Chemical Science Review and Letters ISSN 2278-6783

Research Article

Determination of Ethion and Carbendazim Residues in Farm gate Samples of Apple in Kashmir

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Abstract

Samples of Red Delicious cultivar of apple were collected from three different locations viz., Sangrama, Achabal and Janwari from district Baramulla and Shopian, Murren and Pulwama proper from district Pulwama. The samples were screened for pesticide residues on 0, 10 and 20th day interval and data was analysed statistically. The mean residues of Ethion were present to the tone of 0.370, 0.0.110, 0.257 and 0.108 mg/kg at 0 day at Sangrama, Achabal, Janwari and Shopian, which degraded to 0.307, 0.031, 0.156 and 0.033 mg/kg respectively after 10 days of collection and 0.253, ND, 0.110, and ND mg/kg after 20 days of collection respectively. However, the residues of Ethion could not be detected at Murren and Pulwama proper of district Pulwama. Similarly, the residues of carbendazim were present to the tone of 0.307, 0.411, 0.356, 0.286, 0.420 and 0.243 mg/kg at 0 days in the samples collected from Sangrama, Achabal, Janwari, Shopian, Murren and Pulwama proper respectively. The residues degraded to 0.275, 0.373, 0.318, 0.346, 0.360 and 0.208 mg/kg on 10th day after collection and 0.255, 0.366, 0.302, 0.233, 0.346 and 0.189 mg/kg after 20th day of collection at Sangrama Achabal, Janwari, Shopian, Murren and Pulwama proper respectively.

Keywords: Residues, degradation, Ethion, Carbendazim

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Introduction

Apple (*Malus domestica* Borkh.) the premier fruit and native of South Western Asia and Europe is grown all over the world under temperate climate and is the principal fruit crop of J&K State. Presently the area under apple cultivation in Jammu and Kashmir is 1.57 lakh hectares having annual production of 13.48 lakh metric tonnes. Among the temperate fruits in J&K, apple is the principle crop accounting for more than 43 per cent of area, whereas in terms of fruit production, its share is more than 78 per cent. The percentage share of this fruit in respect of area and production at national level is 2.4 and 2.0 per cent respectively. The Jammu & Kashmir state has created a niche in quality apple production and has made tremendous progress during the last decade as the area in the state has increased 16 times, production by about 60 times and productivity by 5 fold [1].

The most important insect pests attacking apple under Kashmir conditions are Sanjose scale (*Quadraspidiotus perniciosus* Comstock), Woolly aphid (*Eriosoma lanigerum* Haunsman), Hairy caterpillar (*Lymantria obfuscata* Walker), Apple stem borer (*Aeolesthes sarta* Solsky), Leaf rollers (*Archips pomivora* Meyrick) and Blossom thrips (*Taeniothrips rhapalantennalis* Shumshar) [2]. Besides these European red mite (*Panornychus ulmi* Koch) and two spotted spider mite (*Tetranrynhus urticae* Koch) have emerged as major pests of apple for the last few years. In addition to arthropod pests many diseases cause huge economic losses to apple. Principal diseases attacking apple arc apple scab caused by (*Venturia inaequalis* (Cike) Wint.), Alternaria rot caused by (*Alternaria allternata* (Fr.) Keissler), Brown rot caused by (*Sclerotinia fructigina*), Sooty blotch caused by (*Gloeodes pomigena* (Schw.) Colby); and leaf spot caused by (*Allemaria mali* (Lobt.) [2]. Keeping in view the damage caused by pests and diseases to fruits and in order to achieve meendancy over them. the markets of valley are flooded with various types of insecticides and fungicides which are indiscriminately used because they serve as the immediate solution to keep the pest below economic injury level.

Persistence and rate of degradation of pesticides vary with the crop and also with the agroclimatic conditions of the place [3-6]. In a survey carried out by the Indian Council of Medical Research (lCMR), New Delhi, it was found that 51 per cent of the samples of one food commodity were contaminated with pesticide residues and out of these, 20 per cent sample had pesticide residues above maximum residue limits (MRL). In spite ofthe fact that the consumption of pesticides in India is still very low, about 0.5 kg /ha against 6.60 kg/ ha in Korea and 12.00 kg/ha in Japan respectively, there has been a widespread contamination of food commodities with pesticide residues due to nonjudicious use of pesticides [7,8].

In general, the use of pesticide in agro-ecosystem imposes deleterious effects like environmental pollution and residual toxicity, because they possess slow rate of degradation which varies with the temperature and relative humidity of a place [9]. Because of their long persistence in the environment, these pesticides get accumulated in the biosphere and their cumulative build up in the human system causes a great concern to the human welfare. A number of ailments like anemia, dizziness, nephritis etc., develop in the human beings as a result of chronic and acute exposure to these pesticide residues [10].

The problem of pesticide residues becomes very serious when the fruit growers apply the pesticides at higher concentrations and that too close to the time of harvest; with the result, the pesticide does not get enough time to dissipate from the fruit before it is harvested and is ready for consumption.

Bearing in mind the consumer safety, it is important that the pesticide residue levels associated with different edible commodities be monitored regularly. With this background, it was therefore, thought pertinent to undertake the present investigations on Monitoring of pesticide residues in farmgate samples of apple in Kashmir, in order to determine toxicological levels of residues in farmgate samples of apple.

Materials and Methods

The investigations on Monitoring of pesticide residues in farmgate samples of apple in Kashmir were conducted in the toxicological laboratory, Division of Entomology, Sher-e-Kashmir University of Agricultural Sciences and Technology of Kashmir, Shalimar, Srinagar.

Sampling

Farmgate samples of apple were collected from three distinct locations at district Baramulla and district Pulwama. Ten samples of fruits were collected from each location. The samples were put in polythene bags, tied with rubber bands and carried to the laboratory where they were kept at the ambient temperature (10.5 to 20.2°C).

Extraction and clean up

For determination of organophosphate insecticide ethion residues, each sample was chopped and then 3 replicates each consisting of 20 g was drawn for further analysis. Each replicate was blended in a motor driven homogenizer for 2 minutes with 50 ml of acetone and 10 g anhydrous sodium sulphate (Na_2SO_4). The contents were filtered through Buchner's funnel using Whatman filter paper No.1 and re-extracted 2-3 times under vacuum using more contents were filtered. The fililtrates were pooled together and mixed with 50 ml of hexane and subjected to partitioning in 250 ml separating funnels by shaking vigorously for one minute. The lower denser organic layer containing residues in acetone was collected after passing through anhydrous sodium sulphate placed on the glass wool in glass funnel. The extracts were concentrated to 5 ml using Kuderna Danish evaporators and 5 ml of acetone were added so that the final volume of the residue extract was 10 ml. The residues extracted were stored in refrigerator in sterilized glass vials pending clean up process.

Ethion extract was cleaned up to the recommended standard column chromatographic technique, in which glass chromatographic columns (20 x 450 mm) with sintered discs were packed with activated adsorbent at 110°C for 2 hours and celite 545, MgO and sodium sulphate in the ratio of 2:2:1 [11]. About one inch thick layer of anhydrous Na_2SO_4 was loaded at the top of the adsorbent mixture and a mild tapping was given to ensure compactness of the column. Columns were made to run using acetone for equilibration. The samples extracted earlier were then gently loaded on the columns. A fully decolourizcd eluate was collected in 15 ml glass vials which were labelled and stored in refrigerator pending further analysis.

Carbendazim residues were extracted and cleaned up by the technique adopted by All India Coordinated Research Project on Pesticide Residues (AlCRPPR), lCAR, New Delhi. Three replicates weighing 100 g each were taken after initial chopping of the whole sample. 100 g of anhydrous sodium sulphate added to 2.5 ml concentrated ammonia and

200 ml of ethyl acetate was added to the replicate and then it was subjected to blending in a motor driven homogenizer for 3 minutes at a high speed. Sodium sulphate was used to prevent the formation of emulsion during blending. The upper layer was subjected to decantation and then filtered over anhydrous sodium sulphate. The residues left were again extracted with 100 ml ethyl acetate and filtered in a Buchner's funnel under suction. The combined filtrate was reduced to about 80 ml under vacuum at 40-45 ℃. Volume of the extract was made upto 160 ml in a measuring cylinder from which 40 ml was taken in a separating funnel and partitioned twice with 100 ml 0.1 N HCl by shaking vigorously for 2 minutes each time. The lower aqueous phase was pooled in another separating funnel along with 40 ml of ethyl acetate saturated with 30 ml of sodium bicarbonate (80%) solution for getting Hcl neutralized. it was shaken vigorously for 3 minutes and the lower aqueous phase was washed with distilled water and then partitioned with 100 ml of 0.1 N Hcl which was freshly Saturated with ethyl acetate by shaking vigorously for 1 minute.

Residue assay

Ethion residues were quantitatively estimated by para-nitrophenol method [12], as modified by Jain [13]. One ml of aliquot of clean up acetone extracts was taken in a reaction tube. The acetone was evaporated to dryness at 55±5℃ in a water bath. To the dried tube, 0.2 ml of 2 per cent cyclohexylamine solution was added. Micro-columns were then attached to the reaction tubes which were immersed 2 inch in the preheated oil bath at 175℃ and kept for 3 minutes. The tubes were then removed and cooled for 5 seconds in the ice-cold water. Finally, 3 ml of ethyl acetate were added to each tube and the absorbance at 412 nm was recorded in UV-Visible spectrophotometer model DM-108 against distilled water as reference.

Carbendazim residues were quantitatively assayed by a standard technique adopted by "All India Coordinated Research Project on Pesticide Residues (AICRPPR)", ICAR, New Delhi where the absorbance of 0.1 N Hcl extract was recorded in UV-visible spectrophotometer model DM-108 against 0.1 N Hcl which was freshly saturated with ethyl acetate.

Preparation of standard curves

Standard calibration plots for ethion and carbendazim (**Tables 1** and **2**, **Figures 1** and **2**) were prepared by adopting the procedure for residue analysis for each pesticide already described. Analytical grade ethion and carbendazim supplied by Environmental Protection Agency, North Carolina, USA were used for the preparation of standard curves. Different concentrations of ethion, and carbendazim in the range of 4-24 µg were used for the preparation of standard curves.

Table 1 Standard curve for the estimation of ethion residues

Concentration in µg (x)	*Mean O.D ± S.D	Calculated values (y)
4	0.172 ± 0.0045825	0.181
8	0.289 ± 0.006110	0.283
12	0.390 ± 0.008082	0.385
16	0.493 ± 0.01386	0.487
20	0.593 ± 0.011718	0.589
24	0.683 ± 0.02928	0.691
y = regression equation 0.0796 ±0.0255 (x) r = 0.9992 (significant at P = 0.05) *Mean of three replicates		

Table 2: Standard curve for the estimation of carbendazim residues

Concentration in µg (x)	*Mean O.D ± S.D	Calculated values (y)
2	0.22 ± 0.0068	0.245
4	0.384 ± 0.0051	0.360
6	0.490 ± 0.0110	0.476
8	0.591 ± 0.0120	0.592
10	0.697 ± 0.0112	0.707
y = regression equation 0.1297 ±0.0578 (x) r = 0.9992 (significant at P = 0.05) *Mean of three replicates		

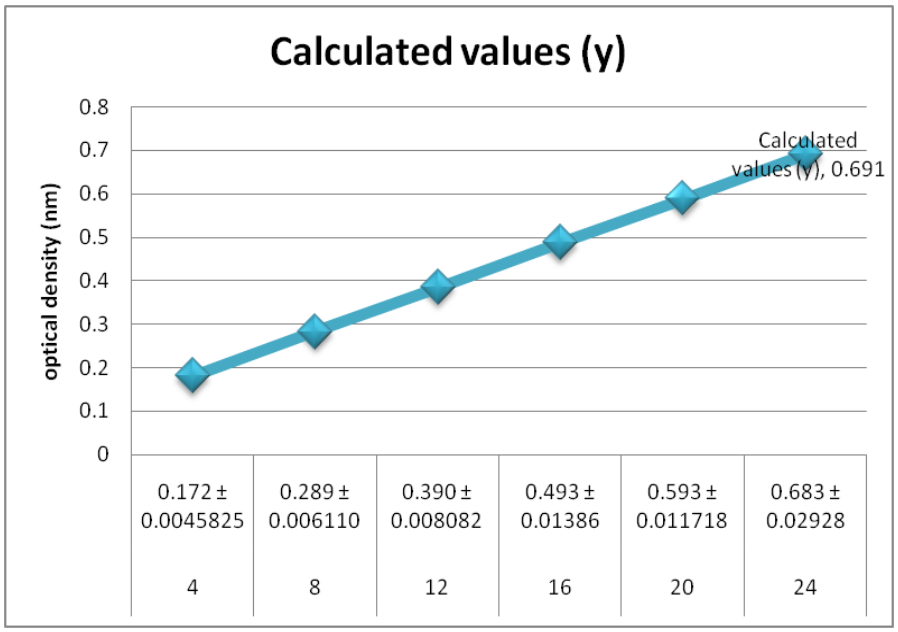

Figure 1 Calibration plot for estimation of Ethion

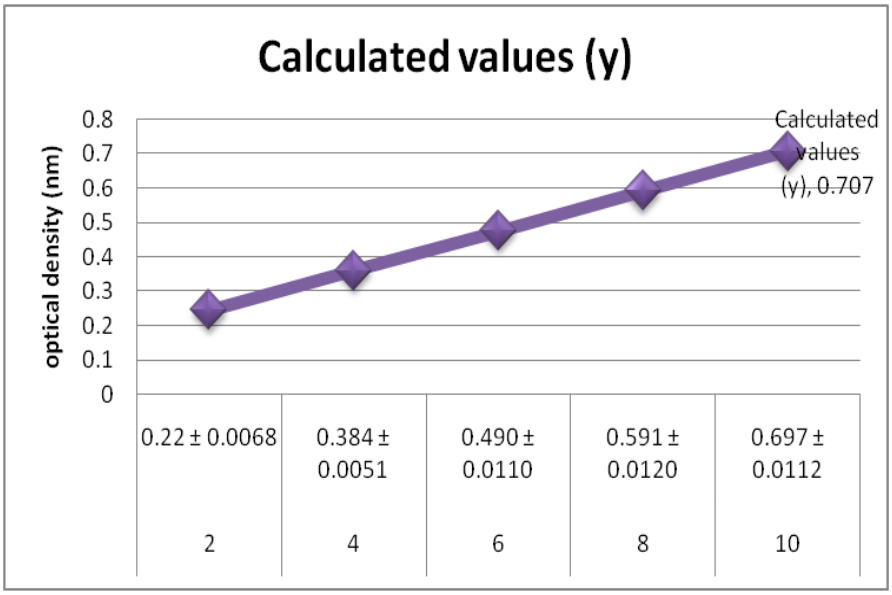

Figure 2 Calibration plot for estimation of Carbendazim

Recovery

Authenticity of the procedure was tested by the recovery of pesticides. Pesticide residues were determined by fortifying 25 g of apple samples individually with 5, 15 and 25 µg of ethion and 2, 4, 6 and 8 µg of carbendazim. After 4 hours, the samples were extracted, cleaned up and assayed for ethion and carbendazim determination by the procedures already described. The mean per cent recovery for fortified apple samples in each pesticide was 92.73 and 86.81 in ethion and Carbendazim, respectively (**Tables 3** and **4**).

Analysis of data

The residues of ethion and carbendazim were quantitavely estimated with the help of following formula:

$$T = \frac{X \times D}{E} \times 100$$

Where, T is the total amount of pesticide present in the extract, X is the µg of the pesticide in the sample aliquot, D is the dilution factor and E is the sample extract.

The residues of pesticides were worked out in ppm by dividing total amount of pesticide in the extract by total weight of fruit in g taken for analysis. T 1/2 values corresponding to the rate of dissipation and T total values corresponding to waiting periods were calculated by different methods [14,15].

The waiting period 'T tol' required to be elapsed for the pesticide deposits to reach the maximum residue limit required for the same consumption of the fruit after pesticide application was also worked out by the alternate method [15].

Table 3 Recovery of Ethion residues from the fortified samples of Apple

Level of fortification (µg)	Amount of Ethion Recovered			*Mean ± S.D	(%) recovery	**Mean (%) recovery
	R_1	R_2	R_3			
5	4.0	4.4	3.7	4.03 ± 0.351	80.6	90.55
15	14.0	14.8	14.0	14.26 ± 0.461	95.06	
25	24.7	23.4	23.9	24.0 ± 0.655	96.0	
*Mean of three replicates; **Mean of three replicates						

Table 4 Recovery of Carbendazim residues from the fortified samples of Apple

Level of fortification (µg)	Amount of Carbendazim Recovered			*Mean ± S.D	(%) recovery	**Mean (%) recovery
	R_1	R_2	R_3			
2	1.80	1.78	1.76	1.78 ± 0.02	89.0	86.81
4	3.40	3.10	3.30	14.26 ± 0.152	81.5	
6	5.20	5.00	5.20	5.13 ± 0.115	85.5	
8	7.20	7.6	7.10	7.3 ± 0.264	91.25	
*Mean of three replicates **Mean of three replicates						

Analysis of data

The residues of ethion and carbendazim were quantitavely estimated with the help of following formula:

$$T = \frac{X \times D}{E} \times 100$$

Where, T is the total amount of pesticide present in the extract, X is the µg of the pesticide in the sample aliquot, D is the dilution factor and E is the sample extract.

The residues of pesticides were worked out in ppm by dividing total amount of pesticide in the extract by total weight of fruit in g taken for analysis. T 1/2 values corresponding to the rate of dissipation and T total values corresponding to waiting periods were calculated by different methods [14,15].

The waiting period 'T tol' required to be elapsed for the pesticide deposits to reach the maximum residue limit required for the same consumption of the fruit after pesticide application was also worked out by the alternate method [15].

Results

Residues of ethion in/on apple (cv. Red Delicious) 0, 10 and 20th day after collectlon in Sangrama, Achabal Janwari (Baramulla) Shopian, Murren, Pulwama proper (Pulwama)

The data on the presence of ethion residues in the Red Delicious cultivar of apple fruits in Sangrama, Baramulla on 0, 10 and 20th day after collection revealed that residues of ethion were present in the apple fruits in Sangrama on 0 day collection and ranged between 0.270 ± 0.017 to 0.447 ± 0.030 mg/kg. Degradation of residues of ethion within 10 days was 0.063 mg/kg and residues ranged between 0.250 ± 0.015 to 0.386 ± 0.057 mg/kg. Further the residues of ethion were present in the fruits analyzed after 20 days of collection ranged between 0.206 ± 0.025 to 0.300 ± 0.045 mg/kg and degradation was 0.117 mg/kg. The composite mean residues of ethion were 0.370, 0.307 and 0.253 mg/kg at 0, 10, 20th day after collection respectively (Table 5). Similarly, residues of ethion were present in the fruits on 0 day collection in Achabal and ranged between 0.066 ± 0.011 and 0.166 mg/kg. Degradation of residues of ethion was

0.079 mg/kg within 10 days after collection and the residues ranged between 0.01 ± 0 to 0.056 ± 0.01 mg/kg. No residues could be detected on 20th day after collection. The composite mean residues of ethion were 0.110 and 0.031 mg/kg after 0 and 10th day of collection respectively (**Table 5**). Also, on 0 day in Janwari, Baramulla residues of ethion were present and ranged between 0.170 ± 0.043 to 0.340 ± 0.040 mg/kg. Degradation of residues of ethion was 0.101 mg/kg within 10 days after collection and residues ranged between 0.106 ± 0.011 to 0.236 ± 0.061 mg/kg. Further the residues of Ethion were detected in the fruits even after a lapse of 20 days and ranged between 0.056 ± 0.040 to 0.196 ± 0.025 mg/kg and degradation was 0.146 mg/kg. The composite mean residues of Ethion were 0.257, 0.156 and 0.110 mg/kg after 0, 10 and 20th day of collection, respectively (Table 5).

In Shopian Pulwama Residues of Ethion were present in the apple fruits on 0 day collection and ranged between 0.073 ± 0.015 to 0.143 ± 0.025 mg/kg on 10th day after collection of samples degradation of residues was 0.075 mg/kg and residues ranged between 0.026 ± 0.020 to 0.040 ± 0.026 mg/kg. On 20‘h day after collection, no residues of Ethion were detected in the fruits. The composite mean residues were 0.108 and 0.033 mg/kg at 0 and 10th day after collection, respectively.

Table 5 Composite mean residues (mg/kg) of Ethion in the (CV. Red Delicious) in the farm gate samples of apple in different districts of Kashmir analyzed at different intervals after collection

S.No	Area	District	Composite mean residues after intervals of analysis in days (mg/kg)		
			0	10	20
1	Sangrama	Baramulla	0.370	0.370 (0.063)	0.253 (0.117)
2	Achabal	-do-	0.1 10	0.031 (0.079)	ND
3	Janwari	-do-	0.257	0.156 (0.101)	0.110 (0.146)
4	Shopian	Pulwama	0.108	0.033 (0.075)	ND
5	Murren	-do-	ND	ND	ND
6	Pulwama proper	-do-	ND	ND	ND

Residues of carbendazim in/on apple (cv. Red Delicious) on 0, 10 and 20th day after collectlon in Sangrama, Achabal Janwari (Baramulla) Shopian, Murren, Pulwama proper (Pulwama)

Carbendazim residues were present in the apple fruits in Sangrama, Baramulla on 0 day collection and ranged between 0.280 ± 0.043 to 0.330 ± 0.017 mg/kg. Degradation of residues of carbendazim was 0.032 mg/kg within 10 days after collection and the residues ranged between 0.260 ± 0 to 0.290 ± 0.010 mg/kg. Further the residues of carbendazim were present in the fruit samples even after 20 days of collection ranged between 0.243 ± 0.015 to 0.280 ± 0.020 mg/kg and degradation was 0.052 mg/kg. The composite mean residues were 0.307, 0.275 and 0.255 mg/kg at 0, 10 and 20th day after collection, respectively (Table). In Achabal, Baramulla residues were observed on 0 day collection and ranged between 0.400 ± 0.017 to 0.423 ± 0.020 mg/kg. Degradation of residues of carbendazim was 0.038 mg/kg within 10 days after collection and the residues ranged between 0.356 ± 0.025 to 0.406 ± 0.020 mg/kg. Further the residues of carbendazim were present in the fruit samples even after 20 days of collection ranged between 0.316 ± 0.005 to 0.353 ± 0.020 mg/kg and degradation was 0.075 mg/kg. The composite mean residues were 0.411, 0.373 and 0.336 mg/kg at 0, 10 and 20th day after collection, respectively (**Table 6**).

In Janwari, Baramulla residues on 0 day collection ranged between 0.336 ± 0.020 to 0.373 ± 0.020 mg/kg. Within 10 days after collection degradation of residues of carbendazim was 0.038 mg/kg and the residues ranged between 0.306 ± 0.015 to 0.333 ± 0.068 mg/kg. On 20th day after collection residues of carbendazim were present in the apple fruits ranged between 0.296 ± 0.011 to 0.316 ± 0.011 mg/kg and degradation was 0.054 mg/kg. The composite mean residues of carbendazim were found to be 0.356, 0.318and 0.302 mg/kg after 0, 10 and 20th day after collection, respectively (Table 6).

In Shopian Pulwama residues of carbendazim were present in the apple fruits on 0 day collection and ranged between 0.276 ± 0.015 to 0.300 ± 0.036 mg/kg. On 10th day after collection of samples, degradation of residues of carbendazim was 0.040 mg/kg and the residues ranged between 0.223± 0.015 to 0.270 ± 0.010 mg/kg. Further the residues of carbendazim were detected in the fruits on 20th day after collection ranged between 0.213± 0.020 to 0.233 ± 0.025 mg/kg and degradation was 0.063 mg/kg. The composite mean residues of carbcndazim were 0.286, 0.246 and 0.223 mg/kg at 0, 10 and 20th day after collection, respectively (Table 6).

In Murrcn, Pulwama residues of carbendazim were present in the apple fruits collected on 0 day and ranged between 0.406 ± 0.015 to 0.436 ± 0.005 mg/kg. Degradation of carbendazim was 0.060 mg/kg within 10 days after sample collection and ranged between 0.340 ± 0.017 to 0.383 ± 0.015 mg/kg. On 20th day after collection residues of

carbendazim were present in the fruits ranged between 0.333 ± 0.005 to 0.363± 0.015 mg/kg and degradation was 0.074 mg/kg. The composite mean residues were found to be 0.420, 0.360 and 0.346 mg/kg alter 0, 10 and 20lh day of collection, respectively (Table 6).

Moreover, carbendazim residues were present in the apple fruits on 0 day collection in Pulwama proper and ranged between 0.223 ± 0.015 to 0.270 ± 0.020 mg/kg. On 10th day after collection, degradation of the residues of carbendazim was 0.035 mg/ kg and the residues ranged between 0.190± 0 to 0.226 ± 0.015 mg/kg. Further the residues of carbendazim were present in the fruits even after 20 days of collection and ranged between 0.170 ± 0.010 to 0.206 ± 0.015 mg/kg and degradation was 0.054 mg/kg. The composite mean residues were found to be 0.243, 0.208 and 0.189 mg/kg after 0, 10 and 20th day after collection, respectively (Table 6).

Table 6 Composite mean residues (mg/kg) of Carbendazim in the (CV. Red Delicious) in the farm gate samples of apple in different districts of Kashmir analyzed at different intervals after collection

S.no	Area	District	Composite mean residues after intervals of analysis in days (mg/kg)		
			0	10	20
1	Sangrama	Baramulla	0.370	0.275 (0.032)	0.255 (0.052)
2	Achabal	-do-	0.411	0.373 (0.038)	0.336(0.075)
3	Janwari	-do-	0.356	0.318(0.038)	0.302(0.054)
4	Shopian	Pulwama	0.286	0.246(0.040)	0.223(0.063)
5	Murren	-do-	0.420	0.360(0.060)	0.346(0.074)
6	Pulwama proper	-do-	0.243	0.208(0.035)	0.189(0.054)

Discussion

The Residues of ethion in different locations of district Pulwama and district Baramulla indicated that residues of ethion were present in the fruit samples collected from all the three locations of district Baramulla ranging from 0.253 to 0.370 mg/kg at Sangrama; 0.031 to 0.110 mg/kg at Achabal and 0.110 to 0.257 mg/kg at Janwari. In district Pulwama residues of ethion were detected in fruit Samples only at Shopian and ranged from 0.033 to 0.108 mg/kg. The ethion residues could not be detected in fruit samples collected from Murren and Pulwama proper. Although the residues of ethion were present in the fruit samples at different locations in both districts but the residues were not present above the prescribed maximum residue limit of 2.0 mg/kg [16]. These findings are in agreement with authors, who reported that ethion, phosalone, azinphosmethyl,, parathon residues were present in market samples of apple but were below the recommended MRL values as per the Canadian Act [17].

Further, the residues of ethion degraded in 10 days after collection and degradation persisted even upto 20th day of collection. Degradation of ethion residues after 10th and 20th day after collection was 0.063 and 0.117 mg/kg at Sangrama; 0.076 mg/kg at Achabal; 0.101 and 0.146 mg/kg at Janwari of district Baramulla and 0.075 mg/kg at Shopian in district Pulwama, respectively. No residues could be detected on 20th day after collection in Achabal of district Baramulla and Shopian of district Pulwama. No residues could also be detected from the fruit samples collected from Murren and Pulwama proper. Non-detection of residues of ethion from the fruit samples collected from Murren and Pulwama proper are attributed to the fact that growers may not have used ethion in their spray schedule, a practice generally adopted by the farmers. The degradation pattern followed was similar to that reported by others, who observed that when pesticide treated samples of apple are CA stored, the persistence of residues prolongs considerably than when stored at ambient temperature [18]. The pattern of presence of residues of ethion in the present investigations draw their support from the number of findings, which detected residues of parathion ethyl and capton in the market samples of apple cultivar Katerine but the residues were below the recommended MRL values[19]. Similar findings have also been reported for dimcthoate and fcnvalerate residues detected at 0.032 and 0.1 mg/kg in apples in the markets in Islamabad [20].

The Residues of carbendazim were present in fruit samples collected from different locations in both districts of Baramulla and Pulwama. In Sangrama, Achabal and Janwari of district Baramulla, the average residues were present to the extend of 0.307, 0.411, 0.356 mg/kg, respectively. While in Shopian, Murren and Pulwama proper of district Pulwama, residues of carbendazim were present to the extent of 0.286, 0.420 and 0.243 mg/kg respectively. Similar type of degradation pattern was observed in case of carbendazim as were observed in case of other pesticides under the present investigations. Degradation of carbendazim residues at ambient temperature on 10th and 20th day after collection was 0.032 and 0.052 mg/kg at Sangrama; 0.038 and 0.075 mg/kg at Achabal; 0.038 and 0.054 mg/kg at Janwari; 0.040 and 0.063 mg/kg at Shopian; 0.060 and 0.074 mg/kg at Murren and 0.035 and 0.054 mg/kg at

Pulwama proper, respectively. In a study, ethylene bisdithiocarbamate fungicide in 5 per cent of sampled apples above the recommended MRL values of 3 mg/kg was detected [21]. But in present investigations, the residues exceeded the prescribed MRL values in none of the samples.

Conclusion

The discriminate use of pesticides and non-adoption of Good Agricultural practices by the apple growers have lead to the persistence of pesticides and their build up in the fruits. Pesticide residues find their entry into the human system through the consumption of these pesticide laden fruits. The present studies were, therefore, carried out to monitor the residues of some commonly used pesticides in the farmgate samples of apple in two districts of valley.

At all locations in district Baramulla, the residues of both pesticides were below the recommended MRL values. Thus there was absolutely no risk involved to the consumers with respect to these pesticides. However, the presence of other pesticides cannot be ruled out. The degradation at the ambient temperature occurred in all samples both l0 days and 20 days after collection. However, maximum degradation occurred in 10 days after collection, thereafter the rate of degradation slowed down gradually, which is evident from the fact that residues of ethion had degraded to 0.307 and 0.253, 0.031 and ND and 0.156 and 0.110 mg/kg at Sangrama, Achabal and Janwari at 10th and 20th day after collection, respectively. By and large similar degradation pattern was also observed in case of earbendazim residues which degraded to 0.275 and 0.255, 0.373 and 0.336 and 0.318 and 0.302 pig/kg in 10 and 20 days after collection at Sangrama, Achabal and Janwari, respectively. Likewise the farmgate samples of Red Delicious cultivar of apple collected from three distinct locations viz. Shopian, Murren and Pulwama proper in district Pulwama were also found laden with the residues of ethion and carbendazim. Residues of ethion were present to the extent of 0.108 mg/kg in the samples collected from Shopian. However, residues of ethion could not be detected from the samples collected from Murren and Pulwama proper. Carbendazim residues were present to the extent of 0.286, 0.420 and 0.243 mg/kg at Shopian, Murren and Pulwama proper, respectively. It is clear that the residues of both pesticides at all the three locations in district Pulwama were well below the suggested MRL values. Thus there was no danger involved in the consumption of the commodity with respect to these pesticides. Now looking at the degradation pattern, degradation occurred in all the samples both at 10 days and 20 days alter collection at the ambient temperature. However, rate of degradation was at maximum within 10 days after collection and thereafter, it slowed down gradually. Thus regular monitoring of faringate samples of fruit is a must both for the safety of the consumers and for the international trade.

References

[1] Anonymous. Packages of practices. Directorate of Skuast-k Shalimar, Srinagar 2013. pp. 23-2
[2] Anonymous. Annual Progress Report. Department of Horticulture J&K Government, Srinagar, 2014. pp.1- 2
[3] Kavadia, V. S. and Lal, R. Residues of malathion on Indian rapeseed. Indian Journal of Agricultural Sciences, 1967. 38: 708-713.
[4] Srivastava, B. P., Kavadia, V.S. and Shanna, G. K. Effect of temperature and humidity on residual toxicity of some insecticides. Indian Journal of Entomology, 1969. 32(2): 127-131.
[5] Boxall, A. B. A. Sinclair, C. J. Fenner, K. Kolpin, D. Maund, S. J. "Peer Reviewed: When Synthetic Chemicals Degrade in the Environment". Environmental Science & Technology, 2004. 38 (19): 368
[6] Bina, G. Rani, M. and Kumar, R. Degradation of thiram in water, soil and plants: a study by high- performance liquid chromatography. Biomed Chromatogram, 2012. 26: 69–75.
[7] Abhilash, P. C. And Singh, N. Pesticide use and application: an Indian scenario. Journal Hazard Mater, 2009. 15;165(1-3):1-12.
[8] Fenner, K. Canonica, S. Wackett, L. P. Elsner, M. "Evaluating Pesticide Degradation in the Environment: Blind Spots and Emerging Opportunities". Science, 2013. 341 (6147): 752.
[9] Van Middclem, C. H. Principal residues and analytical method for pesticides. Plant growth regulators and food additives. Edited by Gunter Zweg. Acad. Press, New York, 1996. 1: 25-45.
[10] Hallenbeck, W.H. and cunnigham, K.M. Pesticides and Human health, 1985. pp. 6-20
[11] Kaihpal, T. S. and Deewan, R. S. Improved clean up technique for the estimation of etidosulfan and ethion residues. Journal of Association official Analytical Chemistry, 1975. 58(1): 1076-78.
[12] Getz, F. M., Molvin, E. and Watts-Randal, R. Application of 4-(P-Nitrobenzyl) pyreridine as a rapid quantitative reagent for the organophosphate pesticides. Journal of Association of Official Analytical Chemistry, 1964. 47(6): 1094-96.

[13] Jain, H. K. Panday, S. Y., Agnihotri, N. P. and Deewan, R. S. Rapid estimation of organophosphorus insecticides. Indian Journal of Entomology, 1974. 54(6): 1186-1190.
[14] Gunther, F. A. and Blinn, R. C. Analysis of insecticides and acaricides. Interscience publishers, London, New York, 1955. pp. 696
[15] Hoskins, W. M. Mathematical treatment of the rate of loss of pesticide residues. Plant Protection Bulletin FAO, 1961. 9: 163-168.
[16] Anonymous, Pesticide residues in food. Report of the Joint Meeting of FAO, Panel of Experts on Pesticide in Food and Environment and WHO Expert Group on Pesticide Residues. FAO Plant Production and Protection paper, 1986. 77: 23-29
[17] Frank, R., Braun, H. E. and Ripley, B. D. Monitoring Ontario grown apples for pest control chemicals used in their production. Food additives and contaminants, 1989. 6(2): 227-234.
[18] Sharma, I. D., Nalh, A. and Koul, J. L. Persistence of carbendazim in apples following post harvest dip-treatment. Pesticide Researcn Journal, 1991. 3(2): 173-175.
[19] Fytianos, K., Konstantinou, J., Knidatizis, J. and Albanis, T. Multiresidue determination of insecticides and fungicides in fruits and vegetables by gas chromatography. Bulletin of Environmental Contamination and Toxicology, 1998. 61: 684-689.
[20] Tahir, S., Anwar, T., lmtiaz, A., Aziz, S., Mohammad, A. and Ahad, K. Determination of pesticide residues in fruits and vegetables in Islamabad market. Journal of Environmental biology, 2001. 22(1): 71-74
[21] Dubey, J. K. and Nuth, A. Monitoring of ethylene-bisdithiocarbomate residues in apple and tomato. Pesticide Research Journal, 1991. 3: 167-168.

Publication History
Received 16th Apr 2017
Revised 27th Apr 2017
Accepted 06th May 2017
Online 30th May 2017