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Estimation of commercially available pesticide residues from Lyari River outfall Karachi, Pakistan

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ABSTRACT
Karachi is largest city of Pakistan and its financial hub. Besides industrial activities, agriculture is also practiced mostly in the outskirts of the city. Karachi basin is drained by two major rivers namely Malir and Lyari which have no fresh water in them and mostly utilized as drains which empties their effluent in the Arabian Sea. Agriculture is being practiced over a large area around these rivers where the farmers are using a large number of conventional pesticides including the Malathion (organophosphate) and Cypermethrin (pyrethroid). Their application is mostly through ground and aerial sprays. The outfall of Lyari river in particular is heavily polluted mostly due to domestic and industrial discharge. A sizeable portion of pesticide is also found in Lyari river effluent. In the present study, 24 effluent samples were collected for a period of one year to identify commercially available pesticide residues. In general, the pH of Lyari river effluent is towards alkaline side, while mean DO concentration was 1.95. The quantitative study reveals two predominant pesticides that were Malathion and Cypemethrin. The mean concentration of Malathion was 21.35 ppm while that of Cypermethrin was 14.73 ppm. This preliminary study suggest that Lyari river effluent contains appreciable amount of pesticides residues which final dumped in to the Arabian sea that may have serious consequences to the marine biodiversity.
Key words: *Lyrai River outfall, Malathion, Cypermethrin, Pesticide.*

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INTRODUCTION

Pakistan has agri-based economy where 70% of the human resource is living in villages and are involved directly or indirectly to the agriculture sector [1]. According to an estimate about 2.5 million tons of pesticides are being used every year in Pakistan. The rate of pesticide usage is keep on accelerating in the current face of world food problem [2]. Pakistan has no exception [3]. At present more than 108 types of insecticides, 30 types of fungicides, 39 types of weedicides, 5 types of acaricides, and 6 different types of rodenticides are being used in Pakistan [4]. The trend in the use of pesticide has been increased to 1169% in the last 20 years [5]. The predicament is that the farmers are indiscriminately using pesticides without considering their toxic effects. Even the pesticides that are banned by the developed countries are still being used by the developing or under developed countries [6]. Karachi is largest city and the financial hub of Pakistan which ranked 6th world largest metropolitan area. City geographic coordinates are 24°51′ N 67°02′ E. Agriculture in Karachi is mostly in the out skirts. Karachi basin is drained by two major rivers namely Malir and Lyari with catchments areas of 2051 and 7045 Km^2 respectively [7]. As there is no more fresh water in these rivers, they are merely used for dumping of liquid and solid wastes of both domestic and industrial origin [8]. Lyari River is the largest watercourse flowing through urban Karachi, which was primarily a seasonal river but now has become a drainage system for the adjoining industries and localities [9].

Lyari River has very mild slope in the outfall reaches touching almost at zero level downstream of Mauripur road bridge. The flow in the river is thus very much influenced by the diurnal rise and fall of the tides. The river carries highly polluted wastewater from the north and west of the city and finally dumped it into the Arabian Sea. Lyari River is about 50 km long, which up till
1950's had clean water [10]. Lyari river drain into the Arabian sea at Manora channel where it remain stagnant during low tide [11]. At present more than 50 squatter settlements are located along both the banks of Lyari river accommodating approximately 0.8 million persons. These unauthorized encroachments create obstruction in the waterway. Ultimately, the water level increases and storm water

drains discharging in Lyari River become ineffective. In many places, Lyari river effluent is being used for unrestricted irrigation. The people of the nearby communities used to cultivate vegetables mostly through the untreated effluent of Lyari River. These vegetables are being supplied to the Karachites.

The farmers mostly used two common and commercially available pesticides namely Malathion and Cypermethrin owing to their efficacy and affordability. Malathion (organophosphate) and Cypermethrin (pyrethroid) are extensively used all over the country. Their application is mostly through ground and aerial sprays [12].

Malathion, S-(1,2-dicarbethoxyethyl) -O, O-dimethyldi-thiophosphate [13]. targets mainly the nervous system of organisms by selectively inhibiting acetylcholinesterase (AChE) [14]. It is commonly used to control a wide range of chewing and sucking insects on a number of crops, stored grain. The United States Environmental Protection Agency, has classified malathion as a toxicity class III pesticide and allowed a maximum amount of 8ppm residue in specific crops used as foods [15].

Cypermethrin, cyano-(3-phenoxyphenyl) methyl 3-(2,2-dichloroethenyl) -2,2 dimethylcyclopropane-1-carboxylate is also widely used in agriculture, forestry, horticulture, public health, and homes, as well as for protection of textiles and buildings [16, 17, 18]. Cypermethrin is toxic to the aquatic environment with concentrations as low as 10 µg/L [19, 20, 21] and reported to have carcinogenic effects [22, 23].

The present research investigation aimed at determining the residual concentration of Malathion and Cypermethrin from the Lyari river effluent samples.

MATERIAL AND METHODS

Sampling

Samples were collected from Layri river outfall (24°51'59.48"N 66°58'20.16"E) these samples were collected twice a month during 2014. In all 24 samples were collected.

Collection of samples

Wastewater samples were collected using Niskin bottle from the surface (approx. 10 cm) at the area approachable through feet. For the collection of samples pre-sterilized amber glass bottles were of 2-litre capacity were used. The samples were collected in a way to avoid floating materials. All samples were grab collection, taken from the pre-designated locations as mentioned in Fig.1.

Physical parameters

The physical parameters of Lyari River tested were, pH and Dissolved Oxygen (DO). pH of the samples was determined using HACH sensation 156 multi parameter dissolved oxygen meter.

Dissolved oxygen was determined using Jenway 630i dissolved oxygen meter. The DO probe was immersed in the sample stream to an adequate depth and in a manner to ensure sufficient sample movement across the probe-sensing element. The above mentioned parameters were determined onsite.

Liquid–liquid extraction (LLE)

For the extraction of pesticide residues in wastewaters, liquid liquid extraction (LLE) method was used following [24] method. One liter wastewater sample was homogenized with 2 g anhydrous NaCl in separating funnel and extracted twice with 50ml of dichloromethane (2 x 50 ml). The lower layer was separated and dehydrated by passing through anhydrous sodium sulfate. The eluent was then allowed to evaporate completely by using a rotary evaporator (BUCHI Rotavapor B-740) at 40°C under vacuum. The dried residue was then dissolved in 10mL analytical grade n-hexane for analysis on GC.

GC Analysis

A Gas Chromatograph (Shimadzu's versatile GC-2014), instrument equipped with a WBI injector, Optima 5 column 6.0m 0.32mm capillary column coated with a 0.25µm film, Column temperature was maintained at 180°C for 1 min and raised to 360°C at the rate of 240°C/min and hold for 1min, The injection port temperature was 260°C. Nitrogen was used both as a carrier gas at a flow rate of 2.11 ml min^{-1} and the make-up gas with a total flow rate of 7.2 ml/min. Electron Capture Detector (ECD) temperature 300°C was used for cypermethrin and Flame Ionization Detector (FID) was used for malathion residue analysis. Each sample was injected three times and standard deviation and standard error were calculated.

GC –MS Analysis

Malathion and Cypermethrin were monitored and confirmed through Gas Chromatography - Mass Spectrometry (GC/MS) system, Agilent 7890A (G3440A) equipped with mass spectroscopy detector (MS Agilent 7000 GC/MS triple quadrupole).

RESULTS AND DISCUSSION

Results of pH and DO are given in Table 1. The minimum and maximum pH values of Lyari river effluent ranged from 7.3 to 7.8. Whereas, the mean pH value was 7.51. The minimum pH value was found in January and October while maximum pH value was obtained in February and May. In general, the pH of Lyari river effluent is towards alkaline side. Lyari River contains effluent from textile industries located at

SITE and Federal B area industrial area. These are the two industrial areas where most of the textile and hosiery industries are located. Alkaline pH of Lyari river is mainly due to textile effluent which generally have a very high pH values.

Table 1. pH and dissolved oxygen values of Lyari river effluent

S. No	Months	pH	Dissolved oxygen (ppm)
1.	January	7.3	1.8
2.	February	7.8	1.7
3.	March	7.6	1.9
4.	April	7.5	2.1
5.	May	7.8	1.6
6.	June	7.4	2.3
7.	July	7.5	2.5
8.	August	7.7	2.9
9.	September	7.4	1.9
10.	October	7.3	1.6
11.	November	7.4	1.5
12.	December	7.5	1.7
Min.-Max.		7.3-7.8	1.6-2.9
Mean		7.51	1.95
Standard error		0.051	0.122
Standard deviation		0.174	0.42

Table 2. Residual concentration of Malathion and Cypermethrin in Lyari river effluent (Mean of two samples)

S. No	Months	Malathion (ppm)	Cypermethrin (ppm)
1.	January	51	BDL
2.	February	BDL	19.5
3.	March	42.5	BDL
4.	April	55	BDL
5.	May	BDL	31
6.	June	BDL	50
7.	July	BDL	30.7
8.	August	BDL	30.9
9.	September	48	BDL
10.	October	59.8	BDL
11.	November	BDL	BDL
12	December	BDL	BDL
Min-Max.		42.5-59.8	19.5-50
Mean		21.35	14.73
Standard Error		6.60	10.99
Standard deviation		26.69	18.30

The mean concentration of DO in Lyari river effluent was 1.95. Whereas minimum and maximum DO concentration were 1.6 (May and October) and 2.9 mg/l (August) respectively. High DO concentration in August might be due to high wind velocity, which is responsible for atmospheric dissolution of dissolved

oxygen. The typical sewage like smell all along the Lyari River particularly at its outfall is an indication of high organic load that is responsible for creating anoxic conditions. No significant variations pertain to DO concentration was observed during entire study. Low DO concentrations could be due to high BOD values which indicate the stress of ecosystem [25, 26]. In general, DO during each month remained less than 3.0 mg/l. It can be claimed that the river is facing hypoxic condition which normally occurs when DO concentration is < 2.0 mg/l [27]. Lower DO (<4.0 mg/l) occurred largely in summer in both the estuary and adjacent coastal waters [28]. Khan et al [29] also reported similar values of DO in Lyari river effluent.

Results of pesticide analysis are presented in Table 2. Fig. 1 represents the standard chromatogram of Malathion and Cypermethrin. Monthly variations in pesticides concentration is presented in Fig. 2 and 3. Malathion peak was observed after the retention time of 15.20 min and Cypermethrin peak was observed after the retention time of 32.79 min. The Malathion and Cypermethrin were also identified and confirmed by GC-MS based on similarity of their fragments and molecular ions with those of corresponding authentic compounds by using documented data from the National Institute of Standards and Technology (NIST) library database. The mass spectrum of Malathion and Cypermethrin is shown in Fig 4 with molecular weight of malathion 284 and cypermethrin 415.

The mean concentration of Malathion was 21.35 ppm while that of Cypermethrin was 14.73 ppm. Minimum and maximum concentration of Malathion ranged between 42.5 to 59.8ppm. Minimum concentration of Malathion was found in March while maximum was obtained in October. It is interesting to note that Malathion was only available in the effluent during January, March, April, September and October. The concentration of Cypermethrin was relatively low as compared to Malathion. The minimum and maximum values of Cypermethrin was 19.5 (February) and 50 ppm (June). The average concentration of both these pesticides in wastewater samples were higher than the NEQS [30] allowable limits (0.15mg/L).

No significant trend was observed in the concentration of both the pesticides during the entire study.

The main source of these pesticides could be the industrial effluents originated from the four industrial zones of Karachi that are Sindh Industrial Trading Estate (SITE) in the north, Landhi Industrial Estate (LITE) in the east, Korangi Industrial area (KIA) in the south and Hub Trading Estate (HITE) between Karachi and Gadani in the west. Karachi city generates more than 350 MGD of domestic and industrial waste, of which only 90 MGD (less than 30% of the total waste generated) is partially treated daily at three waste water treatment plants [31, 32]. These treatment plants are located in SITE town called TP-1 (Sher Shah) in Jamshaid Town called TP-2 (Mahmoodabad) and in Mauripur called TP-3. TP-1 and TP-2 were built in 1960.

Unrestricted irrigation is also common at some places along the course of Lyari River. In particular, the people used to cultivate spinach, corn, tomatoes and lettuce. The unrestricted irrigation fields were found at Hasan square bridge, Lasbella and Ten Hatti Bridge and at Lyrai river outfall. The families consumed their own produce and also sell into the nearby market. It has been observed during the field surveys that the farmers /families indiscriminately using Malathion and Cypermethrin in particular to save their crops from the attack of insects without considering their harmful effects. This unrestricted use of pesticide could be one of the potential sources of pesticides in Lyari River effluent. During the recent epidemic of Dengue fever in Karachi Malathion was also used to kill mosquitoes by Karachi Municipal Corporation. This involves spray in large outdoor areas. Malathion also used to kill beetles found in stored grain [33] particularly wheat. Malathion from wheat granaries located in the city may also enter in the Lyari effluent through washing of the areas.

The haphazard and misuse of pesticides may pollute the water reservoir and eventually entered into the food chain, which cause severe harm to human health, fishes and many other animals, leading to death [34]. The solubility of Cypermethrin within the range of test temperatures (15-25 ^{o}C) was estimated to be in the range 5-10 µg/l [35].

Jing *et al*., [36] detected maximum concentration of cypermethrin (0.969 µg/l) in industrial wastewater samples of Beijing. Cypermethrin is potentially toxic to the aquatic life forms even at a concentration as low as 10 µg/l [37]. It may also have carcinogenic effects [38]. Stephenson, [35] determined Cypermethrin toxicity to some species of fish (*Cyprinus curpio. Scurdinius etytheophthalmus, Salnro goirdneri, Salmo trutta and Tilapia nilotko*). He found 96 hour LC_{50} values were within the range 0.4-2.2 µg/l.

Nuzhat *et al* [39] has reported that Karachi harbor is contaminated with organochlorine pesticide and the residual concentration is considerably higher in the vicinity of the discharge point of Lyari River and adjoining areas.

As such desirable aquatic life forms do not exist in Lyari river, however, the continuous discharge of Lyari river effluent into the Arabian sea is potentially hazardous to marine biodiversity.

From this preliminary study no selective point source of pesticide was detectable however, pesticide

misuse, spillage, and/or inappropriate storage, handling and disposal could be the potential sources of pesticides in Lyari river effluent. Accordingly these sources are responsible, in many cases, for pesticide contamination of water bodies at high concentration levels [40].

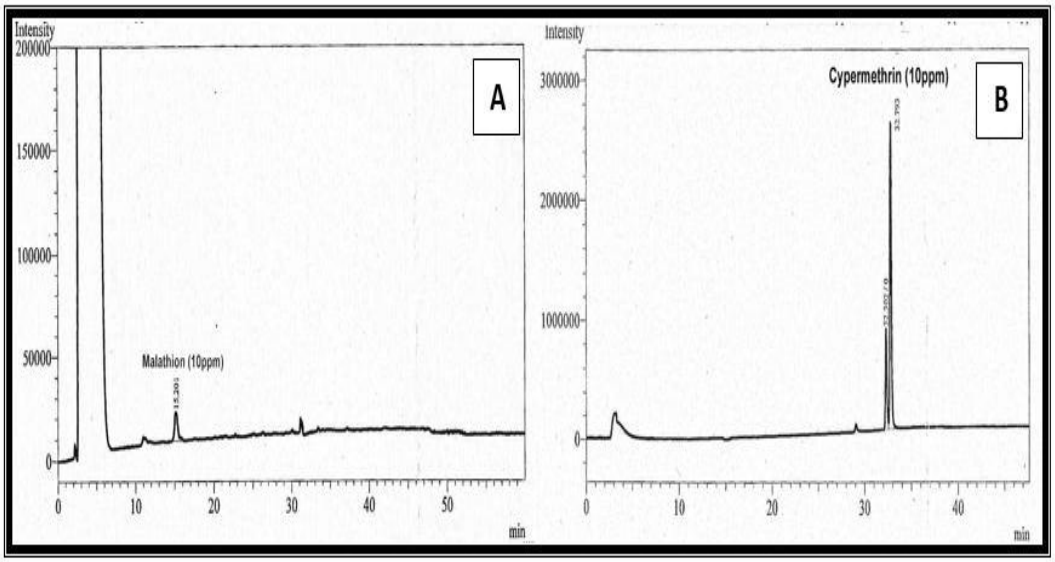

Fig. 1 (A) GC-chromatogram of Malathion standard (10ppm) (B) Cypermethrin standard (10ppm)

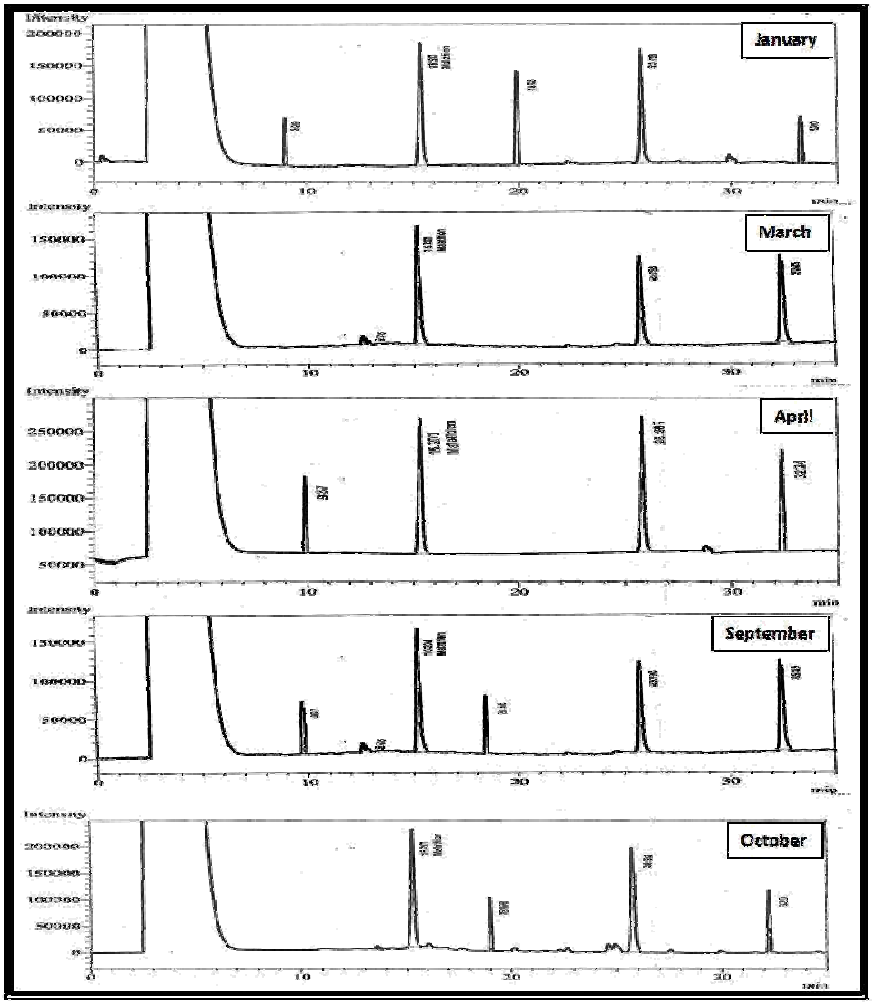

Fig. 2 GC-chromatogram of Malathion residues in wastewater

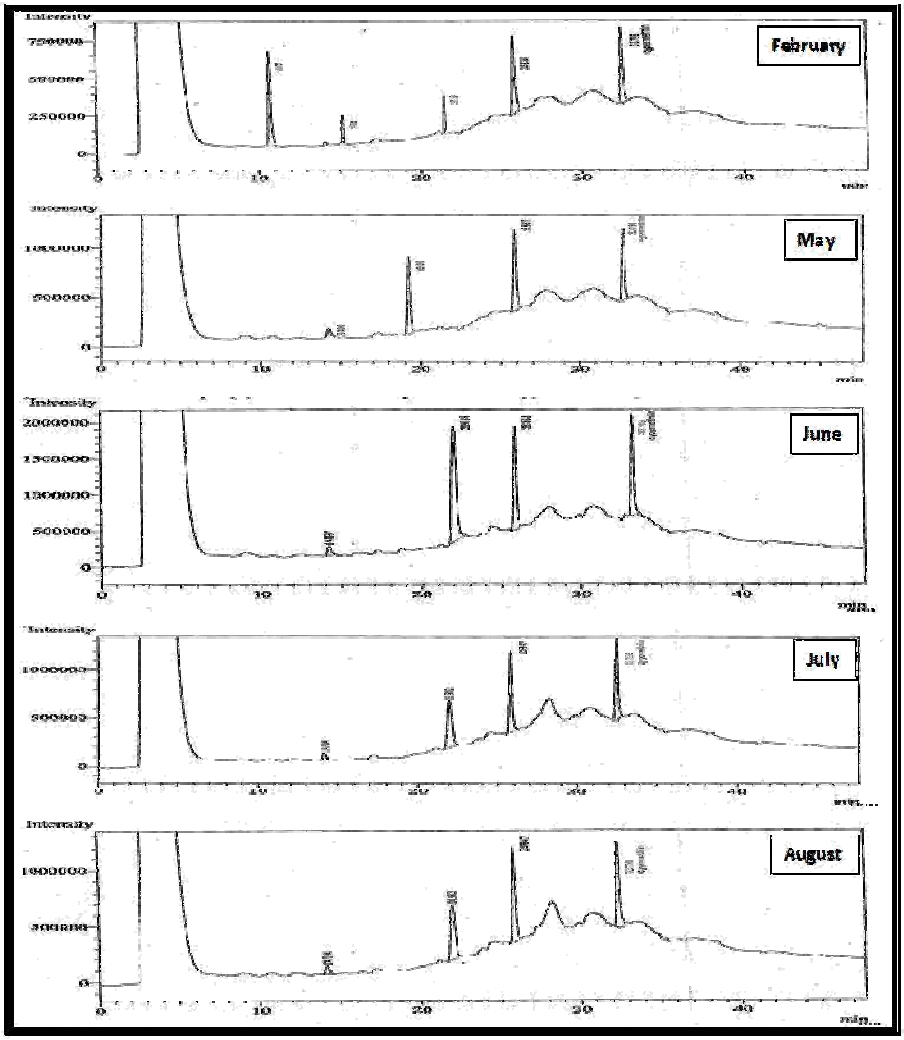

Fig. 3 GC-chromatogram of Cypermethrin residues in wastewater

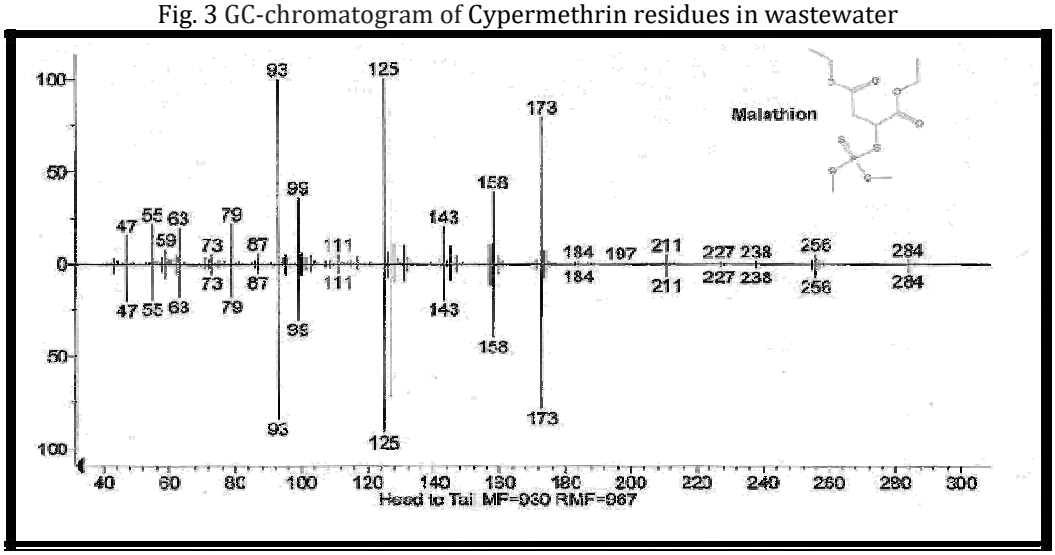

Fig. 4 Mass spectrum of Malathion

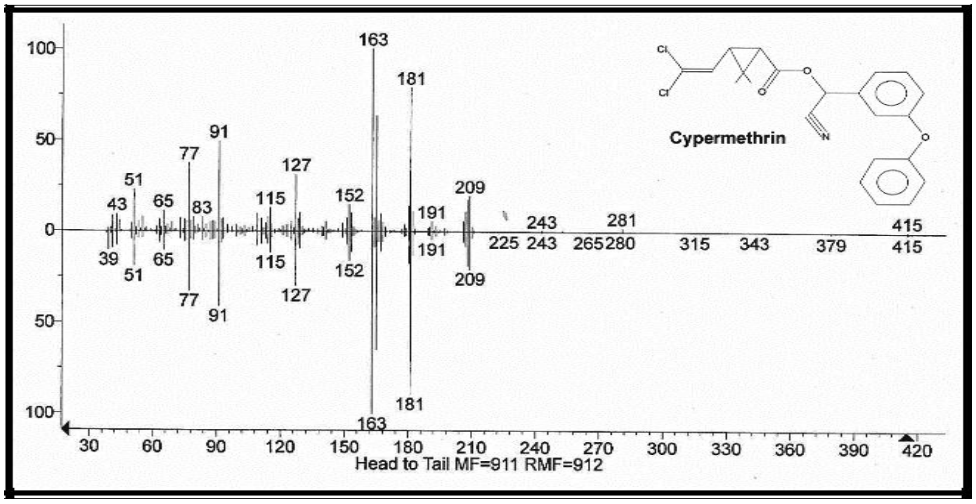

Fig. 5. Mass spectrum of Cypermethrin

CONCLUSIONS

This study will provide a groundwork for establishing a monitoring program for commercially available pesticides. This preliminary study will be helpful for the municipal authorities in setting up relevant management policies.

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