International Journal of Academic Research
ISSN: 2348-7666 Vol.1 Issue.2, August, 2014

Analysis of Pesticide Residues Present in Water Samples in Konaseema Region of Andhra Pradesh.

Dr.A.Venkateswara Rao and Dr.Ch.China Satyanarayana,
Deaprtment of Chemistry, S.K.B.R.College,
Amalapuram , E.G.Dt.-533201,A.P.

Abstract: *The improper methods of using or spraying pesticides by farmers in India seriously affected their health. The author concentrated on the quality of drinking water with reference to the pesticide residues to understand their impact on the health of people in Konaseema area. The pesticide residues were analyzed using Gas Chromatograph with Mass Detector in various seasons of water samples. This comparative study results that detectable pesticide residues were present in water samples by intense agricultural activity in this area. Finally the author tried to indicate the measures to take such that the pesticide residues are below detectable levels for the people are healthy and happy.*

Key words: *agricultural activity, healthy and happy, temperature,*

1. Introduction

Wills et al. [1] reported pesticides persistence on foliage. The amount of applied pesticide intercepted by target plants varies widely depending upon meteorological conditions temperature, wind, rain, solar radiation, spray droplet size, carrier, fall time etc.,. Representative literature values reveal that the percent of applied pesticide intercepted by various targets may be around 62±27% and for ground and axial application is 45±20%. Plant intercepted pesticide may be adsorbed, altered, volatilized or removed by water. The half-life value depends on all these above parameters. Half-life values of pesticides are important in assessing their concentrations in water, soil and agricultural food products. The wide spread use of pesticides inevitably leads to a mixture of pesticides being present in water sources and soil along with their residues on agricultural food products.

Chitra Grace et al. [2] reported that improper methods of using or spraying pesticides by farmers in India seriously affected their health. Unfortunately, the farmers are not aware of the serious health effects of the pesticides. Depending on the nature of pesticide sprayed, the farmers are suffering from different health problems. Carpy et al. [3] reviewed the health risk of low dose pesticide mixtures with special reference to combination toxicology and health risk assessment. They pointed out the synergistic and anti synergistic effects of mixtures of pesticides and argued that both may occur simultaneously at different organs in the same organism. It has been observed that the interaction between components is not a common event at low levels of human exposure such as those that may occur through pesticide residues in food and drinking water. Coronado et al. [4] examined the association between occupational task and organophosphate pesticide residues in

and its affect on the agricultural workers and their children and found that the levels of pesticides are detectable, even though low in concentration, their long time exposure may lead to accumulation and health problems.

Arcury et al. [5] analysed pesticide residues in the urine of children living in farm yards in Eastern North caroline Ina found that substantial proportion of children have 1.0 pg/L (mean value) of parathion or methyl parathion and 1.92 1.tg/L of chioropyriphos or methyl chloropyriphos. This shows that children in farm worker houses experience multiple sources of pesticide exposure. Arcury et al. [5] also reported that for farm workers residues of pesticides used in their farms are a major source of occupational injury and illness. They suggest that proper awareness be created through safety education with special reference to toxicity of pesticides, precautions to be taken while handling, spraying pesticides in the agricultural lands. Simcox et al. [6] reported that pesticides in household dust and soil are exposure path ways for children of agricultural farms. They studied the differences in the concentration of selected pesticides, i.e chloropyriphos, and parathion etc., in dust and soil of houses close to agricultural farms and far off from them and found that the pesticide concentrations are high in houses close to farms and very low in houses far off from them. This clearly establishes that the people and especially children in houses close to the agricultural farms, where pesticides are sprayed, are exposed to higher levels of these pesticides than those that are far away. There are reports [7,8] that exposure to higher levels of pesticides may led to childhood cancers.

2. Experimental Methods

a. Sample collection of Surface water in Crop Holiday

The author concentrated on the quality of drinking water with reference to the pesticide residues to understand their impact on the health of people in Konaseema area. The most important source is surface water i.e canal water which intern feeds all the tanks in the villages. The canal water is likely to be contaminated' by back waters or return waters from agricultural lands. . So, he took up the analysis of the water in the three canals and back water from agricultural lands. The author selected 3 insecticides and 1 fungicide, which are most frequently and commonly. These 4 pesticides are used in huge quantities throughout Konaseema area compared to the other pesticides used. The author collected 25 samples of back waters from the agricultural lands covering different crops, paddy, banana, sugar cane, coconut etc., in crop holiday period during the month of November 2011.

b. Sample collection of Surface water after Crop Holiday

The author also collected 25 samples of back waters from the agricultural lands covering different crops, paddy, banana, sugar cane, coconut etc., after completion of crop holiday period that is again agricultural activities are reassumed during the Rabi season in the month of February 2012

and next Kharif season in the month of November 2012.

3.Instruments

a. GC-MS

Gas Chromatograph Agilent 6890N (USA) with Mass spectrometer Detector Agilent 5975 was used for the determination of pesticide residues in water. The author adopted the following GC and MS conditions to analyze all the four pesticides simultaneously in the standards and samples. Operating conditions of GC-MS in Table1

Table1 Operating conditions of GC-MS

GC *conditions*	
Column	DB-5 MS (5% phenyl polysiloxane),0.25 mm i.di.di.d.x 30.0m Flim thickness:0.25
Carrier gas	Helium at l min^{-1}
Injection	250°C splitess
Temperature programming conditions	100° C (4min)→6°C min→250°C
MS conditions	
Ionization mode	Electron impact ionization(70ev)
Ion source temperature	230°C
Quadrupole temperature	150° C

All the chemicals, reagents, solvents and pesticide standards used for carrying out the analysis were of analytical grade from E. Merck, Germany or India, Sigma Aldrich USA, Qualigens, India and SD fine chemicals India.

a. Solutions

Stock solution (500micro.g/mL) of each pesticide standard was prepared in CH_2Cl_2 and stored at 4°C. A standard stock solution (5micro.g/ml.) containing all of the pesticides were prepared in CH_2Cl_2. Working solutions were prepared by appropriate dilution of the stock solution. The internal standard was prepared by dissolving 500micro.g/mL hexachlorobenzene (HCB) in CH_2Cl_2.

b. Extraction of Pesticide Residues in water samples:

Water samples were shaken well and filtered through No.1 whatman filter paper. pH of the samples was checked and was adjusted to 7. After filtration, I litre of water sample was taken in a 2 litre capacity separating funnel and 30mL of saturated sodium chloride solution was added. The pesticides in water sample were extracted in to 100mL of CH_2Cl_2 in a separating funnel. The layers were allowed to separate and the organic layer was collected in a beaker. The procedure was repeated four times until all the pesticides were completely extracted. The four extracts of CH_2Cl_2 layers were combined and passed through anhydrous sodium sulphate. Later the column was washed with methylene chloride. The methylene chloride solution was

collected as an effluent of the anhydrous Na_2S0_4 column.

c. Clean up:

Cleanup of the CH_2Cl_2 extract was done using (l0g) activated silica gel (2h at 130^0 C) packed between two layers of sodium sulphate (5g each) and the column was eluted with 150 mL CH_2Cl_2. Effluent from the column was collected and concentrated to about ImL using rotary vacuum evaporator and made up to exactly ImL with CH_2Cl_2 in a volumetric flask.

d. Determination of Pesticide residues:

2 micro.l of the CH_2CI_2 solution containing the pesticide residues was analyzed using Gas Chromatograph with Mass Detector. Analyses were performed with selected ion monitoring (SIM) using one target and two qualifier ions. The target and qualifier abundances were determined by the injection of individual pesticide standards under the same chromatographic conditions using full scan with the mass/charge ratio ranging from 60 to 500 m/z. Quantification was based on the ratio of the peak area of the target ion divided by the peak area of the internal standard in samples versus that found in the calibration standard. The SIM program used to determine and confirm pesticides. Pesticides were confirmed by their retention times, the identification of target and qualifier ions and the determination of qualifier to target ratios. The retention times had to be within ±0.2 min of the expected time RT value and the qualifier- to-target ratios had to be within a 20% range for positive conformation. Quantification was performed and compared by using calibrations standards involving standards in a neat solvent, standards added to blank extracts. The blank extracts were fortified with 0.5 mL of the pesticide standard solution and 0.5mL of the internal standard solution. 0.5mL of 1 micro.g/ml, of HCB was used as a internal indicator.

e. Recoveries using the solvent extraction method

The percent recovery of the four pesticides was determined in three different samples, namely distilled water, river water and tap water. 0.5mg of each pesticide was added to 1000 ml of each water sample and solvent extraction was performed using CH_2CI_2 solvent. The extraction procedure repeated five times. During the extraction procedure, no foam was observed. The mean percent recovery rate of seven pesticides was in the range 84-96%. The percent recoveries studies were repeated 5 times and the mean values is presented in the Table 2.

Table2:Percent Recoveries of different pesticides

S.No	Name of the pesticide	Mean Recovery (%)	RSD (%)
1	Malathion	90	±6
2	Chloropyrifos	94	±6
3	Monocrotophos	84	±12
4	Tricyclazole	90	±9

The lower percent recovery of Monocrotophos may be due to its highest solubility in water.

4 Results and Discussion

The results of the analysis of different pesticide residues analyzed in back waters and canal waters are presented in Table 3.3. and 3.4. The minimum and maximum values are presented in order to represent all the analysis data in a consign manner at the same time give a clear picture of the data. The drinking water standards prescribed by Indian Government and other international organizations are presented in Table 5.

It is to be noted that all the 4 pesticides are not detected in all the samples. In the case back waters and canals only few, 1or 2 pesticides are detected where as others are below detectable levels. This is because these pesticides are used in the agricultural lands on various crops at different times.

The author distributed the sampling after crop holiday period the agricultural activity is intense and the use of pesticides is very high. During these months, the back waters that are let into canals and canal water are collected at different fields, points and analyzed. It can be seen from the Table 3 that pesticide residues in back waters or canal water are higher.

Table.3 Concentration different pesticides in various surface water in Konaseema area after crop holiday.

All the values in micro.g/L.(ppb)

S. No	Name and Pesticide Type	Back waters		Surface water					
				Canal-I		Canal – II		Canal – III	
		Min	Max	Min	Max	Min	Max	Min	Max
Organophosphrous insecticide									
1	Chloropyrifos	0.04	0.9	BOL	0.03	BOL	0.09	BOL	0.11
2	Malathion	0.07	0.8	BOL	0.02	BOL	0.06	BOL	0.08
3	Monocrotofos	0.15	2.9	BOL	0.05	BOL	0.05	BOL	0.10
Fungicide									
4	Tricylazole	0.08	1.5	BOL	0.10	BOL	0.17	BOL	0.31

Table.4 Concentration different pesticides in various surface water in Konaseema area during the period crop holiday.

All the values in micro.g/L.(ppb)

S.No	Name and pesticide type	Back waters		Surface water					
				Canal-I		Canal-II		Canal-III	
		Min	Max	Min	Max	Min	Max	Min	Max
Organophosphrous insecticide									
1	Chloropyrifos	0.09	1.1	BOL	0.08	BOL	0.13	BOL	0.15
2	Malathion	0.15	2.1	BOL	0.05	BOL	0.09	BOL	0.12
3	Monocrotofos	0.65	3.5	BOL	0.08	BOL	0.10	BOL	0.14
Fungicide									
4	Tricylazole	0.12	1.9	BOL	0.15	BOL	0.22	BOL	0.38

Table.5:Drinking water standards for pesticides
All values expressed in ppb

Pesticide	IS 10500: 2004	W.H.O	U.S EPA
Endrin	NO	NG	2.0
Dieldrin	0.03	0.03	NO
		-	
Malathion	190	NO	NO
Monocrotofos	1.0	NO	NO
Chloropyrifos	30	NO	NO
Carbofuran	NO	5.0	40
Tricyclazole	NO	NO	NO

NO: *No Guidelines (No standard minimum concentrations prescribed* for these *pesticides*)

The author also distributed the sampling in crop holiday period the agricultural activity has come to a grinding halt and the use of pesticides is very low. During these months, the back waters that are let into canals and canal water are collected at different fields, points and analyzed. It can be seen from the Table 4 that pesticide residues in back waters or canal water are very low when compared with after next coming season of crop holiday from the table 4.

That detectable concentration of these pesticide residues in this comparative study proved that due to intense agricultural activities in konaseema area. Thus the drinking water quality and intern the health of people is likely to be effected by intense agricultural activity in this area.

On interaction with the farmers, the author understood that sometimes the shops may be selling wrong and spurious pesticides to kill a particular pest, and many a time, the shop owners advise them to use more quantities than what is advised by the agricultural officer of that area. Also many of the farmers personally feel that use of higher quantities of fertilizers and pesticides than what is suggested by agricultural officers might result in higher crop yields. This could also be one of the reasons for the presence of pesticide residues in waters in this area. Tricyclazole, a common systemic fungicide, has been analysed in for the first time in the water samples of Konaseema area.

From a through literature survey, there is no published report on the pesticide residues of Konaseema area which is an area with intense agricultural activity in Andhra Pradesh. It is known that the movement of pesticides in water and soil depends on the characteristics of pesticides, their solubility, half life, adsorption coefficient and soil characteristics like texture, permeability, organic matter present etc. Pesticide residues themselves and their transformed products are all present in the water as huge quantities of the pesticides are being used for the last several years in Konaseema area. Due to several constraints, the author monitored only 4 pesticide residues in water.

It can be seen from Table 3 that the pesticide residues are generally high in the back waters compared to canal waters. This is as expected. The canal waters receive huge quantities of such back waters at several points all along the canal. So, even though, the extent of dilution is very high in the canal, the loading of pesticide residues is also high in the canals resulting in pesticide residues in the canal waters. In the canal waters, in all the samples analyzed, the pesticides residues concentrations are lower than the permissible limits. The main sources of contamination is the back waters from agricultural fields, which are let out from the agricultural fields or from waste water drains entering the canals from villages and towns which might also be carrying these pesticide residues.

Even though the individual pesticides residue concentrations are lower than the maximum allowable contamination limits for drinking water in all the canals, it is to be noted that few pesticide residues arc present simultaneously in those waters. The synergistic effects of these pesticide residues on the health of the people are not clearly understood.

Several people, in Konaseema area, depend on the canal water for their drinking purposes. Some of them, mostly poor people drink the water directly after it is fetched in an utensil to the house from the canal or tank.

The author observed that people working in agricultural lands (fields) drink canal water or well or bore well water in the agricultural fields directly. Such people are most valunarble to the pesticide residues and other water quality parameters may also affect their health. In the case of poor people, government must provide perfectly treated water so that they will not suffer from pesticide other contaminants in drinking water.

With the increasing awareness on quality of water and the related health effects, middle class and rich people are using some gadgets to treat the water before drinking. It is possible that the gadgets used by people may be capable of removing the pesticide residues to some extent thus purifying the water used by them for drinking purposes. The efficiency of these gadgets for removing pesticides is not known. It is necessary to understand the efficiency of these gadgets in removing these pesticide residues and finally assess the quality of the water used by people for drinking purposes. The author analysed few samples of out let water used for drinking purposes from water purifying gadgets that contain activated charcoal catridge and found that all the pesticides are below detectable levels in the outlet water.

Thus the author analysed the quality of surface water sources with reference to pesticide residues and attempted to explain the sources and also tried to indicate the measures such that the pesticide residues are below detectable levels and the people are healthy and happy.

REFERENCES

1) G.H. Wills, L L Mc Dowell, *Reviews of Environmental Contamination and Toxicology*, **1987**, 100, 23-73.
2) C.A.Grace, V.R.Muraleedharan, T.Swaminathan., D.Veera Raghavan, Use of pesticide and its

impact on human health: a case of farmers in South India, **2004**.

3) S.A. Carpy, W Kobel, J Doe, *Journal of Toxicology and Environmental Health,* 13,**2001**,3, 1-25.
4) G.D. Coronado, B.Thompson, L.Strong, W.C. Griffith, L.Islas *Environmental Health Perspectives*, **2004**, 112 (2), 142-144.
5) T.A.Arcury ,S.AQuandt, G.B. Russell *Environmental Health Perspectives,* **2002**,110(2),233-240.
6) N.J.Simcox, R.AFenske, S.A. Wolz, I.C.Lee, D.A.Kalman *Environmental Health Perspectives,* **1995**, 103(12), 1126-1134.
7) R.B.Gunier, M.E.Harnly,P.Reynolds, A.Hertz, lV.Behren, *Environmental Health Perspectives,* **2001**,109(10),1071-1078.
8) A. G .Bayer, H.J. Jarczyk. Manual of Pesticide Residue Analysis Vol.I&II, **2004**.