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Evaluation of Pesticide Residues in Farmgate Samples of Vegetables in Karnataka, India

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Abstract Fifty Vegetable samples (Beans, Brinjal, Cabbage and Carrot) grown in Kolar district of Karnataka, India were analysed for 20 pesticide residues by gas liquid chromatography equipped with ECD and FTD. Recovery studies were performed at 0.1, 0.5 and 1.0 mg kg $^{-1}$ fortification levels of each compound and the recoveries obtained ranged from 73.0 % to 96.6 % with relative standard deviations lower than 7.5 %. The method showed good linearity over the range assessed 0.01–1.0 mg Kg^{-1} with correlation coefficient >0.998 and the detection and quantification limits for the pesticides studied varied from 0.0001 to 0.002 mg Kg^{-1}and 0.0001–0.001 mg Kg^{-1}, respectively. All the samples were found to be contaminated, the organo chlorines (97 %) dominated followed by organophosphates (83 %) and pyrethroids (60 %). However, 58 % of the samples were found to contain the residues of these insecticides above their respective maximum residue limits (MRL). It is therefore proposed to perform extensive monitoring studies covering all the vegetable crops from different agro-climatic regions of the Karnataka to know the exact status of pesticide contamination.

Keywords Monitoring · Vegetables · Maximum residue limit (MRL) · Pesticides

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Beans (*Phaseolus vulgaries* L.), Brinjal (*Solanum melongena* L.), Cabbage *(Brassica oleracea var. capitata*) and Carrot (*Daucus carota* L.) are the important vegetable crops of India. These are widely cultivated throughout the sub-tropical parts of south India. These crops are attacked by a number of insect pests that damage crop at various stages of growth. It is well well-known that repeated application of wide range of pesticides may lead to undesirable residues on consumable parts of vegetables (Agnihotri 1999). Also, several hazards associated with the consumption of pesticide treated crops and the consequent impacts are known. Therefore, the sensible suggestion of a pesticide requires that it must not only provide an effective control of pests, but at the same time its residues on the commodity must also be toxicologically acceptable. These residues, when present in excessive, may prove unsafe to the health of the consumers. Chahal et al. (1997, 1999) opined surprisingly that residues of different insecticides, including those which are not recommended for use on vegetables were invariably identified. The analysis of farm gate vegetables by various workers in India have revealed contamination mostly with organo phosphorus (OP) and synthetic pyrethroids (SP), which denotes a clear change in the usage pattern from organochlorine (OC) to other groups (Mukherjee and Gopal 1996; Madan et al. 1996; Parihar et al. 1997; Shah et al. 2000; Kole et al. 2002; Kumari et al. 2003; Deka et al. 2005; Battu and Joia 2006).

An indispensable requisite to ensure quality and reliability of the results in chemical analysis is method validation. The analyst must produce information to demonstrate that a method intended for this purpose is capable of offering adequate specificity, accuracy and precision, at relevant analyte concentrations and in appropriate matrices (Hill and Reynolds 1999; Paschoal et al. 2008).

The aim of this study was to determine 20 pesticides related to Organophosphates, Organochlorines, and Synthetic Pyrethroids in different vegetable samples. Good sensitivity and selectivity of the method were obtained with the limits of quantification 0.0001 mg kg^{-1} in almost of all the cases. This method is reliable, simple, sensitive, accurate and precise, and hence can be applied for routine analysis of vegetables and fruits.

Materials and Methods

All solvents like n-hexane, acetonitrile, petroleum ether and diethyl ether (HPLC grade) were procured from Sigma Aldrich Co. and were glass distilled before use. Sodium chloride (NaCl) and anhydrous sodium sulfate (Na_2SO_4), AR grade was procured from Himedia Pvt. Ltd. India. Before use, anhydrous sodium sulfate (Na_2SO_4) was purified with acetone and heated for 4 h at 400°C in muffle furnace to remove possible phthalate impurities. Florisil, 60–100 mesh, purchased from Merck India limited was activated at 450°C and reheated at 130°C for 5 h before use. The Pesticide Standards were procured from All India Network Project on pesticide residues, Division Of Agricultural Chemicals, Indian Agricultural Research Institute (IARI) Delhi, India. A stock solution of each pesticide was prepared dissolving pure standard in n-hexane. Working standard solutions containing a mixture of the analytes were prepared from the above by appropriate solvent dilutions.

Fifty samples of marketable size vegetables (1 kg each) like Beans, Brinjal, Cabbage and Carrot were collected from the farms of vast vegetable growing areas of Kolar district of Karnataka state, India in 2011. Twelve samples of Beans, Brinjal, Cabbage each and fourteen Carrot samples were analyzed. The samples were kept in a refrigerator below 5°C till analysis. Only the edible parts of each vegetable were processed for residue analysis. All the samples were extracted fresh. The information regarding pesticide applied to vegetable crops was collected from the farmers at the time of sampling. Composite sample consisted of 1 kg was cut into small pieces and macerated in a grinder.

A representative 50 g sample of macerated vegetable was extracted with 100 mL acetonitrile in a warring blender (Super mixer grinder, Model, No. Mx-216E, National, India) for 2–3 min. The supernatant liquid was filtered through a Buchner funnel with What man filter paper. The vegetable residue was re-extracted with 50 mL acetonitrile, two more times. The extracts were pooled and transferred to a separating funnel (1,000 mL). 600 mL of 5 % brine solution was added and the extract was partitioned into 100 mL petroleum ether and partition was repeated with additional 50 mL of petroleum ether twice. The combined organic layers containing the insecticide residues were drained into 500 mL beaker through 5 cm layer of anhydrous sodium sulphate supported on a pre washed glass wool in a funnel. The sodium sulphate was washed with an additional 25 mL of petroleum ether. The combined extract obtained was concentrated to 5 mL in a rotary evaporator at a temperature below 40°C. The extracts so obtained were cleaned up by column chromatography using florisil adsorbent (AOAC 2000). Before use, the florisil was activated at 110°C for 2 h. A glass column (60 cm × 2.0 cm i.d.) was packed with a mixture of florisil (10 g), anhydrous sodium sulphate (10 g) and activated charcoal (0.2 g) supported on a cotton plug was used for cleanup and the sample was wetted with 50 mL petroleum ether. A sample slurry was prepared using petroleum ether and transferred to the column. The glass beaker containing extract was rinsed with acetone and was transferred to the column which was allowed to stand for 45 min. Subsequently the petroleum ether present in the column was eluted drop wise (5 mL/min). When about 5 mL petroleum ether remained on the surface of the adsorbent, the extract was eluted with 200 mL of freshly prepared 6 % solvent mixture (diethyl ether in petroleum ether), 200 mL 15 % solvent mixture (diethyl ether in petroleum ether) and finally 200 mL 50 % solvent mixture successively. The eluents were concentrated to dryness in a rotary evaporator under vacuum and diluted to 10 mL with n-hexane for further analysis.

The quantification of 20 residues, 9-OCs (aldrin, dieldrin, endosulfan -α, endosulfan-β, endosulfansulphate, HCH-α, HCH- β, HCH-γ, heptachlor), 6-OPs (acephate, chlorpyriphos, dichlorvos (DDVP), monocrotophos, phorate, profenofos), 5-SPs (cyfluthrin-β, cyhalothrin-λ, cypermethrin, delta methrin, fenvalerate) were carried out with a gas liquid chromatography (GLC) (Shimadzu Model GC-2010) equipped with an electron-capture detector (ECD) and flame thermionic detector (FTD). Organochlorines (OCs) and pyrethroids (SPs) insecticides were analysed using ECD (63Ni) and a capillary column BP-5 (60 m × 0.25 mm i.d. × 0.25 μm film thickness) with split ratio 1:10. The GLC working conditions were as follows: nitrogen flow rate, 30 mL min^{-1}; injection port, 250°C; and detector, 300°C. The column temperature was initially maintained at 80°C for 5 min, then increased to 260°C at the rate of 10°C min^{-1}, for 5 min and finally increased to 290°C for 5 min. The injection volume was 1 μL. Organophosphates (OPs) insecticides were analysed with FTD and a splitless capillary column DB-5 (60 m × 0.25 mm i.d. × 0.25 μm film thickness). The GLC working conditions involved : nitrogen flow rate, 60 mL min^{-1}; hydrogen flow rate, 3 mL min^{-1}; air flow rate, 150 mL min^{-1}; injection port temperature: 280°C; and detector temperature: 300°C; The column temperature was initially maintained at 180°C for 5 min, then increased gradually to 260°C for 5 min. The injection volume was 1 μL with split ratio of 1:10.

Residues were estimated by comparison of peak heights/areas of the standards with that of the unknown or spiked samples run under similar conditions. Efficiency of the method was validated with recovery precision, specificity, linearity, LOD and LOQ. The accuracy of the method was estimated through recovery experiment. The recovery studies for 5 replicates for each pesticide at three different fortification levels was carried out. For this purpose, samples (Beans, Brinjal Cabbage and Carrot) were spiked with a mixture of 20 insecticides at three levels 1.0, 0.5 and 0.1 mg kg^{-1} and processed separately as per the methodology described above. Matrix-matched calibration solutions were used for all the analysis. The percentage average recoveries of 20 pesticides are in the range of 73.0–96.6.

The precision, expressed as repeatability of the method, was determined in terms of relative standard deviation (RSD, in %) from recovery experiments at each fortification level for 5 replicates of each pesticide, the RSD of 20 pesticides are in the range of 1.3 %–7.5 %. (Table 1). The specificity of the method was determined by analyzing blank vegetable samples. The absence of background peaks, above a signal-to-noise ratio of 3, at the retention times of the target pesticides, showed that no interferences occurred. The linearity of the calibration curves was studied using calibration solutions prepared in the blank/pesticide free matrix extract. The ECD response for all pesticides was linear in the range of concentration studied (0.01–1.0 mg kg^{-1}), with correlation coefficients between 0.998 and 0.999. The limit of detection (LOD) of each pesticide, individually and in a mixture was determined by injecting standard solutions of different concentrations in duplicate to GLC. The lowest concentration of the pesticide that gave peak area five times greater than background level was considered as LOD, and the values are in the range of 0.0001–0.0020 mg Kg^{-1}. The limit of quantification, considered as lowest recovery was assessed with standard results, and the values are in the range of 0.0001–0.010 mg kg^{-1}. The results obtained with these methods are comparable with those reported in vegetables by others (Nakamura et al. 1994; Nguyen et al. 2008; Tao et al. 2009).

Results and Discussion

A multi residue procedure was applied to monitor 20 pesticide residues by GC-ECD and FPD with sufficient sensitivity among four vegetable samples collected in 2011. The targeted twenty pesticides were detected and quantified based on calibration standard at 0.1 mg kg^{-1} and the results of analysis are compared with MRL values of each pesticide fixed by Prevention of food Adulteration Act (PFA) 1954, Govt. of India.

Of the twelve beans samples analysed, all of them contained OCs, 83 % Ops and 60 % SPs. Specially 10 (83 %) samples were highly contaminated with acephate and heptachlor while 2 (17 %) samples were least contaminated with dieldrin, endosulfan-β and chlorpyriphos. Residues of profenofos, cyfluthrin-β, cyhalothrin-λ, cypermethrin, delta methrin and fenvalerate were not detected. Residue levels of monocrotophos was high (1.5448 mg kg^{-1}) while endosulfan-α was least (0.0008 mg kg^{-1}). Seven (58.3 %) out of 12 samples, three contained residues of monocrotophos (MRL value = 0.2, 1.0604–1.5448 mg kg^{-1}) and four phorate (MRL value = 0.05, 0.0604–0.2554 mg kg^{-1}) residues above MRL values (Table 2).

All the twelve brinjal samples were contaminated with OCs, 83 % with OPs and 80 % with SPs. Nine (75 %) samples were highly contaminated with acephate and heptachlor while 3 (25 %) samples were least contaminated with cyfluthrin-β, cypermethrin and deltamethrin. Residues of monocrotophos, profenofos and cyhalothrin-λ were not detected. Residue levels of deltamethrin was high (0.4898–0.9013 mg kg^{-1}) while HCH-β was least (0.0001–0.0019 mg kg^{-1}). Of the 12 samples of brinjal, six (50 %) samples contained phorate (MRL value = 0.05, 0.2448–0.1662 mg kg^{-1}) residues exceeded MRL values.

Among 14 samples of cabbage analysed, OCs, OPs and SPs were present in 100 %, 83 % and 60 % samples, respectively. While 12(86 %) samples were highly contaminated with acephate and 3 (21 %) samples were least contaminated with endosulfan-Sulphate, cyfluthrin-β, cyhalothrin-λ and fenvalerate. Residues of profenofos, cypermethrin, and delta methrin were not detected. Residue levels of dichlorvos (DDVP) was high (0.6687 mg kg^{-1}) while endosulfan was least (0.0003 mg kg^{-1}). Eight (57.1 %) out of 14 samples of cabbage, three contained residues of chlorpyrifos (MRL value = 0.01, 0.0110–0.3557) one dichlorvos (MRL value = 0.15, 0.6687) and four phorate (MRL value = 0.05, 0.1084–0.0959) values are above tolerance levels.

In 12 samples of Carrot analysed, 89 % contained OCs, 83 % OPs and 60 % SPs. Eight (67 %) samples were highly contaminated with acephate and aldrin while 2 (17 %) samples were least contaminated with fenvalerate. Residues of HCH-β, monocrotophos, cypermethrin and delta methrin were not detected. Residue of acephate was high (1.1377 mg kg^{-1}) while HCH-α was least (0.0011 mg kg^{-1}). Out of 12 samples of Carrot, four contained residues of chlorpyriphos, (MRL value = 0.2, 0.4888–0.9920) and four contained residues of phorate, (MRL value = 0.05, 0.6378–0.8057) of above tolerance levels.

In general, among 50 samples, 100 % contamination was found with one or other residues. However, the residues of Ops exceeded the MRL value in 58 % samples i.e. 2 % dichlorvos, 6 % monocrotophos, 14 % chlorpyriphos

Table 1 Average recoveries and R.S.Ds, % of different insecticides from three samples of Beans, Brinjal, Cabbage and Carrot fortified at 1.0, 0.5 and 0.1 mg kg^{-1} Levels

	Insecticide(s)	Beans(n = 3)			Brinjal(n = 3)			Cabbage(n = 3)			Carrot(n = 3)		
		Mean recovery ± R.S.D			Mean recovery ± R.S.D			Mean recovery ± R.S.D			Mean recovery ± R.S.D		
		Level of fortification (mg kg^{-1})			Level of fortification (mg kg^{-1})			Level of fortification (mg kg^{-1})			Level of fortification (mg kg^{-1})		
		1	0.5	0.1	1	0.5	0.1	1	0.5	0.1	1	0.5	0.1
1	Aldrin	90.6(3.8)	86.1(3.8)	87.4(3.7)	85.3(4.4)	86.4(3.6)	91.1(3.3)	89.7(4.7)	88.8(2.3)	89.3(3.2)	83.3(2.2)	86.4(3.6)	89.1(6.2)
2	Dieldrin	82.7(5)	95.6(2.5)	82.5(5.1)	83.9(3)	97.5(1.8)	84.3(3.5)	89.9(5.6)	91.8(1.8)	84.2(3.7)	84(3.3)	95.5(2.3)	86(5.5)
3	Endosulfan-α	73(4.5)	94(1.4)	77.6(2.1)	81(3.3)	93.7(1.7)	76.9(3.6)	85.6(5.5)	82.6(4.3)	83.7(3.9)	84.5(5)	93.5(0.9)	75.9(5.8)
4	Endosulfan-β	78.8(2.1)	91.7(5.6)	80.6(3.6)	83.7(4.9)	92.9(6)	81.1(2.7)	85.4(6.2)	87.8(3.4)	83.1(2.7)	90(3.3)	91.8(5.7)	80.6(3.6)
5	Endosulfan-Sulphate	85.2(3)	96.2(1.4)	88.5(5.6)	83.7(5.3)	96.2(1.5)	88.5(5.6)	87.7(4.8)	92.7(0.9)	86(3)	86.1(3.3)	96.2(1.4)	88.5(5.6)
6	HCH-α	77.1(4.9)	88.7(5.6)	80.4(3.5)	84.1(3.8)	90.1(3.2)	95.8(1.3)	80.5(3.1)	87.4(2.4)	80.4(1.7)	86.9(3.2)	88.7(5.6)	79.3(5.6)
7	HCH-β	83.8(3.2)	81.9(1.1)	85.6(3.5)	83.7(1.5)	81.8(1.3)	85.1(4.6)	83.3(3.6)	82.5(3.8)	85.7(1.2)	84.2(2.3)	81.8(1.3)	85.1(4.6)
8	HCH-γ	79.1(6.2)	93(2.5)	76(1.5)	82.8(2.2)	94.9(4.1)	76.1(1.4)	85.3(5.5)	91(3.4)	85(1.7)	85.3(3.7)	93(2.5)	75.9(1.6)
9	Heptachlor	89.4(5.5)	95.2(0.7)	90.7(2.1)	83.9(4.4)	96(0.8)	83.6(3.7)	83.5(3.8)	92.7(1.6)	92.2(3.1)	95.2(3)	95.2(1.7)	83.6(3.7)
1	Acephate	80.7(2.4)	89.2(6.2)	82.3(2.2)	80.4(1.9)	89.4(6.6)	82.9(2.9)	85.9(1.7)	87.4(3.6)	87.4(1.8)	88.1(2.5)	89.2(6.2)	82.4(2.2)
2	Chlorpyriphos	86.4(1.4)	92.9(4.7)	84.5(5.4)	84.6(3.1)	91.6(7.5)	84.5(5.4)	83.4(5.6)	87.2(2.4)	86.6(1)	84.8(1.7)	94.6(3.4)	84.5(5.4)
3	Dichlorvos (DDVP)	96.6(1.8)	92.2(2.3)	92.4(4.8)	88.7(7.3)	92.2(2.3)	92.4(4.8)	92(6.7)	87.2(2.6)	94.4(2)	89.9(1.9)	92.2(2.3)	92.4(4.8)
4	Monocrotophos	88.4(1.5)	86.9(5)	88.4(1.5)	89.1(2.8)	88.3(4.9)	90.3(3)	88.6(6.1)	85.6(2.5)	87.2(2.1)	92.7(2.8)	88.4(3.6)	88.4(1.6)
5	Phorate	84.3(5.9)	92.1(0.3)	85.6(3.5)	83.4(4.7)	92.7(1.4)	84.5(5.9)	84.1(2.8)	87.4(1.7)	87.1(3.8)	87.7(1.8)	92.1(1.3)	84.3(6.1)
6	Profenofos	80.3(3.1)	88.5(2.7)	80.3(3.1)	80(2.8)	88.5(2.7)	80.3(3.1)	81.1(2.2)	85.8(2.7)	84.6(2.8)	84.7(1.7)	88.5(2.7)	80.3(3.1)
1	Cyfluthrin-β	81.1(2.4)	86.9(5)	83(3.7)	86.1(3.5)	89.9(9.6)	83(3.7)	87.7(5.7)	87.1(1.3)	84.1(3.3)	83.8(3.5)	86.9(5)	83(3.7)
2	Cyhalothrin	85.7(6.5)	82.6(2.2)	85.7(1.4)	87.2(3.9)	82.6(2.2)	85.8(1.5)	87.9(6.5)	84.7(1.7)	93.1(2.7)	84.5(3.4)	82.7(2.2)	82.7(7.8)
3	Cypermethrin	86.2(2.6)	83.4(3.4)	93.9(2.6)	86.2(3.6)	83.4(3.4)	86.2(2.6)	84.7(2.7)	86.3(2.8)	87.2(2.6)	85.6(1.1)	83.4(3.4)	89.1(7.8)
4	Delta methrin	92.9(4.6)	91.5(1.6)	93.4(4.3)	90.9(3.3)	92.1(1.4)	94.5(3.7)	91.9(2.2)	87.3(2.9)	92.3(2.1)	93.5(1.6)	91.9(2)	91.3(7)
5	Fenvalerate	76.1(1.6)	88.8(2.4)	77(2.6)	74.3(1.6)	90.3(1.4)	77.2(2.6)	82.4(5.8)	87(2.3)	88.3(1.2)	85.8(4.3)	88.8(2.4)	77(2.6)

Table 2 Retetion time, MRLs values and pesticide residues (mg/kg) detected in farm gate samples of Beans, Brinjal, Cabbage and Carrot in 2011

			Beans (n = 12)							Brinjal (n = 12)						
			No of samples		Residue range (mg/kg)			Samples		No of samples		Residue range (mg/kg)			Samples	
	Pesticides	RT (min)	a	b	Min	Max	Mean	MRLs	>M	a	b	Min	Max	Mean	MRLs	>M
1	Aldrin	20.7	8	67	0.0015	0.0306	0.0112	0.1	Nil	7	58	0.0024	0.0067	0.0039	0.1	Nil
2	Dieldrin	22.6	2	17	0.0047	0.0063	0.0055	0.1	Nil	7	58	0.0010	0.0190	0.0097	0.1	Nil
3	Endosulfan-α	22.2	4	33	0.0008	0.0108	0.0052	2	Nil	6	50	0.0016	0.0034	0.0024	2	Nil
4	Endosulfan-β	23.2	2	17	0.0013	0.0027	0.0020	2	Nil	5	42	0.0007	0.0058	0.0027	2	Nil
5	Endosulfansulfate	24.4	5	42	0.0031	0.0074	0.0077	2	Nil	5	42	0.0005	0.0021	0.0015	2	Nil
6	HCH-α	17.6	6	50	0.0011	0.0117	0.0076	1	Nil	6	50	0.0159	0.0277	0.0239	1	Nil
7	HCH-β	18.4	3	25	0.0025	0.0039	0.0031	1	Nil	4	33	0.0001	0.0019	0.0010	1	Nil
8	HCH-γ	19.0	5	42	0.0027	0.0043	0.0035	1	Nil	8	67	0.0009	0.0090	0.0038	1	Nil
9	Heptachlor	19.8	10	83	0.0040	0.0210	0.0104	0.05	Nil	9	75	0.0005	0.0428	0.0182	0.05	Nil
1	Acephate	14.5	10	83	0.2406	0.4705	0.3326	NA	Nil	9	75	0.0113	0.5101	0.3363	NA	Nil
2	Chlorpyriphos	20.6	2	17	0.1647	0.1801	0.1724	0.2	Nil	4	33	0.0128	0.0827	0.0617	0.2	Nil
3	Dichlorvos (DDVP)	11.6	4	33	0.0012	0.0157	0.0090	0.15	Nil	6	50	0.0028	0.0037	0.0035	0.15	Nil
4	Monocrotophos	17.5	3	25	1.0604	1.5448	1.2370	0.2	3	ND	ND	ND	ND	ND	0.2	Nil
5	Phorate	17.6	4	33	0.0604	0.2554	0.1947	0.05	4	6	50	0.0605	0.2448	0.1662	0.05	6
6	Profenofos	22.4	ND	ND	ND	ND	ND	NA	Nil	ND	ND	ND	ND	ND	NA	Nil
1	Cyfluthrin-β	30.1	ND	ND	ND	ND	ND	NA	Nil	3	25	0.0093	0.1058	0.0417	NA	Nil
2	Cyhalothrin-λ	26.8	ND	ND	ND	ND	ND	NA	Nil	ND	ND	ND	ND	ND	NA	Nil
3	Cypermethrin	30.7	ND	ND	ND	ND	ND	NA	Nil	3	25	0.0017	0.0468	0.0197	0.2	Nil
4	Delta methrin	34.5	ND	ND	ND	ND	ND	NA	Nil	3	25	0.4898	0.9013	0.6999	NA	Nil
5	Fenvalerate	33.2	ND	ND	ND	ND	ND	NA	Nil	4	33	0.0082	0.0237	0.0164	2	Nil
			Cabbage (n = 14)							Carrot (n = 12)						
			No of samples		Residue range (mg/kg)			Samples		No of samples		Residue range (mg/kg)			Samples	
	Pesticides	RT (min)	a	b	Min	Max	Mean	MRLs	>M	a	b	Min	Max	Mean	MRLs	>M
1	Aldrin	20.7	8	57	0.0066	0.0713	0.0221	0.1	Nil	8	67	0.0205	0.0973	0.0634	0.1	Nil
2	Dieldrin	22.6	4	29	0.0004	0.0015	0.0012	0.1	Nil	8	67	0.0014	0.0775	0.0188	0.1	Nil
3	Endosulfan-α	22.2	5	36	0.0003	0.0110	0.0044	2	Nil	6	50	0.0074	0.0877	0.0228	2	Nil
4	Endosulfan-β	23.2	5	36	0.0075	0.3274	0.1776	2	Nil	5	42	0.0885	0.2228	0.1887	2	Nil
5	Endosulfansulfate	24.4	3	21	0.0025	0.0067	0.0047	2	Nil	3	25	0.0014	0.0019	0.0017	2	Nil
6	HCH-α	17.6	9	64	0.0024	0.0239	0.0133	1	Nil	6	50	0.0011	0.0559	0.0272	1	Nil
7	HCH-β	18.4	7	50	0.0004	0.0081	0.0028	1	Nil	ND	ND	ND	ND	ND	1	Nil
8	HCH-γ	19.0	4	29	0.0016	0.0038	0.0027	1	Nil	6	50	0.0014	0.0022	0.0019	1	Nil
9	Heptachlor	19.8	5	36	0.0009	0.0063	0.0034	0.05	Nil	6	50	0.0017	0.0036	0.0026	0.05	Nil

Table 2 continued

	Pesticides	RT (min)	Cabbage (n = 14)							Carrot (n = 12)						
			No of samples		Residue range (mg/kg)			Samples		No of samples		Residue range (mg/kg)			Samples	
			a	b	Min	Max	Mean	MRLs	>M	a	b	Min	Max	Mean	MRLs	>M
1	Acephate	14.5	12	86	0.1256	0.5277	0.3154	NA	Nil	8	67	0.1144	1.1377	0.4284	NA	Nil
2	Chlorpyriphos	20.6	4	29	0.0110	0.3557	0.2290	0.01	3	5	42	0.0914	0.9920	0.6317	0.2	4
3	Dichlorvos (DDVP)	11.6	6	43	0.0014	0.6687	0.1224	0.15	1	7	58	0.0026	0.0144	0.0076	0.15	Nil
4	Monocrotophos	17.5	4	29	0.0477	0.1849	0.1400	0.2	Nil	ND	ND	ND	ND	ND	0.05	Nil
5	Phorate	17.6	4	29	0.0787	0.1084	0.0959	0.05	4	4	33	0.6378	0.8057	0.7291	0.05	4
6	Profenofos	22.4	ND	ND	ND	ND	ND	NA	Nil	3	25	0.0038	0.0053	0.0046	NA	Nil
1	Cyfluthrin-β	30.1	3	21	0.0030	0.0413	0.0257	NA	Nil	3	25	0.0086	0.0103	0.0092	NA	Nil
2	Cyhalothrin-λ	26.8	3	21	0.0012	0.0032	0.0022	NA	Nil	3	25	0.0011	0.0014	0.0012	NA	Nil
3	Cypermethrin	30.7	ND	ND	ND	ND	ND	2	Nil	ND	ND	ND	ND	ND	NA	Nil
4	Delta methrin	34.5	ND	ND	ND	ND	ND	NA	Nil	ND	ND	ND	ND	ND	0.02	Nil
5	Fenvalerate	33.2	3	21	0.0200	0.0346	0.0278	NA	Nil	2	17	0.0138	0.0197	0.0168	NA	Nil

RT retetion time, *ND* not detected, *NA* not assigned, n no. of samples analysed *a* contaminated, *b* % of contamination

MRLs = MRLs Values (mg/kg) by PFA, >M = No. of samples > MRLs

and 36 % Phorate, OCs and SPs not exceeded the MRL value in any sample. This exhibits the shift from OC to OP and SP insecticides and the restricted use of OC insecticides. Slightly low level of pesticidal contamination was noticed (Kumari et al. 2001), in case of summer vegetables viz. okra, brinjal, bitter gourd etc., where 23 % samples were found to contain OP insecticide residues above MRLvalues. Acephate (78 %) is highly contaminated followed by Aldrin (62 %) and 2 % of each of profenous, cypermethrin, deltamethrin are least. The contamination is mainly due to frequent use of organo chlorine followed by organophosphorus and synthetic pyrethroid insecticides. The results obtained in the present investigations are in agreement with earlier reports (Fytianos et al.1985; Gupta et al.1998). Intensive cultivation technologies produce high infestation of crops by some pests and diseases, trigger off major losses of quality crops and initiate the use of more pesticides. The increase in frequency and magnitude of residues in the four vegetables could be attributed to indiscriminate and over use of pesticides by farmers despite efforts by various concerned agencies. It also indicates that farmers are neither observing recommended waiting periods nor following good agricultural practices (GAP) (Bhanti et al. 2004). It is further concluded that Indian farmers lack awareness regarding safe use of pesticides. Therefore, an effective way of educating the farmers via training and electronic media is advised particularly in view of the export potential of the crop. Also, Monitoring studies are essential to know actual levels of contamination due to toxic pesticide residues for future policies as well as to strengthen the confidence of consumer in quality of food. It is therefore, suggested that such studies may be extended to other vegetables grown in different agroclimatic regions of Karnataka.

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