International Journal of Research in Advent Technology, Vol.6, No.10, October 2018
E-ISSN: 2321-9637
Available online at www.ijrat.org

Identification of Pesticide Residues in Water Samples of Gugal Barrage Cum Bridge of Deodurga Taluk, Raichur District, Karnataka, India

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Abstract- Agriculture is one of the major practices in India hence different types of pesticides are widely used to prevent and control the crop loss due to pest attack which leads to the contamination of water bodies. The present study is conducted to identify and analyze the pesticide residues in water samples of gugal barrage/bridge of Deodurga taluk, raichur district, Karnataka. Pesticides are biological or chemical product that is used to control and kill the pests. Pesticides help farmers in yielding the quantitative and qualitative crops but it also carries the drawbacks of causing environmental hazards like water pollution, toxicity to food chain thereby leading to health issues in living organisms. Pesticides are one of the reasons for pollution in water bodies which require precautions and measures to overcome the pollution caused due to the pesticide usage in cultivation land. Also there is need for alternate sources for pesticide which can be pollution free and environmental friendly. This paper intends to highlight the pesticide residue identified from water source called Gugal Bridge cum barrage and discuss some properties of the pesticides detected from the water sample. Finally, recommending the alternate way to overcome the pesticide usage in the conclusion part of the paper.

Keywords- Gugal barrage cum bridge, Pesticide residues, GC-MS/MS, LC-MS/MS, Krishna river

1. INTRODUCTION

Pesticides are the substances that are meant to control the pests. Most pesticides are intended to serve as plant protection products (crop protection products) which in general protect plants from weeds, fungi, or insects. Pesticides can be biological agent or chemical agent that will prevent or kills pests. Pesticides can cause delayed and severe health impacts like affecting the reproductive systems, nervous system, and also issues that might lead to cancer. Pesticides can reach other than actual target group that is like water, soil, air. Pesticides are one of the causes of water pollution and are a persistent organic pollutant [7, 8]. The objective of the study is to identify and analyze the presence of pesticides residues from the water samples collected from gugal barrage/bridge, deodurga taluk, raichur district, Karnataka, India.

India is one of the leading foods producing country in the world. Agriculture is one of the major important sectors of Indian economy where agriculture sector alone contributes 18% to the India's GDP and also it provides major employment opportunity to the rural population. Agriculture has important role to play in overall development of socio-economic reforms of India. Karnataka is eight largest states in geographical area. In Karnataka agriculture is major occupation for majority of the rural population [1]. Even though agriculture is considered as backbone of India, farmers has to overcome many challenges in the agriculture sector. Most of the rural population in India is dependent on agriculture practices to lead the life.

There are many hurdles to overcome by the farmers before the crops reach the market. One of the challenges the farmer has to overcome is the

protection of crops by the pests attack. In order to yield high quality crops to the market farmers should ensure that crops reach the market in good condition. Farmers rely on the pesticides to control the pests attack. This leads to the soil contamination and also pesticides get in to the water by the surface water runaway. This paper aims to detect and analyze the pesticides residues from the sample water collected from Gugal Bridge cum barrage, Deodurga taluk, Raichur district, Karnataka, India.

2. MATERIALS AND METHODS

2.1 ***Study area*:-** The present study is conducted for monitoring pesticide residues in gugal barrage/bridge across river Krishna which is located near gugal village, deaodurga taluk, Raichur district, Karnataka, India. Gugal barrage is located near gugal village of deodurga taluk of Raichur district with latitude 16^{o} 28' 30'' North, Longitude 77^{o} 8' 39'' East, across river Krishna a high level barrage with vertical gates measuring 810mts of length. The sole aim of construction of this barrage is to provide water for irrigation, groundwater recharge & drinking water facility for villages along the back water. people of shapur taluk of yadgir district & deodurga taluk of Raichur district were benefited by gugal barrage[20].

2.2 ***Sample collection:*** Using one liter of clean container was used to collect the samples from the sampling area during early hours of the day. The sample was firmly packed and sent for laboratory to test the pesticides residue content.

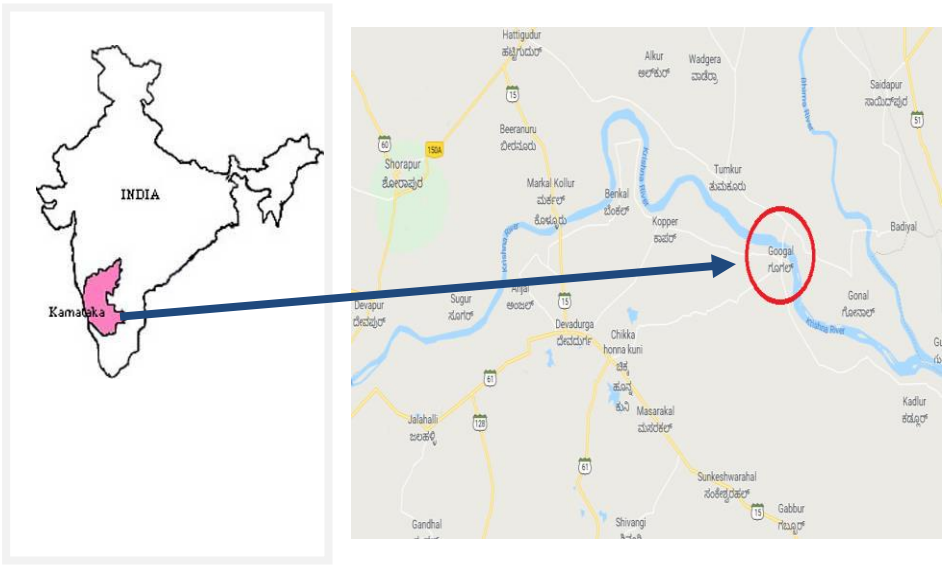

Fig. 1: Map of Gugal Bridge cum barrage location

3. RESULTS AND DISCUSSION

3.1 *METHOD-1: LC-MS/MS (Liquid Chromatography Tandem Mass Spectrometry)*

Liquid chromatography-Mass spectrometry (LC-MS) is an analytical chemistry approach that combines the physical separation capabilities of liquid chromatography with mass analysis capabilities of mass spectrometry. Coupled chromatography is important in chemical analysis because the individual capabilities of each technique are enhanced synergistically. Liquid chromatography separates the mixtures with multiple components and mass spectrometry provides structural identity of the

individual components with high molecular specificity and detection sensitivity [2].

Table 1: Pesticide residues tested and detected using LC-MS/MS approach

Sl. No.	Pesticide residue	LC MS/MS based pesticide residue Results (µg/L)	Indian standard for pesticide residue Limit (µg/L) [6]	Prohibited in other countries [21]	Prohibited in India
1	Carbendazim	115.4	Data Not Available	-	-
2	Imidacloprid	2.51	Data Not Available	-	-
3	Phosphomidon	18.63	Data Not Available	US (restricted use)	-

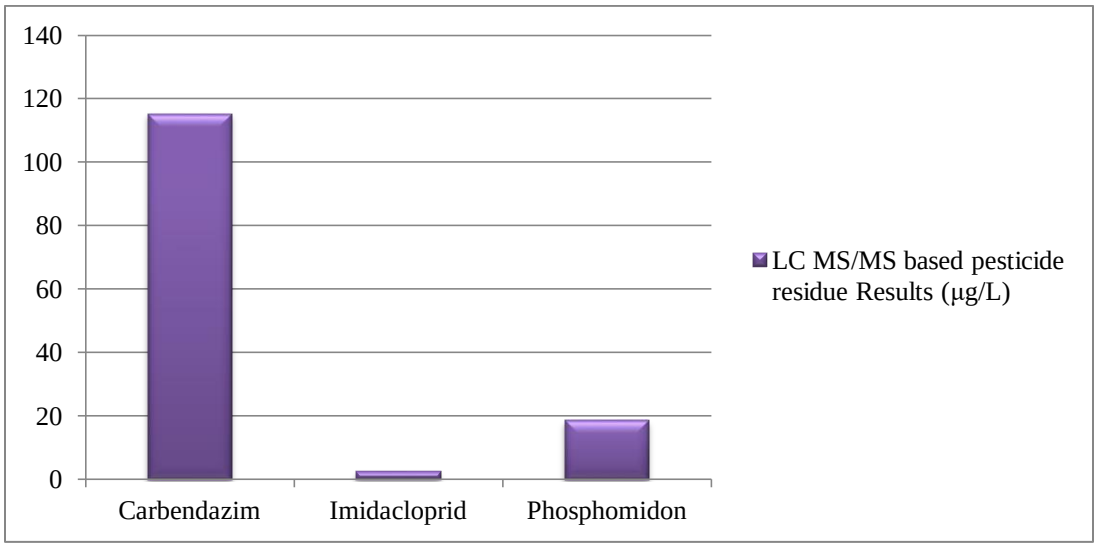

Fig 2: LC MS/MS based pesticide residue Results (µg/L)

3.2 *Discussion about the pesticide residues detected by LC –MS/MS technique*

Imidacloprid : is a neonicotinoid compound which is similar to nicotine is used as an insecticide for crop protection. Neonicotinic chemicals are selective in nature that is they cause less toxic to humans and more toxic to insects, pests that are nicotinic receptors in nature [3]. Imidacloprid is less toxic to mammals but still high dosage in humans can cause effects on testes, pancreas, and thymus [4]. The pesticide residue detected is 115.4 µg/L and there is no data found which indicates the permitted limit for the same by the Indian standards. Since this pesticide has little impact on humans, this might be the reason for the high quantity of pesticide is found in the sample compared to the other two.

Carbendazim: is a fungicide used to act upon the fungal diseases like Septoria, Fusarium. It is persistent in water systems under certain conditions. Fungicides are less toxic to humans but still slight impact can occur like skill irritation and eye irritation. When inhaled in dust form might cause throat irritation, coughing etc [5, 22]. This is found in

least quantity compared to other two pesticides and even in this case also did not find permitted limit as such.

Phosphamidon: is an organophosphate insecticide which is combination of (*Z*)-isomer and (*E*)-isomer [10]. Phosphamidon insecticide is used to destroy the sap feeding insects like rice leaf beetles, sugar cane beetles which are generally found in citrus fruits, nuts, commercial crops like cotton and also deciduous fruits. Typically organophosphorus pesticides are in form of liquids that have different vapour pressures at room temperature and have different kinds of hazards due to inhalation from compound to compound. Health complications are more when exposed to dust form than dilute sprays. Phosphamidon is found to be at moderate level in the sample tested but table 1 indicates that this pesticide is restricted in US and that's an alarm for the other countries to review about the pesticide usage in agriculture.

Table 2: Pesticide residues tested and not detected using LC-MS/MS approach

Sl. No.	**Pesticide residue tested and Not Detected**	**Sl. No.**	**Pesticide residue tested and Not Detected**	**Sl. No.**	**Pesticide residue tested and Not Detected**
1	Thiacloprid	14	Carbaryl	27	Tetraconazole
2	Buprofezin	15	Triazophos	28	Quinalphos
3	Metalachlor	16	Carbofuron	29	Profenofos
4	Dimethoate	17	Bitertenol	30	Pendimethalin
5	Coumatetryl	18	Bendiocarb	31	Difenconazole
6	Triademenol	19	Benalaxyl	32	Pretilachlor
7	Triademefon	20	Acephate	33	Penconazole
8	Thiobencarb	21	Pymetrozine	34	Paclobutrazole
9	Spinosad	22	Omethoate	35	Malathion
10	Phosalone	23	Metribuzin	36	Hexaconazole
11	Methoxyfenzide	24	Metalaxyl	37	Chlorantraniliprole
12	Hexythiazox	25	Isoproturon	38	Flubendiamide
13	Fenpyroximate	26	Emamectin Benzoate		

From table 1 and table 2 it is clear that using LC-MS/MS technique 41 types of pesticide residues were tested and sample was found with 3 types Imidacloprid**,** Carbendazim, Phosphamidon. This is good sign that water is less pollutant with pesticides and more scope exists for the aquatic life to sustain and flourish.

3.3 ***METHOD-2: GC-MS/MS (Gas Chromatography - Tandem Mass Spectrometry)***

Samples analyzed by GC-MS/MS are separated in gaseous state using different physical and chemical properties of interest and there interaction with analytical column's stationary phase. After termination of analytical column the analytes enters the tandem mass spectrometer which is of two scanning mass analyzers segregated by cell collision. Fragments resulted in the earlier analyzer are reacted with an inert gas using cell collision which in turn results further fragmentation.

Table 3: Pesticide residues tested and detected using GC-MS/MS approach

Sl. No.	**Pesticide residue**	**GC MS/MS based Pesticide residue Result (µg/L)**	**Indian standard /WHO standard for pesticide residue Limit (µg/L) [6,9]**	**Prohibited/ Restricted use in other countries [17, 21]**	**Prohibited in India / restricted use only**
1	Alachlor	7.657	20	US	-
2	Aldrin	133.072	0.03	US	YES
3	Allethrin	14.233	Data Not Available	-	-
4	Bifenthrin	2.076	Data Not Available	US(restricted)	-
5	Butachlor	6.464	125		
6	Cypermethrin-I	6.907	Data Not Available	US(restricted), Europe	To be used only through Pest Control Operators and not allowed to be used by the General Public
7	Delta-BHC	5.85	Data Not Available	US	Benzene Hexachloride
8	Deltamethrin	12.504	Data Not Available	US(restricted.), Europe	-
9	Dichlorvos	6.268	20 (WHO)	US(restricted)	-
10	Etofenprox	20.859	Data Not Available	US(restricted)	-
11	Iprobenfos	15.141	Data Not Available		-
12	Lambda-Cyhalothrin	6.64	Data Not Available	US(restricted), Europe	-
13	o,p'-DDT	103.287	1	US, UK, Europe	Use of DDT in Agriculture is withdrawn. In very special circumstances warranting the use of DDT for plant protection work
14	P,p' – DDT	1.897	1	US, UK, Europe	
15	Permethrin-I	23.665	30 (WHO)	-	-
16	Permethrin-II	39.047	30 (WHO)	-	-

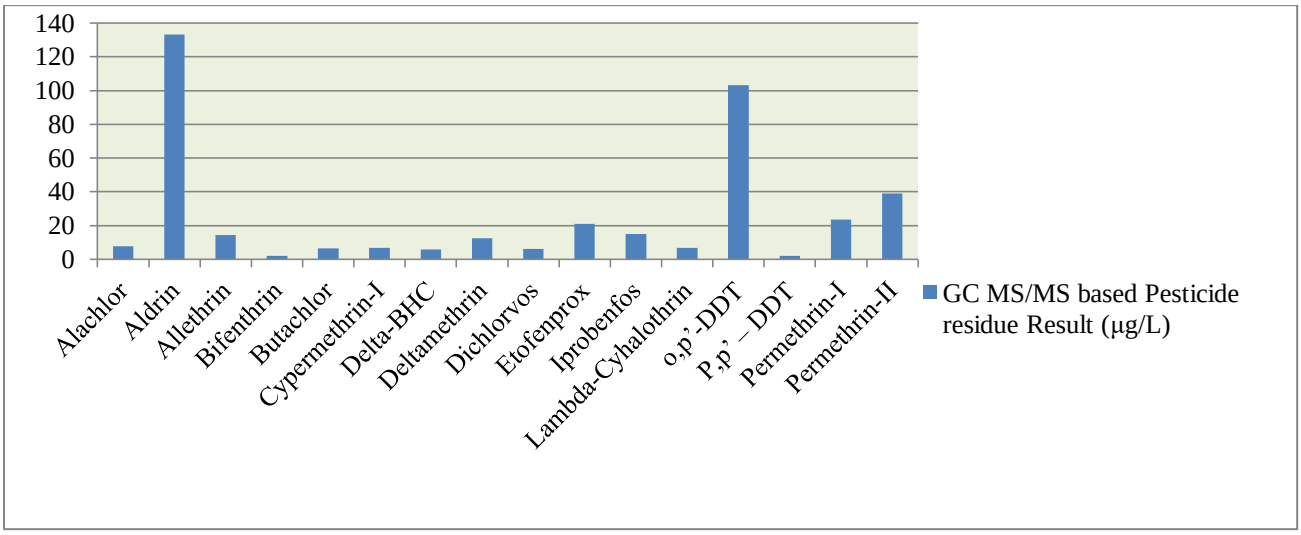

Fig 3: GC MS/MS based Pesticide residue Result (µg/L)

3.4 *Analysis of the pesticide residues detected by GC –MS/MS technique*

Dichlorvos: is an agricultural insecticide used to control the pest and protect the stored products from insects and animals. It is also used as an insecticide for pest control at homes using pest strips which releases the pest chemical slowly to surroundings. Dichlorvos exterts toxic effects in humans and animals by inhibiting the enzyme called acetyl cholinesterase [11].

Delta BHC (benzene hexachloride): Hexachlorocyclohexane (HCH), also known as benzene hexachloride (BHC), is a artificial chemical that occurs in different chemical forms called isomers. It used on fruits, vegetables and crops as insecticides. This chemical has the potential to accumulate in food chain through soil, water and food items and excess accumulation is toxic to human health causing headaches, mental disorders, and blood disorders [11]. This insecticide is not permitted to use in many countries including US as given in table 3.

Iprobenfos: An organic thiophosphate that is the S-benzyl O, O-diisopropylester of phosphorothioic acid. Iprobenfos is used to control leaf and ear blast in rice fungicide. This kind of pesticides might have affects on plants and also other non-target organisms. Aquatic lives also have the immediate environment contamination. [12]

Alachlor: is an aniline herbicide which is used to destroy the unwanted plants and to control the annual grasses in the field. It is a selective systemic herbicide that kills only the unwanted plants leaving the desired plants uneffected. The compound works by interfering with plants ability to produce protein and by interfering with elongation [13].

Aldrin: It is an organ chlorine insecticide used as a pesticide to treat seed and soil. This is named after the german scientist called kurt Alder. The insecticide acts on the surface soil of the plants which inturn reaches the digestive tracts of insects; aldrin is strong insecticide as it oxidizes to epoxide dieldrin. Its solubility in water is around 0.027 mg/L which persists in the environment [14].

Allethrins: is a group of synthetic insecticide which is combination of group of similar compounds. It is type of pyrethroids that are similar to synthetic form of chemical found in chrysanthemum flower. Allethrin is generally used in homes and gardens to kill flies, mosquitoes, and also to control flying or

crawling insects. Another structural form d-trans-isomer of allethrin is highly toxic to insects and also used to control the parasites living within animal systems. It effects the stomach and respiratory in the insects before insects are killed. This is also used in mats, aerosol sprays, mosquito coils etc. [13].

Butachlor: is a herbicide used as selective pre emergent herbicide. It is extensively used in India in rice cultivation during post emergence herbicide [15].

P,p' – DDT (para, para DDT), o,p'-DDT (Ortho, para DDT): **(**Clofenotane; Chlorophenothane; Dichlorodiphenyltrichloroethane) DDT used as pesticide to control and kill insects in agriculture. It is pesticide that is highly resistant to light and oxidation. This is highly unstable in nature and has the ability to accumulate in ecosystems. It is water insoluble and poses challenges in residue removal from soil, food items and water. Exposure to DDT mainly affects the nervous system resulting in vomiting, tremors, seizures etc [11].

Bifenthrin: is a type of synthetic insecticide that is generally used kill ants that is found at agricultural fields. This pesticide is highly poisonous to aquatic environment. Bifenthrin is least solutable in water and usually remains in soil. Bifenthrin has effect on vector mosquitoes and also it is hardly soluble in water thereby remains staying on the surface level. Even in small quantity of befenthrin can impact the fish and other aquatic life [16].

Lamda-Cyhalothrin: is an insecticide belonging to set to chemicals called pyrethroids that are similar to natural insecticides pyrethrins. Pyrethroids disrupt the functionality of nervous system in the organisms. This insecticide has toxicity nature in high temperature [18].

Permethrin-I, Permethrin-II, Cypermethrin-I: This is constituent of variety of insecticide range that can destroy and control different kinds of insects. By nature this is same as lamda-cyhalothrin in functionality. It is less toxic to living organisms and this is created using chrysanthemum flowers to mimic the chemical characters of naturally occurring insecticide pyrethrum.

Etofenprox or 2-(4-ethoxyphenyl)-2-methylpropyl 3-phenoxybenzyl ether is a type of insecticide with low toxicity with chemical compound of carbon, hydrogen and oxygen. This is used as product for flea medication for animals like cat and also has impact on variety of pests causing effect to the nervous system in the insects and pests [19].

Deltamethrin: is pyrethroid insecticide that has main function in controlling the vector mosquitoes causing malaria and also used to manufacture long lasting insecticidal mosquito nets. This is one of safest type of synthetic pesticide class and also helps to prevent the diseases spreading which is carried by tick infested burrow animals, prairie dogs. This is also helpful in preventing and controlling the different types of household pests like spiders, ants, bees, bedbugs, fleas etc [11].

Table 4: Pesticide residues tested and not detected using GC-MS/MS approach

Sl. No.	**Pesticide residue tested and Not Detected**	**Sl. No.**	**Pesticide residue tested and Not Detected**	**Sl. No.**	**Pesticide residue tested and Not Detected**
1	Phenol, 4-bromo 2-chloro	10	Parathion methyl	19	Beta-Endosulfon
2	Trifluralin	11	Heptachlor	20	Profenofos
3	Alpha-BHC	12	Fenitrothion	21	P,p' – DDE
4	Beta-BHC	13	Chlorpyrifos	22	Endrin

5	Fluchloralin	14	Parathion	23	p,p'– DDD
6	Diazinon	15	Tetraconazole	24	Endosulfon sulphate
7	Tri-allate	16	(E)-Chlofenvinfos	25	Fenpropathrin
8	Clorpyrifos methyl	17	Phenthoate	26	Cyfluthrin-I
9	Propanil	18	Alpha-Endosulfon	27	Fenvalerate

From table 3 and 4, it is evident that using GC-MS/MS technique sample was tested with 43 types of pesticides residues and we were able to detect 16 types of pesticides where it is observed that some pesticides are below the permitted limit like Alachlor, Butachlor, Dichlorvos, Permethrin-I and some pesticides have exceeded the limit like Aldrin, o,p'-DDT, P,p' – DDT, Permethrin-II. Most of the detected pesticides fall to the category of restricted and prohibited one. Referring to usage of DDT, from table 3, it is withdrawn from Indian government for agriculture purpose but still can be used for plant protection which might be the cause for pesticide residue beyond permitted limit.

4. CONCLUSION

From the above results and discussions, we found that out of 84 pesticides tested using both LC-MS/MS and GC-MS/MS method the sample was detected with total of 19 pesticides and 65 pesticides types are undetected i.e. rate of detection of pesticides residue is 22.6% from the sample collected. Even though rate of detection of pesticides residue looks small there are some pesticides which have exceeded the permitted limit and there is need to take measures to reduce the pesticides usage as par possible. These pesticides have the potential to enter in the food chain and consumption of food stuff contaminated with pesticides has drastic impact on the human health causing severe hazards.

To protect the environment and the biodiversity from harmful effect of pesticide residues, farmers should be encouraged for organic cultivation where the primary aim is to use the organic wastes like crop, animal, farm wastes, and aquatic wastes etc for cultivating the land so as to keep the soil health in good condition along with raising the crops with quality which is free of chemicals also. Organic cultivation also includes use of other biological materials and beneficial microbes like biofertilizers to release nutrients to crops for increased production with eco-friendly pollution free environment.

It is necessary to frequently monitor the pesticide residues from different environmental samples in order to assess the condition of pesticides in ecosystem and also there is need to take suitable steps to minimize or neutral the usage of pesticides by switching towards the alternate ways to control the pests and insects without causing impact on the natural resources.

ACKNOWLEDGMENTS

Authors would like to thank Pesticide residue and Food quality analysis laboratory, University of Agricultural sciences, Raichur, Karnataka, India. Authors also thank the editors for giving valuable suggestions.

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