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Insecticide Residues in Vegetable crops Grown in Kothapalli Watershed, Andhra Pradesh, India : A case Study

G.V. Ranga Rao, K.L. Sahrawat, Ch. Srinivasa Rao*, Binitha Das, K. Kirankumar Reddy, B.S. Bharath, V. Rameshwar Rao, K.V.S. Murthy and S.P. Wani

International Crops Research Institute for the Semi-Arid Tropics, Andhra Pradesh - 502 324, India.

**Central Research Institute for Dryland Agriculture, Hyderabad - 500 059, Andhra Pradesh, India*

ABSTRACT: Investigation on the pesticide residues in vegetable (brinjal, cucumber, okra, ridge gourd and tomato) and water samples collected from Kothapally Adarsha watershed in Rangareddy district, Andhra Pradesh, India during 2007 revealed the presence of monocrotophos (range 0.001-0.044 mg kg^{-1}), chlorpyrifos (0.001 to 5.154 mg kg^{-1}), cypermethrin (0.001 to 0.352 mg kg^{-1}) and endosulfan (0.001 to 0.784 mg kg^{-1}). The residues of monocrotophos and endosulfan were below maximum residue limit (MRL) in all the 59 vegetable samples, while the residues of chlorpyrifos were above MRL in 4 samples and cypermethrin in 2 samples. The water samples also revealed the presence of pesticide residues, but were below MRLs.

Keywords: Pesticide residue, monocrotophos, chlorpyrifos, endosulfan, and cypermethrin.

Ever increasing demand for food, feed and fiber due to increased population in India demands an increase in crop productivity on a sustained basis. With the advent of improved technology including high yielding crop varieties, use of fertilizers and pesticides, considerable success has been achieved in boosting agricultural production. In the process of enhancing productivity, the use of agrochemicals became an integral part of the modern agriculture. Approximately 2.5 million tons of pesticides are used in agriculture annually throughout the World (Meena *et al.*, 2008). An indiscriminate use of pesticides over a long run resulted in the development of resistance in insect pests to pesticides (Kranti *et al.*, 2002). The exposure of farmers and farm workers to agrochemicals and their ill effects is a central issue of debate.

In general about 50% of the chemical pesticides that are applied to the crops directly go into the soil and other non-target species. The chemical residues from the soil find their way to the aquatic systems or accumulate in plant products. Chlorinated compounds are more persistent in nature than other organophosphorus, carbamate and pyrethroid compounds. The basic problem in plant protection is the negligence of safety intervals in after pesticidal sprays and also the lack of knowledge on pesticide residue monitoring in the farm produce (Ranga Rao *et al.*, 2002).

There have been many studies on determining the ill effects of pesticide exposure (McCauley *et al.*, 2006). The World Health Organization and the UN Environment Programme estimate that each year, 3 million farm workers in the developing world experience severe pesticide poisoning of whom about 18,000 were fatal (Miller, 2004). The study with 23 school children shifted to organic food from normal diet dramatically reduced the levels of organophosphorus pesticide levels (Lu C *et al.*, 2006).

Information from India showed that about 51% food material is contaminated with residues in comparison to 21% world wide, of which 20% were above MRL prescribed by FAO standards (Anon, 1999). This contaminated food was not thrown out in developing countries, but was consumed due to the ignorance and innocence. Lack of awareness on consequences of pesticide contaminated food, could be one of the reasons for increased incidences of cancers in developing world. Besides the damage to human health, indiscriminate use of chemical pesticides adversely affects the natural bio-diversity that resulted in the reduction of natural enemies (Ranga Rao *et al.*, 2005).

In the past few decades with the benefits of synthetic pesticides being clearly recognized, usage has steadily increased from 2.2 g ha^{-1} active ingredient (a.i) in 1950 (David, 1995) to the level of 381 g ha^{-1} by 2007 i.e about 270 fold (Anon, 2009). The poisonous effects of insecticides like DDT, BHC (banned), edosulfan, malathion, methyl parathion, monocrotophos, quinolfos, dimethoate, phosphomidon, cypermethrin and envelerate have been reported even in blood samples of human beings and a significant increase in chromosomal aberrations were observed (Srivastava *et al.*, 1995).

For maintaining quality of any commodity, it is essential to keep the produce free from any pesticide residues. A zero level residue in the finished product is not only desired but also needed for eco- preservation and human health as well. The necessity of pesticide residue analysis in various agro-based commodities has become more relevant in the present context. Implementation of IPM strategies will help to reduce the dependence on toxic pesticides associated with agriculture to enhance productivity of healthy products and profitability.

In view of the above-stated ill effects associated with plant protection using chemical pesticides, a study on monitoring and management of pesticide residues in different crops was undertaken in Kothapally watershed (longitude 78° 5′ E and latitude 17° 20′ N), Ranga Reddy district, Andhra Pradesh during 2007. Watershed activities were initiated in this village during March 1999. Kothapally has 465 ha land of which 430 ha are cultivated and the rest is wasteland. The total population in this watershed is 1492 with 270 cultivating and 4 non-cultivating families. The average landholding per household is 1.4 ha. Bore wells were common means of irrigation but open well irrigation was also followed by few farmers (Wani *et al.*, 2003).

Materials and Methods

During this investigation residues of monocrotophos, chlorpyrifos, cypermethrin and endosulfan insecticides used in vegetable production (brinjal, cucumber, okra, ridge gourd and tomato) were monitored in 59 vegetable and 6 well water samples from Kothapally Adarsha watershed using Gas Chromatography - Mass Spectroscopy (Shimadzu model GC-17A, GCMS-QP5050). Preparation of the samples and determination of insecticide residues was based on the method described by Association of Official Analytical Chemists (AOAC, 1990).

Sampling Procedure

About 1 kg of each vegetable sample was collected randomly from the farmers' fields in cloth bags field. The history of the pesticides applied to the field was collected through a participatory rural appraisal (PRA) survey conducted before the initiation of the study; and the inference was used for drawing conclusions. Water samples from bore wells and open wells were collected in glass bottles at periodic intervals. The plant and water samples were stored in deep freeze maintained at –10 ± 2°C.

Analysis of pesticide residues in vegetables by multi-residue methods (MRMs) (nonfatty high moisture commodities)

Principle

Most non-ionic insecticide residues were extracted with acetone and were partitioned from aqueous acetone to methylene chloride/ petroleum ether phase. After removing traces of methylene chloride, the final extract was made up with acetone. Organophosphate, organochlorine and synthetic pyrethroid residues were cleaned up by Florisil catridges and determined by GC-MS.

Procedure

- 100g of chopped/ground sample was taken and blended with 200ml acetone for 2 min at high speed (for the vegetables which contain moisture <75%, extraction was carried out with 35% water in acetone).
- The extract was filtered with suction through Buchner funnel fitted with filter paper. Filtration was completed in <1min.
- The sample extract (80ml) was transferred to 1L Separatory funnel and the insecticide residues were extracted with 200ml mixture of petroleum ether:

methylene chloride (1:1, v/v) by a vigorous shaking for one min, the lower aqueous phase was transferred to another 1L Separatory funnel.

- The organic phase from the first Separatory funnel was dried by passing through approximately 1.5″ sodium sulfate supported on per-washed cotton in 4″ funnel.
- To the Separatory funnel containing aqueous phase, 7g of sodium chloride was added and shaken vigorously for 30 sec until dissolved. To the above, 100 ml methylene chloride was added, shaken vigorously and the lower organic phase was dried by passing through sodium sulfate. The procedure of extraction and drying was repeated more than once.
- Sodium sulfate was rinsed with about 50ml methylene chloride. The extract was concentrated using vacuum rotary evaporator. Concentration step was repeated in the presence of petroleum ether to remove all traces of methylene chloride, and then repeated again to produce final extract (2ml) in acetone solution. Solution was not allowed to get dried during the process.
- Florosil catridges were used for cleanup. Catridge was first pre-wetted with hexane and 2ml of the extract was then passed through it. Catridge was eluted finally with eluant acetone (HPLC grade). Florisil eluate was concentrated to 2ml. The extract was suitable for the determination of organophosphorus, organochlorine and synthetic pyrethroid residues by GC-MS.

Multi residue method for water

- 500ml of water was transferred to 1L Separatory funnel. Ground water or sample drawn from river / pond was filtered to remove particulate matter.
- 50g of Sodium chloride was added and shaken until completely dissolved.
- The residues were extracted thrice with methylene chloride (50:25:25ml), each time shaking vigorously for 1 minute.
- The lower organic layer was dried by passing through about 1.5" sodium sulfate supported on washed glass wool in 4" funnel.
- The organic layers were combined and concentrated to 1ml using vacuum rotary evaporator. Concentration step is repeated thrice in the presence of hexane to remove all traces of methylene chloride.
- The final volume of the extract (1ml) was made up to 2ml with hexane. The extract is then suitable for determination by GC-MS.

Results and Discussion

Determination of Pesticide Residues in vegetables

Residues of monocrotophos, chlorpyrifos, endosulfan and cypermethrin were detected in all the 59 samples collected from five vegetables (brinjal, cucumber, okra, ridge gourd, and tomato) (Table 1). The monocrotophos residues ranged from 0.001-0.044 mg kg^{-1}, chlorpyrifos from 0.001 to 5.154 mg kg^{-1}, endosulfan from 0.001 to 0.784 mg kg^{-1}, and cypermethrin from 0.001 to 0.352 mg kg^{-1}. The residues of monocrotophos and endosulfan were below maximum residue limit (MRL) in all the 59 vegetable samples, while those of chlorpyrifos was above MRL in 4 samples and that of cypermethrin in 2 samples. The main reason for low levels of monocrotophos and endosulfan could be due to low utilization of these conventional chemicals in the recent years. Studies conducted by Yahong Bai *et al.*,(2006) in vegetables in the Shaanxi area of China revealed the occurrence of residues of five organophosphorus pesticides ranging from 0.004-0.257 mg kg^{-1} and 18 of 200 samples had residue levels in excess MRLs. In another case Jagadeshwar Reddy (1998) found endosulfan residues in vegetables collected from Srikakulam and cypermethrin residues in vegetables from farmers field around Hyderabad and Guntur, but they were below MRL levels. The findings of Mukherjee (2003) also brought out contamination of vegetables in Delhi with various pesticides, of which 31% samples had residues above MRL.

A comparison of the residue levels in samples of the five vegetable crops indicated higher residues of chlorpyrifos and endosulfan in okra and monocrotophos and that of cypermethrin in ridgegourd (Table 1). In tomato, the residues of these chemicals ranged from 0.003 to 0.064, while it was from 0.004 to 0.066 mg kg^{-1} in cucumber.

Table 1: Pesticide residues in vegetable samples collected from farmers' fields, Kothapally village, Ranga Reddy district during 2007.

Crop (No. of samples)	Range of pesticide residue level (mg kg^{-1})			
	Monocrotophos	**Chlorpyrifos**	**Endosulfan**	**Cypermethrin**
Brinjal (10)	0.003 (<0.001-0.007)	0.008 (<0.001-0.040)	0.019 (<0.001-0.089)	0.052 (<0.001-0.283)
Cucumber (10)	0.004 (0.001-0.011)	0.066 (0.001-0.330)	0.019 (0.002-0.030)	0.010 (0.001-0.034)
Okra (10)	0.013 (<0.001-0.044)	0.605 (0.001-5.154)	0.130 (0.001-0.784)	0.025 (<0.001-0.112)
Ridgegourd (6)	0.015 (<0.001-0.041)	0.050 (0.001-0.223)	0.021 (0.002-0.061)	0.086 (0.001-0.352)
Tomato (23)	0.005 (<0.001-0.025)	0.035 (<0.001-0.151)	0.032 (<0.001-0.466)	0.024 (<0.001-0.141)

< 0.001 = below detectable levels (Values in the parenthesis denote the range)

Residues of four insecticides at different intervals

The results (Table 2) revealed the presence of residues of the four pesticides in all the samples collected at different intervals. Monocrotophos residues ranged from 0.006 to 0.009 mg kg^{-1}during May to July. The residues of chlorpyrifos and endosulfan increased from 0.023 and 0.015 in May to 1.329 and 0.215 mg kg^{-1}in July, respectively. While the residues of cypermethrin decreased from 0.039 in May to 0.006 mg kg^{-1} in July. In general, the insecticide residue concentration increased over the season, which could be due to the cumulative effect of pesticide application during the vegetable growing season. These findings are in conformity with the results reported by Neela Bakore *et al.*, (2002), who detected maximum organochlorine insecticide residues in the tomato crop (17.1 mg kg^{-1}) at the end of the season in Rajasthan, India.

Residues in IPM and Non-IPM fields

Comparison of residues of these four pesticides in samples collected from IPM and non-IPM fields of tomato indicated 0-741% higher residues in non-IPM samples (Table 3). Monocrotophos residues were similar in both the treatments, while endosulfan residues were 741% higher in non-IPM samples compared to IPM samples of tomato. The residues of chlorpyriphos and cypermethrin were 21% and 22% higher in Non-IPM samples of tomato compared to IPM samples. In cucumber the Non-IPM samples recorded 25 to 292% higher residues compared to samples collected from IPM fields. In case of cucumber samples monocrotophos residues were 25% higher in Non-IPM samples compared to IPM. Chlorpyrifos residues were 292% higher in Non-IPM samples compared to IPM. Endosulfan residues were 136% higher in Non-IPM samples compared to IPM. The residues of Cypermethrin were 33% higher in Non-IPM samples than IPM. The residues in IPM fields ranged from 0.004 to 0.027, while it was 0.005-0.106 in non-IPM fields. In case of IPM fields the presence of residues may be due to the left over residues in the soil and water used for the crops before growing vegetables. Another reason could be the presence of Non-IPM fields closer to IPM fields.

Table 2: Residues of four pesticides in samples of tomato and cucumber at different intervals, Kothapally village, Ranga Reddy district, 2007.

Month (No. of samples)	Residue levels (mg kg^{-1})			
	Monocrotophos	**Chlorpyrifos**	**Endosulfan**	**Cypermethrin**
May (30)	0.006	0.023	0.015	0.039
June (25)	0.009	0.084	0.051	0.025
July (4)	0.005	1.329	0.215	0.006

Table 3: Pesticide residues in two vegetable samples collected from IPM and farmers practice plots, Kothapally village, Ranga reddy district, Andhra Pradesh, 2007.

Crop	Treatment (No. of samples)	Residue levels (mg kg^{-1})			
		Monocrotophos	Chlorpyrifos	Endosulfan	Cypermethrin
Tomato	IPM (18)	0.005	0.034	0.012	0.023
Tomato	Non-IPM (5)	0.005	0.041	0.101	0.028
Cucumber	IPM (5)	0.004	0.027	0.011	0.009
Cucumber	Non-IPM (5)	0.005	0.106	0.026	0.012

Residues in water samples

All the water samples recorded the insecticidal residues but they were below MRL. Residue concentration of monocrotophos ranged from <0.001 to 0.004 mg kg^{-1}, chlorpyrifos from <0.001 to 0.018, endosulfan from <0.001 to 0.005, and cypermethrin from <0.001 to 0.029 mg kg^{-1} (Table 4). Nwankwoala and Osibonjo (1992) studied the organochlorine pesticide residues in surface waters in Ibadan (Nigeria). In another study Karam-Ahad *et. al.* (2000) monitored insecticide residues (chlorpyrifos, endosulfan, dihlorvos, and dimethoate) in ground water of Mardan Division, Pakistan. Contamination levels in all sites were found to be below MRL. However, Ganesh Shukla *et al.*, (2006) reported that ground water samples collected from city of Hyderabad, India were found to be contaminated with four pesticides i.e. DDT, β-endosulfan (0.21&0.87μg/L), α-endosulfan and lindane (1.34&2.14μg/L) which are above their respective acceptable daily intake (ADI) values for humans. This may be due to the indiscriminate use of chemicals in those areas. Mahapathra *et al.*, (1994) while examining the Ganga water near Farrukhabad in Northern India detected monoctophos in many samples and frequently found malathion and monocrotophos in ground water samples. This perhaps could be contamination from local as well as up stream areas.

Residues in water samples collected from different sources

Residues of all the four pesticides were found higher in bore well water compared to open well samples (Table 4). Residues of endosulfan were higher by 300%, cypermehrin by 89%, monocrotophos by 50% and chlorpyrifos by 9% in bore wells compared to samples collected from the open wells. The total residue concentrations of all the four pesticides were greater in water samples from bore wells (0.036 mg kg^{-1}) than water samples from the open wells (0.023 mg kg^{-1}). Low levels of residues in open wells could be due to greater exposure to environment there by more scope for degradation. These studies brought about the status of selected conventional pesticides used for farming activities. Though the levels of toxicity in several samples were below MRL's considering their occurrence in all samples one should critically look into the eco system to make sure the crops and the agro eco-system were free from the toxicants.

Table 4: Pesticide residue levels in water samples collected from open and bore wells of Kothapally village, Ranga Reddy district.

Source of water sample	Residue levels (mg kg^{-1})*				Total
	Monocrotophos	Chlorpyrifos	Endosulfan	Cypermethrin	
Bore well	0.003 (<0.001-0.004)	0.012 (<0.001-0.018)	0.004 (<0.001-0.005)	0.017 (<0.001-0.029)	0.036
Open well	0.002 (<0.001-0.002)	0.011 (0.004-0.017)	<0.001 (<0.001)	0.009 (<0.001-0.009)	0.023

* Mean of four open and two bore wells, Values in the parenthesis denote the range

Conclusions

In conclusion, this study has revealed that with increased water availability in rainfed areas farmers diversify the cropping systems with high-value crops such as vegetables for enhancing their incomes through increased water use efficiency. Changes in land use pattern are bringing in new pest and disease management practices using pesticides which are resulting in the presence of pesticide residues in the vegetables as well as in groundwater. There is an urgent need to educate the farmers to use integrated pest management practices to minimize the use of chemical pesticides in order to avoid adverse effect of pesticide residues in food chain. The IPM practices when adopted have demonstrated its effectiveness in reducing the use of chemical pesticides in vegetables which resulted in lower pesticide residues.

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