0.17	0.11	0.13	0.14		0.26	0.30	0.35	0.20	0.24	0.33
	Cymoxanil	0.27	0.32	0.35	0.23	0.26	0.29		0.54	0.64	0.68	0.50	0.59	0.65
Product	Pesticide	P1			P2			Product	P1			P2		
		pf (RD)	pf (DD)	pf (TD)	pf (RD)	pf (DD)	pf (TD)		pf (RD)	pf (DD)	pf (TD)	pf (RD)	pf (DD)	pf (TD)
Grape Nectar	Lufernon	0.46	0.53	0.62	0.35	0.39	0.43	Grape Squash	0.78	0.84	0.89	0.73	0.78	0.86
	Mandipropamid	0.27	0.32	0.37	0.20	0.23	0.26		0.46	0.59	0.60	0.42	0.48	0.55
	Bifenthrin	0.21	0.25	0.27	0.16	0.18	0.20		0.39	0.40	0.49	0.33	0.39	0.43
	Acetamiprid	0.38	0.47	0.52	0.28	0.33	0.37		0.58	0.75	0.81	0.55	0.70	0.78
	Difenconazole	0.27	0.30	0.33	0.20	0.22	0.24		0.47	0.51	0.58	0.42	0.45	0.50
	Chlorpyriphos	0.20	0.24	0.27	0.14	0.17	0.20		0.36	0.39	0.50	0.32	0.36	0.42
	Cymoxanil	0.41	0.48	0.57	0.30	0.35	0.41		0.80	0.85	0.89	0.64	0.76	0.85
	Lufernon	0.43	0.48	0.56	0.31	0.46	0.51		0.66	0.72	0.82	0.59	0.63	0.77
	Mandipropamid	0.25	0.29	0.32	0.18	0.21	0.23		0.44	0.50	0.57	0.39	0.46	0.51
	Bifenthrin	0.19	0.23	0.26	0.14	0.17	0.18		0.37	0.39	0.48	0.30	0.37	0.41
	Acetamiprid	0.36	0.42	0.47	0.29	0.32	0.38		0.55	0.70	0.75	0.56	0.64	0.69
	Difenconazole	0.23	0.27	0.31	0.17	0.20	0.22		0.41	0.47	0.50	0.36	0.42	0.47
	Chlorpyriphos	0.18	0.24	0.29	0.14	0.16	0.20		0.32	0.38	0.43	0.29	0.32	0.35
	Cymoxanil	0.38	0.44	0.50	0.28	0.33	0.37		0.74	0.79	0.84	0.60	0.70	0.72

P1 = processing level-1; P2 = processing level-2; pf = processing factor; RD = recommended dose; DD = double dose; TD = triple dose.

the prominent pesticide dissipating mechanisms. Statistical analysis indicated highly significant impact of varieties and jam processing on residues with all interactions (pesticide × processing × variety), and significant difference between the three doses of pesticides applied. The interactions of processing × variety were non-significant at DD and TD in grape jam. P2 represented commendable pesticide decline as compared to P1; and Black expounded adequate results than Perlette which can be due to acidic nature, recipe formulation, and product type. Overall percent reductions indicated maximum loss in chlorpyrifos and bifenthrin with 69.47 and 70.94% in Perlette, while similar maximum loss with values of 71.40 and 71.94% in Black, respectively. Nonetheless, lufenuron depicted minimum loss with 28.01% in Perlette and 35.55% in Black. Overall reduction in processing indicated acidity level-2 caused more loss (58.66%) than acidity level-1 (50.96%), respectively. Overall residues reported 5.81 ± 0.72 and 5.26 ± 0.67 mg kg^{-1} differences from Perlette and Black, respectively. PFs were also calculated for three doses of pesticides in which Table 1 reports that all PFs were below 1, thus depicting that processing was effective. Moreover, jam processing indicated difenconazole dissipation to MRL in only P2 of RD in Perlette, while in both processing of Black variety difenconazole went below MRL.

Squash

Squash, being indigenous product mostly used in summer, is prepared from various fruits according to consumers' choices. Two selected varieties were processed into grape squash using two acidity levels of pulp without heat processing. Acidity levelling was designed to access dissipation whether residues approached MRLs or not. Statistical analysis indicated highly significant impact of varieties and squash processing on residues with interactions (pesticide × processing × variety), and significant difference between the three doses of pesticides applied. The interactions of processing × variety were non-significant at RD and TD in grape squash. P2 of squash showed appreciable pesticide reduction as compared to P1, and Black illustrated sufficient loss of pesticides than Perlette which could be due to variety, composition, product type, processing method, and additives. Overall percent of reductions indicated comparable maximum loss of 59.56 and 60.97% in bifenthrin and chlorpyrifos from Perlette, while 61.54 and 65.39% in Black; whereas minimum loss occurred in cymoxanil (26.84%) in Black contrary to Perlette where minimum loss occurred in lufenuron (18.83%) and cymoxanil (20.25%). Likewise, in other products of grapes assessed in the present work, level two (47.04%) reported more loss as compared to level one (41.10%). Results showed significant difference for Perlette and Black with values 6.48 ± 0.75 and 5.90 ± 0.69 mg kg^{-1}, respectively. Processing factors (Table 1) clearly defined the dissipation at three doses where PFs were found to be below 1. Only P2 of RD degraded difenconazole under MRL in Black grapes.

Raisins

Raisins are popular around the globe owing to their culinary uses and nutritious nature. Numerous grape varieties are known today but not all is suitable for raisins or drying purposes. Usually, Perlette and Black grapes along with some other cultivars are being used to produce dehydrated grapes. The present work explored the impact of two drying methods i.e. solar and hot air dryer on pesticide residues. Statistical analysis indicated highly significant impact of varieties and raisin processing on residues with all interactions (pesticide × processing × variety), and significant difference between the three doses of pesticides applied. The interactions of processing × variety were non-significant at RD and TD in grape raisins. SAD (solar air dryer) for grape drying indicated excellent pesticide reduction as compared to HAD (hot air dryer), and Black grapes showed more loss of pesticides than Perlette, which can be due to initial dip, drying equipment type, drying mechanism as well as varietal influence. Overall reduction percentages indicated maximum loss in SAD as compared to HAD but in Perlette, bifenthrin (72.84%) and chlorpyrifos (74.05%) showed comparable maximum loss as compared to Black with 74.02 and 75.92%, respectively. Lufenuron and cymoxanil showed comparable minimum losses in both varieties with 39.92 and 45.54% in Perlette, and 44.04 and 49.96% in Black, respectively. The overall mean values of 5.47 ± 0.72 and 5.03 ± 0.67 mg kg^{-1} were reported on Perlette and Black, respectively, thus showing more loss of pesticides in Black. Table 2 shows the results regarding moisture and PFs of pesticides, where pf > 1 indicated concentration of residues owing to moisture removal as results were calculated on fresh weight of grapes. Most non-systemic pesticides had pf of < 1 or near to 1 as compared to systemic ones. Current findings reported exception of (systemic) mandipropamid and difenconazole whose PFs in SAD were less than 1 in Black but close to 1 in Perlette regarding RD and DD, but > 1 in TD of both methods except chlorpyrifos. Moreover, RD of seven residues depicted tendency of < 1 pf as compared to DD and TD. Nevertheless,

Table 2. Moisture content before and after drying of grapes.

Moisture Contents Before and After Drying				Methods	
Initial moisture contents				HAD	SAD
Perlette grapes		Black grapes		2.70^{NS}	
74.87 ± 2.54%		78.46 ± 2.87%			
After drying by two methods				Variety	
HAD		SAD		Perlette grapes	Black grapes
Perlette grapes	Black grapes	Perlette grapes	Black grapes	9.48*	
17.82 ± 0.55%	19.32 ± 0.45%	16.59 ± 0.95%	18.65 ± 0.35%		

Processing factors after processing of grapes into raisins								
Variety	Product	Pesticide	Processing factors as function of dose					
			HAD			SAD		
			pf (RD)	pf (DD)	pf (TD)	pf (RD)	pf (DD)	pf (TD)
Perlette	Raisins	Lufernon	2.63	3.04	3.40	1.81	2.18	2.53
		Mandipropamid	1.57	1.83	1.99	1.07	1.25	1.45
		Bifenthrin	1.20	1.36	1.56	0.85	0.99	1.10
		Acetamiprid	2.13	2.59	2.95	1.56	1.81	2.05
		Difenconazole	1.56	1.97	2.12	1.08	1.17	1.28
		Chlorpyriphos	1.13	1.28	1.50	0.79	0.94	1.09
		Cymoxanil	2.51	2.82	2.98	1.68	1.94	2.18
Black		Lufernon	2.38	2.75	3.15	1.60	1.88	2.07
		Mandipropamid	1.38	1.61	1.85	0.94	1.09	1.21
		Bifenthrin	1.09	1.26	1.47	0.73	0.86	1.01
		Acetamiprid	1.99	2.45	2.78	1.35	1.63	1.69
		Difenconazole	1.28	1.49	1.66	0.87	1.01	1.13
		Chlorpyriphos	1.04	1.19	1.32	0.69	0.80	0.90
		Cymoxanil	2.24	2.52	2.68	1.44	1.63	1.86

HAD = hot air dryer; SAD = solar air dryer; pf = processing factor; RD = recommended dose; DD = double dose; TD = triple dose.

raisin processing lost the difenconazole to MRL in only P2 of RD from Perlette while in Black grapes only P2 of RD dissipated lufenuron to MRL and both processings of RD degraded difenconazole to MRL.

Discussion

Five products were developed from two grape varieties; each sprayed with RD, DD, and TD of supervised pesticides with the objective to know the dissipation pattern of residues after various processings such as juicing, fruit nectar processing, jam processing, raisining and squash processing. Based on the obtained findings, it was recipe, acidity, heat processing, pesticide nature, and pesticide dose which mainly affected the fate of pesticides as residues. Among the supervised pesticides, difenconazole (3,000 µg kg^{-1}), lufenuron (1,000 µg kg^{-1}), cymoxanil (300 µg kg^{-1}), mandipropamid (2,000 µg kg^{-1}) decayed to MRLs in some products as previously discussed, while in some products they displayed stanch behaviour. It was found that juice lost greater amount of pesticides as compared to nectar due to greater recipe dilution so same processing levels for both further degraded the residues satisfactorily at even higher doses. Previously, Kong *et al*. (2012) determined the effect of home processing of apple and reported 81 to 84% reduction of cypermethrin and 15 to 36% reduction in acetamiprid, chlorpyrifos, carbendazim, and tubeconazole. Earlier, Miliadis *et al*. (1995) determined the impact of juice processing from apricot on field-applied pesticides and found 20% residues of tetradifon after processing. Furthermore, preparatory operations like blanching and washing reduced the residues by approximately 50% in food matrices like tomato, asparagus, peppers, and spinach but peaches exhibited varied behaviour (Chavarri *et al*., 2005).

Fruit jam is semisolid form of fruit pulp and sugar which dissipated pesticide residues to greater extent. As inferred from present findings, the recipe and processing diluted the residues as acidity level might have caused hydrolysis and heat processing might have decayed the pesticide. Moreover, acidity may disturb the ring structure, functional group ionisation, or aromatic moieties of particular chemical causing degradation or breakdown. Similarly, co-distillation, thermal degradation, or volatilisation may be effective in residue decaying. Rimeeh (2013) determined the residues of imidacloprid from juice, jam, and syrup, and reported jam processed from concentrating juice amplified the residues which could be due to juice concentration during jam cooking. Nonetheless, the data is scarce on jam processing and pesticide loss. Nevertheless, processing directly from fruit pulp and from juice confer different behaviours to end-product pesticide residues.

Raisin is processed from grapes using various drying techniques, but mostly solar drying and hot air drying are applied. In the present work, solar air dryer removed pesticides to greater extent since during drying, volatilisation, evaporation, co-distillation, thermal decay of pesticides could be the main routes. But in hot air dryer, decay could be due to thermal degradation and evaporation by hot air which picked volatile residues along with moisture. Moreover, initial chemical dip of grapes before processing into raisins also influenced the pesticide decay. Besides, more loss of pesticide in solar can be attributed to sun heat as well as solar panel fitted with fan producing hot air convectional currents further augmenting the process of pesticide decay.

Özbey *et al*. (2017) demonstrated 82% degradation by sun drying in methidathion, 73% in chlorpyrifos, 92% in diazinon and 39% in dimethoate while oven drying was excellent at 70 and 80°C causing > 90% reduction in residues in minimum time. Earlier, McDonald *et al*. (1983) explored behaviour of chlorpyrifos and malathion on Sultana grapes during drying and reported concentration of residues owing to moisture removal. Lately, grape processing into different products was studied for fungicide degradation behaviour and findings showed procymidone, phosalone, metalaxyl, and benalaxyl residues were almost the same as on fresh after sun drying but became concentrated i.e. in iprodion and decreased in dimethoate and vinclozoline. Oven drying depicted procymidone and iprodione were reduced in raisins as compared to fresh grapes (Cabras and Angioni, 2000). Recently, Zhao *et al*. (2018) explored 11 pesticides during four processing techniques of jujube and indicated 11.4 to 95.1% reduction. They reported that microwave drying as effective as compared to freeze drying, oven drying, and sun drying. Additionally, dimethoate behaviour was explored in leaves of yerba maté (a type of tea) during two drying stages revealing 22.7% decline in residues (Schmalko *et al*., 2002).

Squash processing in the present work also indicated the loss of pesticides through dilution and acidic hydrolysis since no heat processing was involved. Additives also played a crucial role in pesticide dissipation. No research has been reported regarding dilution of pesticide residues during fruit squash processing. Moreover, contribution of residues in squash may be due to retention of chemical residues in pulp and skin of grapes which become available in blend or mix used for squash development. Utture *et al*. (2011) studied the pomegranate and reported the confinement of residues to rind portion with difenconazole and carbendazim, but contained azoxystrobin in inner parts.

Conclusion

The product development effectively dissipated the residues but indicated high initial deposits may cause more persistence and less degradation of pesticides. Raisins which are mostly eaten all around the globe were processed from Perlette and Black grape varieties using two methods, in which solar air dryer depicted the best dissipation level than hot air dryer when fruit was initially treated with preliminary chemicals like antimicrobials, water losing agents, and berry protecting agents. Conclusively, the following product dissipation pattern (juice > nectar > raisin > jam > squash) was revealed in the present work. Overwhelmingly, cumulative reductions regarding P1 and P2 were calculated as 64.66 and 73.78% in nectar, 75.24 and 79.56% in juice, 50.96 and 58.66% in jam, 41.10 and 47.04% in squash, and 51.78 and 68.79% in raisin, respectively. Both varieties showed similar trend of pesticide dissipation during product development, but Black variety revealed more degradation than Perlette. Overall mean residues as function of processing formed ladder product-wise as follows; juice (4.38 ± 0.70 mg kg^{-1}), nectar (4.88 ± 0.70 mg kg^{-1}), raisin (5.47 ± 0.72 mg kg^{-1}), jam (5.81 ± 0.72 mg kg^{-1}), squash (6.48 ± 0.75 mg kg^{-1}) from Perlette; and juice (4.09 ± 0.67 mg kg^{-1}), nectar (4.54 ± 0.66 mg kg^{-1}), raisin (5.03 ± 0.67 mg kg^{-1}), jam (5.26 ± 0.67 mg kg^{-1}), and squash (5.90 ± 0.69 mg kg^{-1}) from Black. Difenconazole and cymoxanil dissipated to MRLs in juice while mandipropamid and difenconazole approached MRLs in nectar. Jam processing attenuated difenconazole only to safety limit whereas difenconazole was reduced to MRL only in Black grapes during squash processing. Furthermore, raisin processing also reported difenconazole and lufenuron sensitivity to be lost during drying to MRLs. However, pesticides not reduced to MRLs should be applied according to prescribed dose on raw produce, and safety waiting period (after which residues decay themselves on raw produce) should be observed.

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References

Abass, K., Turpeinen, M., Rautio, A., Hakkola, J. and Pelkonen, O. 2012. Metabolism of pesticides by human cytochrome P450 enzymes in vitro - a survey. In Parveen, F. (ed). Insecticides - Advances in Integrated Pest Management, p. 166-194. United Kingdom: IntechOpen.

Almeida, I., Guiné, R. P. F., Gonçalves, F. and Correia, A. C. 2013. Comparison of drying processes for the production of raisins from a seedless variety of grapes. In ICEUBI 2013 - International Conference on Engineering. Portugal: University of Beira Interior.

Cabras, P. and Angioni, A. 2000. Pesticide residues in grapes, wine, and their processing products. Journal of Agricultural and Food Chemistry 48(4): 967-973.

Chavarri, M. J., Herrera, A. and Ariño, A. 2005. The decrease in pesticides in fruit and vegetables during commercial processing. International Journal of Food Science and Technology 40(2): 205-211.

Chen, F., Zeng, L., Zhang, Y., Liao, X., Ge, Y., Hu, X. and Jiang, L. 2009. Degradation behaviour of methamidophos and chlorpyrifos in apple juice treated with pulsed electric fields. Food Chemistry 112(4): 956-961.

Doymaz, I. 2006. Drying kinetics of black grapes treated with different solutions. Journal of Food Engineering 76(2): 212-217.

El-Behissy, E. Y., King, R. D., Ahmed, M. M. and Youssef, A. M. 2001. Fate of postharvest-applied dichlorvos in stored and processed dates. Journal of Agricultural and Food Chemistry 49(3): 1239-1245.

Hendawi, M. Y., Romeh, A. A. and Mekky, T. M. 2013. Effect of food processing on residue of imidacloprid in strawberry fruits. Journal of Agricultural Science and Technology 15: 951-959.

Jaga, K. and Dharmani, C. 2006. Ocular toxicity from pesticide exposure: a recent review. Environmental Health and Preventive Medicine 11(3): 102-107.

Kamrin, M. A. 1997. Pesticide profiles: toxicity, environmental impact, and fate. 1st ed. United States: CRC Press.

Kong, Z., Li, M., Chen, J., Gui, Y., Bao, Y., Fan, B., … and Dai, X. 2016. Behavior of field-applied triadimefon, malathion, dichlorvos, and their main metabolites during barley storage and beer processing. Food Chemistry 211: 679-686.

Kong, Z., Shan, W., Dong, F., Liu, X., Xu, J., Li, M. and Zheng, Y. 2012. Effect of home processing on the distribution and reduction of pesticide residues in apples. Food Additives and Contaminants: Part A 29(8): 1280-1287.

Kumar, R., Bawa, A., Rajeswara Reddy, K., Kathiravan, T., Subramanian, V. and Nadanasabapathi, S. 2015. Pulsed electric field and combination processing of mango nectar: effect on volatile compounds and HMF formation. Croatian Journal of Food Science and Technology 7(2): 58-67.

Líska, D. and Kolesár, D. 1982. Toxicological classification of pesticides. Czechoslovak Medicine 5(3): 137-145.

McDonald, G., Buchanan, G. A. and Griffiths, G. R. 1983. Insecticide application and degradation in sultana grapes grown for drying. Pesticide Science 14(5): 528-536.

Miliadis, G. E., Aplada-Sarlis, P. G. and Liapis, K. S. 1995. Disappearance of tetradifon from field-sprayed apricots and the apricot juice produced from them. Journal of Agricultural and Food Chemistry 43(6): 1698-1700.

Montgomery, D. C. 2012. Design and analysis of experiments. 8th ed. United States: Wiley.

Özbey, A., Karagöz, Ş. and Cingöz, A. 2017. Effect of drying process on pesticide residues in grapes. GIDA - The Journal of Food 42(2): 204-209.

Pan, R., Chen, H.-P., Zhang, M.-L., Wang, Q.-H., Jiang, Y. and Liu, X. 2015. Dissipation pattern, processing factors, and safety evaluation for dimethoate and its metabolite (Omethoate) in tea (*Camellia sinensis*). PLoS One 10(9): article ID e0138309.

Poiana, M.-A., Moigradean, D., Dogaru, D., Mateescu, C., Raba, D. and Gergen, I. 2011. Processing and storage impact on the antioxidant properties and color quality of some low sugar fruit jams. Romanian Biotechnological Letters 16(5): 6504-6512.

Poulsen, M. E., Hansen, H. K., Sloth, J. J., Christensen, H. B. and Andersen, J. H. 2007. Survey of pesticide residues in table grapes: determination of processing factors, intake and risk assessment. Food Additives and Contaminants 24(8): 886-895.

Rajendran, S. 2016. Acute toxic effect of pesticides on human beings: a review. Research and Reviews: Journal of Chemistry 5(2): 99-106.

Randhawa, M. A., Anjum, F. M., Asi, M. R., Butt, M. S., Ahmed, A. and Randhawa, M. S. 2007. Removal of endosulfan residues from vegetables by household processing. Journal of Scientific and Industrial Research 66(10): 849-852.

Saber, A. N., Malhat, F. M., Badawy, H. M. and Barakat, D. A. 2016. Dissipation dynamic, residue distribution and processing factor of hexythiazox in strawberry fruits under open field condition. Food Chemistry 196: 1108-1116.

Schmalko, M. E., Ramallo, L. A., Ferreira, D. and Berlingheri, R. D. 2002. Dimethoate degradation in plants and during processing of yerba maté leaves. Brazilian Archives of Biology and Technology 45(4): 419-422.

Singh, D. K. 2012. Pesticide chemistry and toxicology. United Arab Emirates: Bentham Science Publishers.

Utture, S. C., Banerjee, K., Dasgupta, S., Patil, S. H., Jadhav, M. R., Wagh, S. S., … and Adsule, P. G. 2011. Dissipation and distribution behavior of azoxystrobin, carbendazim, and difenoconazole in pomegranate fruits. Journal of Agricultural and Food Chemistry 59(14): 7866-7873.

Zhao, L., Liu, F., Ge, J., Ma, L., Wu, L. and Xue, X. 2018. Changes in eleven pesticide residues in jujube (*Ziziphus jujuba* Mill.) during drying processing. Drying Technology 36(8): 965-972.