

OCCURRENCE AND DISTRIBUTION OF COMMERCIALY AVAILABLE PESTICIDES AND HARMFUL BACTERIA AT WESTERN BACKWATER OF KARACHI COAST, PAKISTAN

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ABSTRACT

This study aims at preliminary analysis of pesticide pollution of western backwater at Karachi coast. Karachi coastal area is known for its ecological importance. The coastal area receives >350 MGD of wastewater through Lyari and Malir rivers. The effluent of Lyari and Malir Rivers often carries agriculture runoff from the nearby agriculture fields of these Rivers. Samples were collected from 12 different sites at the western backwater of Karachi coast for the occurrence and distribution of commercially available pesticides. The pesticides used in the present study were OCPs (organochlorine pesticides) including aldrin, dieldrin, endrin, endosulfan, Hexachlorobenzene (HCB), HCH (Hexachlorocyclohexane), heptachlor, Methoxychlor, p,p'-DDT and transchlordan. Pesticides were determined through gas chromatographic technique. The highest mean concentration was that of Endosulfan (0.63 µg/l) while lowest concentration was of Endrin (0.046 µg/l). The residual pesticide concentrations were in the order Endosulfan>Heptachlor> DDT> HCH> Dieldrin> Aldrin> Transchlordan> Methoxychlor> Endrin. HCB was not detected in any sample. It noteworthy that DDT was also found in the samples that remains persistent in the environment for decades. The continuous accumulation of pesticide residues at Karachi coast may lead to serious health and environmental implications that cannot be ruled out. The bacterial load of total coliform and faecal coliform was also markedly high. Therefore, it is suggested that strict policy guidelines be enforced to restrict the pollution of this water body that is so closed to human settlements.

Keywords: Pesticides, pollution, effluent, backwater, Karachi coast

INTRODUCTION

Pakistan coastline stretches from west at the boarder of Iran and on the east at Indian border measuring about 970 Km. The EEZ (Exclusive Economic Zone) of Pakistan spreads over an area of 196,600 km². The coastline is divided between Makran coast (Baluchistan province) and Sindh coast (Sindh province) having an approximate length of 800 km and 250 km respectively. The continental shelf of Sindh and Makran coast is about 150 and 40 km respectively.

Karachi being the beta city is the most populous city in the country having an estimated population of 14.9 million according to 2017 census. However, unofficial reports suggested that the city has a population of 21.2 million. Karachi is the economic hub of Pakistan having a coastline of about 135 km of the Sindh coast. Karachi coast is bestowed with rich and diverse tropical marine/estuarine ecosystem. The mangrove ecosystem comprises of moderately wide belt ranging from 10-60 m (Barkati and Rahman, 2005).

The environmental pollution at Karachi coast is overwhelmed due to excessive pollution load originating from both domestic and industrial activities (Mashiatullah *et al.*, 2009; Qari *et al.*, 2005; Saifullah, 2002). Rapid urbanisation, unsustainable development, dilapidated infrastructure and continuous dumping of liquid and solid waste at the Karachi coast is deteriorating the coastal ecosystem. Karachi is the most affected area along the coast of Pakistan (Khan, *et al.*, 2001).

Karachi generates >350 MGD of wastewater of which only an insignificant portion is receives a preliminary treatment while the rest is dumped in to the sea without any treatment (Alamgir *et al.*, 2017). Karachi basin is drained by two major rivers namely Malir and Lyari with catchments areas of 2051 and 7045 km² respectively. These rivers play an important role in the natural drainage of Karachi City. However, at present they are merely used to dump the untreated wastewater into the sea (Sirajuddin, *et al.*, 2016). In Pakistan the issue of industrial water pollution is overwhelmed and uncontrolled. This is mainly due to the fact that Government has given a little or no incentives for industries to treat their effluents (WWF, 2007).

Ensink *et al.*, (2004) reported that wastewater produced in the country is directly used for irrigating an area of about 32,500 ha while Karachi is no exception. The approximate amount of wastewater directly used in agriculture is $0.876 \times 10^9 \text{ m}^3/\text{year}$ (<http://www.wds.worldbank.org>).

In Karachi the agricultural activities can be found in the suburbs of Karachi. Within the city agriculture is practised at Gadap and Malir valley close to Malir River (Kausar, *et al.*, 2014), while at different places at the entire stretch of Lyari river. These agricultural activities are mostly restricted to vegetable cultivation. The summer crops include tomato, pepper, brinjal, okra, gourd and bitter gourd. These crops are sown in February and March and harvested in September. The winter vegetables include cabbage, cauliflower, carrot, radish, turnip, peas, spinach and coriander.

Pesticide demand in the country is escalating owing to the emergence of new insects and pests while the existing pests have developed multiple pesticide resistance. At present about 45 multinational companies and 13 local pesticide industries are trying to meet the existing demand. The worrying issue is however, neglected. Since majority of the farmers are uneducated therefore, they are using pesticides indiscriminately without understanding the consequences of these applications.

The commonly used pesticides in the country include Chlorinated Hydrocarbon Pesticides and Organophosphate pesticides. The former ones includes Aldrin, Dieldrin, Endrin, Chlordane, DDT, lindane, Heptachlor and Thiodane while the later used include Ethion, Usathion, Arathion, Imecron, Formathion, Azodrin, Nexion, Arbicron, Diptrex, Diazinon, Malathion, Methyl Parathion, Metasystox, and Phosdrin etc. These pesticides are available both in liquid (95%) and powder form (5%).

In the areas like Karachi, unrestricted irrigation is unchecked and the farmers are using huge quantities of pesticides not only to protect their crops but also to increase crop yield. As such only a limited amount of pesticides are used to kill the target insects and pests whereas, the amount in excess remains in the field from where it ultimately finds its way to sea through agriculture runoff. Agricultural runoff normally empties into the Lyari and Malir Rivers and the associated drains from where the untreated effluent is dumped into the sea without any treatment.

It is with this aim the present research was undertaken to i. determine the extent of pesticide pollution at the western backwater of Karachi coast, ii. Access the degree of bacterial pollution.

MATERIAL AND METHODS

Study area

The study area comprises of western backwater that receives the effluent from Lyari River. It is located at $24^{\circ}50'18.24''\text{N}$ and $66^{\circ}57'7.88''\text{E}$. This area comprises of thick mangrove cover. The area receives untreated effluent mainly from the Lyari River, Macher colony, Karachi shipyard, Karachi fish harbour, west wharf and other adjoining areas. Due to extensive and indiscriminate use of pesticides, there is an urgent need to evaluate the risk assessment so that the effect of pesticides and bacterial pollution on Karachi harbour ecosystem can be evaluated.

Pesticides use in the present study

The water samples were collected from the western backwater for the detection of OCPs (organochlorine pesticides including aldrin, dieldrin, endrin, endosulfan, Hexachlorobezene (HCB), HCH (Hexachlorocyclohexane), heptachlor, Methoxychlor, p,p'-DDT and tanschlordan.

Sampling

The samples were collected during 2015 survey from 12 different sampling points using deterministic sampling programme. The sites of sample collection are presented in Table 1 and Fig.1. Sampling involved grab collection. The samples were collected after every four months from the pre-designated locations. In all 36 samples were collected. Water sample were collected in a pre-sterilized amber glass bottle (2.0 litre capacity) from the surface using Niskin bottle.

Approximately 1.0 litre of sample was collected in separate sterilized glass container for microbiological analysis. MPN technique was used for the determination of Total coliform count (TCC), Total faecal coliform count (TFC) and Total faecal streptococci count (TFS) as per method described in Standard Methods for Examination of Water and Wastewater (APHA, 2005).

The sampling containers were kept in an ice box and transported to the Department of Chemistry, University of Karachi.

Extraction of seawater sample for the determination of pesticides

The samples were subjected to the extraction procedure prior to the determination of pesticides (OCPs) in accordance with the method described in US-EPA (2007). The extraction procedure was repeated at least three times to obtain pesticides residues in the samples.

Analysis of pesticide residue

Pesticides residues were detected by a Gas Chromatograph (Perkin Elmer Clarus-500) supported by ^{63}Ni ECD detector and auto sampler. The carrier gas used was Nitrogen having a flow rate of 30 ml/min.



Fig. 1 Sites of sample collection.

Table 1. Sampling sites of the study area at Karachi coast.

Sampling site	Coordinates	Site adjacent to
S-1	24°48'34.27"N, 66°57'21.66"E	Mangrove area (Manora)
S-2	24°50'14.72"N, 66°55'13.35"E	Mangrove area (sandspit to Manora)
S-3	24°51'4.98"N, 66°54'54.41"E	Western backwater Lyari
S-4	24°51'18.42"N, 66°54'16.97"E	Western backwater Lyari
S-5	24°51'1.46"N, 66°53'22.84"E	Western backwater Lyari (Sandspit)
S-6	24°51'20.41"N, 66°52'46.21"E	Western backwater Lyari (Sandspit)
S-7	24°51'40.84"N, 66°51'59.09"E	Western backwater Lyari endpoint (Sandspit)
S-8	24°50'53.21"N, 66°58'23.33"E	Karachi fish harbour
S-9	24°51'44.64"N, 66°57'37.23"E	Lyari outfall
S-10	24°48'32.73"N, 66°59'0.37"E	KPT Coastal Area
S-11	24°47'44.98"N, 67° 2'2.68"E	Sea View near Mac Donalds
S-12	24°47'54.86"N, 67° 4'50.98"E	Gizri Creek

RESULTS AND DISCUSSION

The results of the composite analysis of all the samples are shown in Table 2. In all 36 samples were collected from 12 different sites for the above mentioned pesticides. Concentration of individual pesticides was calculated as well as the totality of their isomeric arrangements. Importantly, these may transform in the environment and often likely to deviate from their target thereby affecting the surrounding ecosystem. Due to this regular transformation cycles they persist in the environment for long duration of time and induce toxicity to the non-target living forms (Sankararamakrishnan *et al.*, 2005).

HCB is persistent OCP that may accumulate in the food chain. It is also reported to be carcinogenic (Kelly *et al.* 2007; Zhao *et al.*, 2010). HCB was not found in any sample. The presence of HCB in surface water was however, confirmed by Tariq *et al.* (2004) and Eqani *et al.* (2012). HCB has only limited usage in agriculture; it is mostly used as a fungicide.

The occurrence and distribution of HCH is dependent on the region, climatic conditions, surface water runoff and industrial discharges (Kaushik and Cuervo, 2012). In the present case the prime source of HCH in the western backwater is the effluent of Lyari River. The minimum and maximum concentrations of HCH were 0.119 and 0.813 µg/l respectively. The average concentration was 0.565 µg/L. HCH is banned in the country but its presence indicated that it is still illegally used. Lal *et al.*, (2010) suggested that α -HCH is found to be most persistent in the environment. Said *et al.* (2008) and Vryzas *et al.* (2009) suggested that the concentration of HCH varies from traces to higher concentration throughout the world. The results of the present study corroborate the findings of Turgut and Fomin (2002) who reported similar values of HCH in the effluent of Kucuk Menderes River. Awofolu and Fatoki (2003) however, reported elevated concentration of HCH in Eastern Cape, Africa. In another study Bulut *et al.*, (2010) reported trace amounts of HCH in water samples. Osterreicher *et al.* (2003) opined that HCH occurrence and distribution in water bodies is largely dependent on pH, temperature, organic matter content and microbial degradation of HCH.

Termite problem is invariably insistent in the city for which heptachlor is commonly used. Even though heptachlor is known to be persistent in the environment. Agriculture farm workers also use heptachlor extensively without knowing its toxic effect and its persistence in the environment. The formation of heptachlor epoxide from heptachlor due to physical, chemical and biological processes is even more toxic than heptachlor itself (Singh *et al.*, 2005; Pandit *et al.*, 2001), and it has a tendency to deposit in fatty tissues. The mean concentration of heptachlor was 0.628 µg/l whereas minimum and maximum concentration ranged between 0.886 to 0.209 µg/l respectively. The highest concentration was reported at S-4 which represents the site close to Lyari River outfall. Ahad and Aslam (2005) and Singh *et al.* (2005) also reported higher concentrations of heptachlor in Pakistan and India particularly in water bodies.

The mode of action and toxicological properties of Aldrin, Dieldrin and Endrin are quit comparable. They are reported to be highly persistent in the environment. The average concentration of the above OCPS was 0.285, 0.3066 and 0.046 µg/L, respectively. Whereas, their minimum and maximum concentrations fluctuated in the range of 0.184 to 0.823, 0.1059 to 0.55 and 0.060 to 0.17 µg/L, respectively. It should be mentioned that Aldrin has never been registered in Pakistan However, its presence in the samples indicated that it is easily available in the market. Dieldrin is formed from Aldrin through microbial action, activities of insects, mammals and sunlight under natural environmental conditions (Turgut, 2003). During the entire study period the lowest concentration was that of Endrin. Endrin is also banned in the country but its presence in the water samples clearly indicates its use in the agriculture. Ismail *et al.* (2014) reported a maximum concentration of 0.036 µg/L of Endrin in water samples in the city. Dieldrin can attach with the soil particles due to which, it breaks down only very slowly. From the soil it may also be taken up by the plants. While in case of human and animals it may store in the fatty tissues and excrete very slowly.

Endosulfan is an endocrine disruptor which may affect developmental and reproductive stages of human and animals. Endosulfan contains α - and β isomers however, β -endosulfan has higher water solubility with a half-life of 150 days. α -isomer is found to be 3 times more toxic than β -isomer. Jayashree and Vasudevan (2007) reported higher concentration of endosulfan residues in water samples in India. The mean concentration of endosulfan is 0.638 µg/L whereas, its minimum and maximum concentration ranged between 0.1087 to 0.763 µg/L. The maximum concentration of endosulfan was recorded at S-6 (Western backwater Lyari; Sandspit). The occurrence and distribution of elevated concentration of endosulfan reveals its wide-spread use in agriculture in the suburbs of Karachi.

Chlordane although never registered in Pakistan, its occurrence indicates its use in agriculture. It is less soluble in water having a half-life of 18 hours. In soil however, it can strongly bind with soil particles where it may last for as long periods. The average concentration of transchlordane in all the sample was 0.2646 µg/L while minimum

and maximum concentration were fluctuated in the range between 0.1304 to 0.59 µg/l. Transchloradane is widely used as an insecticide to control termites. Eqani *et al.* (2012) reported much lower values of chloradane as compared to the present study. The recent and on-going use of chloradane can be determined by the ratio of cis and trans-chlordane as reported by Bidleman and Leone (2004).

Table 2. Composite results of the pesticides analysis (all months)

Sites	Pesticides µg/L									
	HCB	HCH	Hepta-chlor	Aldrin	Dieldrin	Endrin	Endosulfan	Transchlordane	4,4-DDT	Methoxychlor
S-1	BDL	0.583	0.693	0.110	0.253	0.070	0.717	0.220	0.415	0.190
S-2	BDL	0.540	0.723	0.317	0.357	0.053	0.577	0.125	0.620	0.217
S-3	BDL	0.703	0.796	0.183	0.407	0.060	0.487	0.413	0.540	0.227
S-4	BDL	0.546	0.886	0.243	0.333	BDL	0.747	0.180	0.710	0.180
S-5	BDL	0.520	0.636	0.270	0.223	BDL	0.710	0.170	0.440	0.160
S-6	BDL	0.756	0.413	0.823	0.210	BDL	0.763	0.160	0.720	0.190
S-7	BDL	0.560	0.713	0.293	0.230	0.050	0.657	0.230	0.690	0.195
S-8	BDL	0.793	0.843	0.230	0.287	BDL	0.573	0.320	0.320	0.217
S-9	BDL	0.331	0.154	0.347	0.550	0.150	0.557	0.313	0.950	0.230
S-10	BDL	0.119	0.713	0.213	0.213	BDL	0.713	0.200	0.340	0.207
S-11	BDL	0.520	0.450	0.110	0.217	BDL	0.720	0.255	0.280	0.220
S-12	BDL	0.813	0.523	0.287	0.400	0.170	0.435	0.590	0.927	0.273
Grand mean	---	0.565	0.628	0.285	0.3066	0.046	0.638	0.2646	0.579	0.208
Std. Dev.	---	0.119	0.154	0.11	0.21	0	0.435	0.125	0.28	0.16

Table 3. Bacteriological quality of seawater at Karachi coast

Variable mg/l	Mean	Median	Min.	Max.	Lower Quartile	Upper Quartile	Quartile range	Std. Dev.
TCC MPN/100ml	1188.7	780	75	2400	157.5	2400	200	1103.55
TFC MPN/100ml	147.25	75	21	460	40	240	0	135.7693
TFS MPN/100ml	0	0	0	0	--	--	--	--

Under aerobic condition DDT can be transformed into DDD or DDE (Eqani *et al.* 2012). DDT although, banned all over the world is still available in the local market with different brand names having different percentages of DDT (Khwaja *et al.*, 2006). It is interesting to note that during the green revolution in 1960's DDT was extensively used by the farmers without knowing its harmful effects and its persistent nature. DDT has a half-life of up to 10 years (Longnecker *et al.*, 2005).

The average concentration of DDT in all the samples was 0.579 µg/l whereas its minimum and maximum concentration ranged between 0.227 to 0.95 µg/l. Highest concentration of DDT was recorded at S-9 (0.95 µg/l). The presence of DDT in all the samples indicates its usage in the city. The prime source of DDT in the samples may not be the agriculture runoff alone it may come from other anthropogenic activities as well. The concentration of DDD and DDE along with DDT (The parent compound) is used to determine the possible source of contamination and its recent or old application. Asi *et al.* (2008) reported elevated concentration of DDT in the water samples collected from district Khanewal central Punjab). Aydin *et al.* (2013) described that water sample of Konya Basin (Turkey) were found to be contaminated with DDT and its metabolites. Badach *et al.* (2000) reported higher concentration of DDT, lindane, heptachlor and methoxychlor in drinking water samples in rural regions of Poland.

The mean Methoxychlor concentration in the samples is 0.16 µg/L while the minimum and maximum concentration were in the range between 0.029 to 0.273 µg/L, respectively. The highest concentration of Methoxychlor was found at S-12 (0.29 µg/L) this site represents Malir River outfall. This river carries agriculture runoff along with the domestic and industrial effluent and discharges at Gizri creek area. Extensive agriculture can be seen on both the banks of Malir River. The farmers mostly cultivate vegetables that are supplied to the nearby markets. The people are consuming the raw vegetables that contain pesticides residues in them. Therefore, the risk factor and its impact on health and environment cannot be ruled out.

From Tables 3 it can be seen that all the sea water samples were contaminated with the organisms of public health importance. Bacteriological analysis reveals that there is an increase in contamination due to organisms of public health importance after rain. This could possibly be due to the runoff from the surroundings providing favourable conditions for the organisms to sustain and multiply. However, faecal streptococci were absent in all the samples. The reason of faecal contamination could be the anthropogenic activities near the lagoon. In general, during the rainfall and flood conditions the microbial load of the flowing water increases which depreciates the water quality (Kistemann, *et al.*, 2001). The water pollution of sea water in Pakistan mainly originates from anthropogenic sources as water pollution through natural processes is insignificant in Pakistan. The results of PCA analysis (composite including all months) is shown in Table 4 and Fig. 2. For the total data set the first three components explained 83.73 % of the total cumulative variance. The first and second principal components explained 49.60 and 19.94% of the total variance. The first component is primarily a function of Endrin, Endosulfan, Methoxychlor, Transchloradane and Dieldrin, whereas the second component is largely a function of Aldrin, Heptachlor, DDT, Transchloradane and Endosulfan. The third component is primarily governed by HCH, Aldrin, Heptachlor, Dieldrin and transchloradane, seems to be more or less a repetition of the second component.

Table 4. Results of Principal component analysis of pesticides data.

Component	Eigenvalue	Percentage variance	Cumulative percentage variance	First 5 eigenvector coefficients	Associated variables
1	4.4648	49.6097	49.6097	0.9172	Endrin
				-0.8810	Endosulfan
				0.85881	Methoxychlor
				0.8343	Transchloradane
				0.6956	DDT
2	1.7950	19.9451	69.5549	0.8097	Aldrin
				0.6877	Heptachlor
				-0.5631	DDT
				0.3642	Transchloradane
				-0.3383	Endosulfan
3	1.2760	14.1780	83.7329	0.8952	HCH
				0.5088	Aldrin
				0.2703	Heptachlor
				-0.2651	Dieldrin
				0.1532	Transchloradane

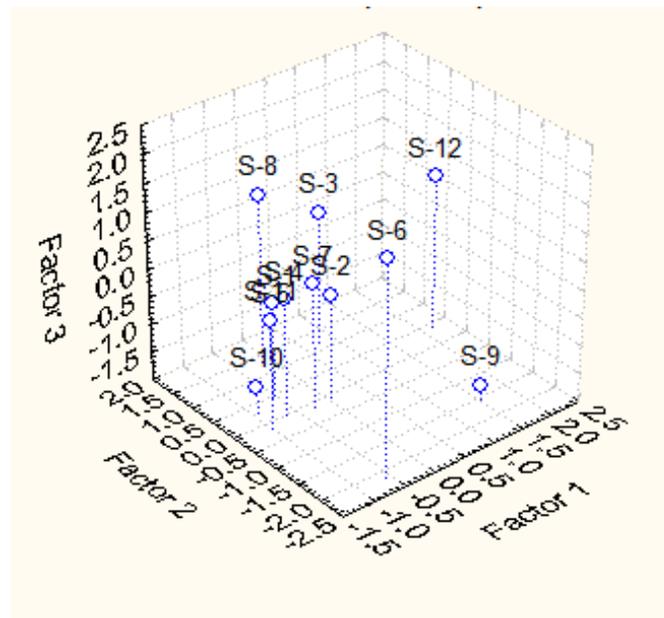


Fig. 2 Principal component analysis (3D;) of pesticide analysis of 12 different sites along the Karachi coast.

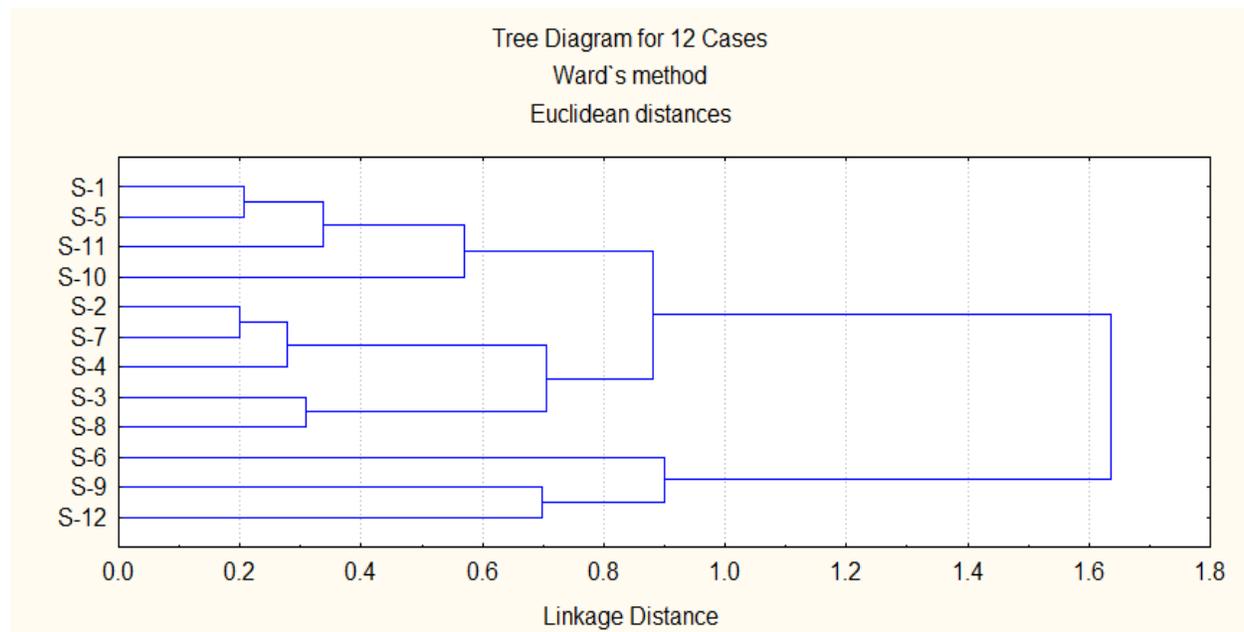


Fig. 3 Dendrogram derived from Ward's method of pesticides analysis of 12 different sites along the Karachi coast.

The dendrogram of composite analysis (all months) is presented in Fig.3. This dendrogram comprises of 3 major group. Group 1 consists of S-1, S-5, s-11 and S-10 having relatively lower concentrations of pesticides. S-2, S-7, S-4, S-3 and S-8 are clustered in Group 2 indicating moderate concentrations of pesticides. While Group 3 comprises of S-6, S-9 and S-12 that depict higher concentration of pesticides. The results of the multivariate analysis further confirms the findings that S-9 and S-12 are the sites having maximum concentration of pesticides. S-12 represents the sites which receive effluent from Malir River.

The results of microbial analysis are presented in Table 3. The mean total coliform count (TCC) were 488.7 for all samples while mean total fecal coliform count were 147.25 which indicates substantial bacterial load from the viewpoint of human health.

CONCLUSIONS AND RECOMMENDATIONS

The investigation concluded that western backwater of Karachi coast is polluted with pesticides residues. The accumulation of pesticide is attributed to unregulated dumping of untreated disposal of Lyari and Malir River effluent. The effluent of Lyari and Malir River often carries agriculture runoff from the nearby fields where the farmers are using pesticides indiscriminately without knowing the harmful effects of these chemicals. These pesticides tend to accumulate in marine invertebrates (e.g. crabs) and vertebrates (e.g. fish). Due to extensive use of pesticides not only in agriculture but also for domestic purpose, there is a dire need of pesticide risk identification so that the impacts of pesticides on human health and environment could be evaluated. Additionally appropriate measures be taken for reduction in the use of pesticide without compromising the crop quality and yield. It must be kept in mind exposure to pesticides, even at low doses, is associated with a wide variety of health issues.

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