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OCCURRENCE AND DISTRIBUTION OF ORGANOCHLORINE PESTICIDES IN KARACHI COASTAL WATER

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ABSTRACT

Organochlorine pesticides (OCPs) remain persistent in the environment for a very long period and induce their toxicity to human and environment so preferred only for a limited use. But in developing countries, these compounds are extensively used in agriculture sector for the control of pests' infestation. The present study aims to assess levels of pesticide pollution at Karachi coast, Pakistan by considering 9 different OCPs that are potentially considered as highly toxic. OCPs were analyzed by Gas chromatography through electron capture detector (GC-ECD). This two-year analysis revealed that although these pesticides are banned and obsolete but are still found in the costal environment in an order of Endosulfan > DDT > HCH > Heptachlor > Aldrin > Dieldrin > Transclordane> Endrin and Methoxychlor. The spatial distribution shows Creek avenue and Channa creek sites are heavily contaminated among all other location with respect to pesticides pollution. The indiscriminate and illegal use of OCPs should be strictly monitored and critically control to avoid seawater contamination to secure marine ecosystem.

Keywords: Organochlorine, Pesticide, Seawater, Pollution, DDT, Toxicity

INTRODUCTION

Organochlorine pesticides (OCPs), the frequently used pesticide across the globe for the removal of agricultural pests applied for many years but after recognizing the possible adverse effects on human, animals and environment, these compounds have been banned in mid 1970s in the developed world (Koureas *et al*., 2016). Due to their durability and persistence in the environment, the OCPs are still a big concern as these can transfer in the food chain affecting each individual of trophic level for example, the metabolite of DDT i.e. pp 'DDE stays in greater that 95% populace (Zubero *et al*., 2015).

Worldwide, the researchers have concerned over the resistance of pesticides in the aquatic environment entered through agricultural discharge, found that the OCPs residues remain in the environment for many years (Wu *et al*., 2014; Agarwal *et al*., 2015; Ali *et al*., 2016). The pesticide pollution of a water body mainly arises from non point sources while these persistent organic pollutants have the ability to travel long distances from their point of origin Kuranchie-Menash *et al.*, 2012). According to European Union guidelines (80/778) a limit of 0.10 μg/L of individual pesticides and their metabolites is suggested for water (Directives Council, 1980).

The level and distribution of obsolete pesticides in various compartments of environment have been studied all over Pakistan indicates the illegal usage of banned pesticide for agricultural purposes. These researches include the presence of pesticides in water bodies (Ahad *et al*. 2010; Alamdar *et al*. 2014; Ali *et al*. 2016; Baqar *et al*. 2018), Indus Basin (Sultana *et al*. 2014), soil, sediments and air (Eqani *et al*. 2011; Syed and Malik, 2011; Syed *et al*. 2013; Syed *et al*. 2014) and urban atmosphere (Nasir *et al*. 2014).

The coastal area of Sindh province is situated at the southeastern part of Pakistan which is about 350 km and stretches between Sir Creek on the east and Hub River on the west at Balochistan coast. The coastal area can be broadly divided in to Karachi coast and the Indus delta creek. Karachi coastline is about 135 km long that is overwhelmed with the pollution and is considered as most polluted area all along the Pakistani coastline (Khan and Khan, 2001). The ecosystem of Karachi coastal area is gravely disturbed due to the continuous discharge of untreated domestic and industrial effluents and agricultural run-off.

Karachi coastal area is facing tremendous pressure that is affecting both the ecosystem and human health through untreated effluents discharge that leads to introduction of pesticides, high nutrient loads, hazardous chemicals and pathogens that is responsible for adverse public health, environmental and socio-economic problems. An estimated more than 350 million gallons of wastewater is dumped into the Karachi costal area without any significant treatment (Alamgir *et al.,* 2017).

The city of Karachi was being blessed through natural drainage basin comprises of Lyari and Malir River. However, due to exponential increase in human population, massive encroachments in these natural drainage basins and dilapidated physical infrastructure, these rivers are now merely considered as wastewater discharge channels that empty city wastewater into the coastal area along the Arabian Sea. The treatment plants located in Karachi are

TP-1 (Sher Shah), TP-2 (Mahmoodabad) and TP-3 (Mauripur). It has been reported that these treatment plants are not working efficiently and can treat only 30 % of the wastewater while the remaining is dumped in the sea without any significant treatment (Saleem, 2002). No significant improvements have been made so far in the wastewater treatment systems in Karachi (Hameed *et al*., 2102).

In Pakistan, the research on pesticides pollution on water bodies and coastal ecosystems is very limited. Therefore, there is a dire need to monitor the pesticide pollution of coastal areas on continuous basis. It is therefore, with this aim the present research work is undertaken to determine the levels of OCPs in Karachi coastal waters. The suburbs of Karachi are extensively used for agriculture. The worrying issue is that the farmers mostly use untreated wastewater of both domestic and industrial origin for the cultivation of vegetables and other crops. In such cases the attack of insects and pests is inevitable for which they indiscriminately used pesticides to improve the crop yield. Most of the farmers have limited knowledge about the hazardous effects of these pesticides. It is anticipated that high concentration of these pesticides finally finds its way through the effluents of Malir and Lyari rivers that ultimately find its way into the sea. This study, therefore, provides the baseline regarding the occurrence and distribution of pesticides along the Karachi coast.

MATERIALS AND METHODS

Sample collection

Sea water samples were collected deterministically from pre-designated locations as shown in Table 1 and Fig.1. In all 20 samples were collected during the period of 2017 and 2018. These samples were collected in triplicates. The water samples were collected in clean plastic bottles. Approximately 2.5 L of sample was collected in each bottle. The sampling containers were labeled and transported to the laboratory of Institute of Environmental studies for subsequent analysis. These samples were stored at low temperature 4^0C in refrigerator prior to the analysis.

Extraction of seawater samples for OCPs analysis

OCPs were extracted from the seawater samples as per method described in US-EPA (2007). The samples were filtered through Whatman No. 1 filter paper and then transferred to a separatory funnel in which 80 ml of NaCl (saturated solution) was added to make salt out effect followed by the addition of 160 mL dichloromethane (80:40:40). The sample was shaken vigorously for 5 minutes. This procedure was repeated at least thrice to collect all the pesticide residues. Moisture content was removed by the addition of anhydrous Na_2SO_4 . This step was carried out in a rotary vacuum evaporator . The final volume of the sample was 2.0 ml. The extracted sample was subjected to activated alumina/silica column.

Approximately 4.0 g silica gel was activated at 130^0C for 16 h which was packed into a glass column of about 10 mm diameter. Later 2.0 g of anhydrous aluminum oxide was added from the top of chromatographic column. Before the transfer of extracted sample to the column, 40.0 mL hexane was added to the column. The concentrated extract was transferred to the column and eluted with 20 mL aliquots of n-hexane followed by 20 mL (15%) of dichloromethane-n-hexane (1:9) to get the organochlorine fraction.

The gentle stream of nitrogen was used to evaporate the eluted fraction that has left the pesticide residues in a glass vial. The dried sample of pesticide extract was made again in 2 mL of hexane. The vials were labeled and sealed for subsequent pesticides analysis. The pesticides samples were analyzed by gas chromatography.

Organo chlorine pesticide residues analysis

The analysis of pesticide residues were conducted in Perkin Elmer Clarus-500 Gas Chromatograph. The details of which are given in Table 2.

RESULTS AND DISCUSSION

The seawater samples were analyzed for the detection of organochlorine pesticides (OCPs). The commercially available pesticides considered for this research were Hexachlorocyclohexane (HCH), Heptachlor, Aldrin, Dieldrin, Endrin, Endosulfan, Transchlordane, p,p′-DDT and Methoxychlor. These are highly persistent pesticides and remain in the environment but can be transformed. Their transformation deviate them from target and affect other species of the ecosystem hence cause trouble for all other organisms. The descriptive analysis of pesticides residues is shown in Table 3 and 4.

Hexachlorocyclohexane is commonly available as technical grade used together with Lindane in agricultural fields. Both are used in combination to have greater affect against pests of livestock, seeds, forestry and food products (Kang and Cheng, 2015). The HCH levels found in sea water in 2017 are in a range of 0.51 to 0.76 µg/L with a mean of 0.66 µg/L. The highest concentration was found from site near Chinna creek. However, in 2018, the average value declined to 0.56 µg/L with a maximum concentration of 0.72 µg/L (S-1, S-8) and minimum of 0.36 µg/L (S-10). Similar findings have also been reported recently in a study where the concentrations of α-HCH was in a range of 0.013-0.776 µg/L, γ-HCH in between 0.033 and 0.419 µg/L) while δ-HCH was <0.010-0.059 µg/L in Lake Naivasha, Kenya (Madadi *et al*., 2017). However, in Japan, the Blubber samples of spotted seals contained high levels of HCH and its isomer that indicates the contamination of food chain (Trukhin and Boyarova, 2020).

Table 1. Description of sampling sites.

Sample	**Latitude °N**	**Longitude °E**	**Area**
S-1	24.843684	66.793658	Arabian Road
S-2	24.859959	66.836882	Jamali Goth
S-3	24.843777	66.900465	Kakapir
S-4	24.797249	66.967858	Manora
S-5	24.815324	66.974437	Kemari Basin
S-6	24.849118	66.975794	Karachi Fish Harbour
S-7	24.844181	66.991664	Under Native Jetty Bridge
S-8	24.841153	66.998628	Channa Creek (near Lalazar)
S-9	24.820482	67.017941	Boat Basin
S-10	24.802205	67.079315	Creek Avenue (near Ghizri Creek)

Table 2. Operating conditions of the gas chromatograph.

S.No.	Parameters	Characteristics
1	System	Perkin Elmer 500
2	Detector	Electron capture
3	Column	DB-5 fused silica capillary column (30 m length 0.32 mm i.d.× .25 µm film thickness)
4	Carrier gas	Nitrogen (99.99%)
5	Carrier gas pressure	10.5 psi
6	Injector temperature	2000C
7	Injection	2 µL
8	Detector temperature	3200C
9	Temperature programme	Initial temp 1800C at a rate of 40C min to 1000C (held for 5 min), then at a rate of 500C/min to 3000C

Table 3. Descriptive statistics of the commercially available pesticides (µg/L) found in the sea water of Karachi coastal area (2017), (Mean ± S.E).

2017	Pesticides (µg/L)								
	HCH	Hepta-chlor	Aldrin	Dieldrin	Endrin	Endosulf-an	Trans chlordane	4,4-DDT	Methoxy chlor
S-1	0.67±0.01	0.69±0.09	0.15±0.02	0.38±0.04	0.04±0	0.73±	0.26±0.02	0.40±0.01	0.00±0
S-2	0.65±0.02	0.56±0.12	0.46±0.02	0.17±0.09	0.00±0	0.65±0.02	0.33±0.02	0.00±0	0.00±0
S-3	0.73±0.04	0.00±0	0.28±0.01	0.49±0.02	0.21±0.03	0.54±0.02	0.22±0.01	0.00±0	0.28±0.01
S-4	0.68±0.01	0.61±0.08	0.22±0.02	0.43±0.10	0.60±0.45	0.73±0.03	0.22±0.03	0.62±0.04	0.27±0.01
S-5	0.74±0.03	0.66±0.10	0.33±0.02	0.28±0.01	0.00±0	0.88±0.02	0.00±0	0.52±0.02	0.29±0.01
S-6	0.63±0.08	0.57±0.13	0.44±0.02	0.36±0.02	0.24±0.02	0.84±0.05	0.00±0	0.76±0.02	0.26±0.01
S-7	0.67±0.03	0.54±0.14	0.36±0.02	0.41±0.01	0.00±0	0.73±0.03	0.33±0.02	0.00±0	0.27±0.03
S-8	0.76±0.07	0.00±0	0.27±0.01	0.00±0	0.19±0.01	0.67±0.02	0.00±0	0.40±0.01	0.36±0.01
S-9	0.51±0.10	0.50±0.09	0.36±0.02	0.59±0.04	0.15±0.03	0.67±0.03	0.31±0.01	0.00±0	0.45±0.01
S-10	0.51±0.08	0.68±0.05	0.33±0.02	0.29±0.01	0.00±0	0.92±0.02	0.28±0.03	0.92±0.02	0.30±0.01
Min	0.51	0	0.15	0	0	0.54	0	0	0
Max	0.76	0.69	0.46	0.59	0.6	0.92	0.33	0.92	0.45
Mean	0.66	0.48	0.32	0.34	0.14	0.74	0.20	0.36	0.25
Std. Dev	0.09	0.26	0.09	0.17	0.19	0.12	0.14	0.35	0.14

The two years pesticide estimation show heptachlor concentration in seawater as 0.48 µg/L and 0.69 µg/L for 2017 and 2018, respectively. The maximum of two year analysis was found to be 0.91 µg/L from the site S-3 adjacent to Kakapir from 2018 but surprisingly, this pesticide was not found in 2017 i.e. 0 µg/L from this site. Levels of heptachlor in water were below the WHO maximum allowable limits for surface water Nairobi, Kenya (Ndunda *et al*., 2018). Heptachlor is also found as 0.023-0.055 µg/L in shallow aquifer of Semarang coastal areas (Rochaddi *et al*., 2018). A recent study shows heptachlor degrading microorganism (Strain H) can degrade it up to 88.2% under neutral to slightly alkaline pH (Qiu *et al*., 2018) which can also be applied in our study area on large-scale.

Aldrin and Dieldrin are not likely to be associated with human carcinogenicity (van Amelsvoort *et al*., 2009). In 2017, the maximum levels of Aldrin were found as 0.46 µg/L and minimum as 0.15 µg/L whereas in 2018, this pesticide was in a range of 0.27 to 0.73 µg/L. The average concentration of Dieldrin is estimated as 0.38 µg/L and 0.34 µg/L from 2018 and 2017, respectively. Another study conducted to estimate OCPs show 0.001 to 2.42 ng/L for cyclodienes (Aldrin, Dieldrin, Endosulfan I, and Endosulfan II) Tiber River Italy (Montuori *et al*., 2016). Endrin pesticide is absent from four sites i.e. S-2, S-5, S-7 and S-10 in 2017 with an average value of 0.14 µg/L but in 2018, these mentioned sites become contaminated except S-10. The average concentration in 2018 was recorded as 0.13 µg/L. There exist researches on microbe assisted degradation of Aldrin and Dieldrin and discussed that the degradation rate is faster by fungi as compared to bacteria (Purnomo, 2017).

The endocrine disruptor Endosulfan is a persistent organic pollutant presents at all the sampling locations along Karachi coastal waters with an average concentration of 0.55-0.82 µg/L in 2018 and 0.54-0.92 µg/L in 2017. Creek avenue samples reported highest values of Endosulfan. Riaz *et al*. (2018) also reported Endosulfan presence in Pakistan and Agnaou *et al*. (2018) from Agadir Bay Morocco. Endosulfan cause neurological disorders with low sensorium, seizures and other organs toxicity including hepatic transaminase elevation, leukocytosis, metabolic acidosis and azotemia (Moses and Peter, 2010).

The oral and dermal exposure to chlordane can cause serious human health effects that include nervous, respiratory, digestive system disorders and affect liver (ATSDR, 2018). The estimation of transchlordane for the year 2018 shows the range of 0 to 0.65 µg/l and an average of 0.25 µg/L while 2017 reported 0 to 0.33 µg/L and an average of 0.20 µg/L slightly lower than 2018. Eqani *et al*. (2012) detected lower values of chlordane as compared to our study.

The banned pesticide DDT was declared as probable human carcinogen by International Agency for Research on Cancer (IARC, 1991) but it is still available in market by different brand names (Khwaja *et al*., 2006). The highly persistent DDT was found in a range of 0 µg/L (S-2, S-3, S-7) to 0.92 (S-10) µg/L in 2017 and 0.44 µg/L (S-1) to 0.68 µg/L (S-6) in 2018. Lower levels of this compound either indicates the conversion of DDT to DDE or pointing towards the less usage in recent years. Siddiqi *et al*. (2017) found DDT in fishes from marine environment of Karachi that shows the risk of food chain with this pesticide. However, similar finding i.e. 1 µg/L DDT from water samples near disposal sites at Kyrgyzstan has also been reported (Toichuev *et al*., 2018).

Methoxychlor is banned due to its greater toxicity i.e. LC_{50} is around 10 µg/L for fishes and less than 1 µg/L for invertebrates that are the most sensitive group (HSDB, 2009; USEPA 2019). But it is still detected in south Asian and African countries (Nerves *et al*., 2018; Zeng *et al*., 2018; Luo *et al*., 2016). The mean concentration of methoxychlor was found as 0.25 and 0.42 µg/L for 2017 and 2018, respectively. In a recent, comparatively lower concentration can be seen from North Pacific Ocean that reported 0.001 µg/L (Gao *et al*., 2019). However, it has stated that methoxychlor is used as an alternative for p,p'-DDT and its usage has been increased after the strict ban of DDT specially in developed world (Oh, 2009).

Table 4. Descriptive statistics of the commercially available pesticides (µg/L) found in the sea water of Karachi coastal area (2018), (Mean ± S.E).

2018	Pesticides µg/l								
	HCH	Hepta-chlor	Aldrin	Dieldrin	Endrin	Endosulf-an	Transch-lordane	4,4-DDT	Metho-xychlor
S-1	0.72±0.03	0.71±0.01	0.27±0.01	0.54±0.01	0.00±0.0	0.62±0.03	0.23±0.01	0.44±0.05	0.65±0.03
S-2	0.49±0.03	0.64±0.02	0.36±0.02	0.55±0.01	0.25±0.02	0.70±0.04	0.00±0.0	0.63±0.02	0.45±0.10
S-3	0.65±0.03	0.91±0.03	0.73±0.06	0.47±0.04	0.00±0.0	0.82±0.03	0.47±0.03	0.60±0.03	0.48±0.11
S-4	0.50±0.02	0.85±0.01	0.46±0.02	0.39±0.03	0.31±0.0	0.62±0.08	0.00±0.0	0.64±0.05	0.51±0.10
S-5	0.57±0.01	0.64±0.01	0.51±0.03	0.26±0.02	0.20±0.1	0.70±0.02	0.26±0.02	0.52±0.04	0.52±0.10
S-6	0.55±0.02	0.48±0.04	0.61±0.04	0.35±0.02	0.07±0.07	0.68±0.04	0.00±0.0	0.68±0.02	0.00±0.0
S-7	0.64±0.04	0.67±0.01	0.46±0.05	0.25±0.02	0.22±0.01	0.65±0.04	0.25±0.01	0.64±0.04	0.37±0.03
S-8	0.72±0.04	0.77±0.04	0.49±0.01	0.32±0.02	0.25±0.02	0.68±0.03	0.34±0.01	0.58±0.03	0.56±0.05
S-9	0.42±0.04	0.54±0.01	0.49±0.01	0.45±0.04	0.00±0.0	0.55±0.02	0.34±0.01	0.67±0.05	0.35±0.06
S-10	0.36±0.02	0.69±0.01	0.63±0.05	0.23±0.01	0.00±0.0	0.71±0.01	0.65±0.06	0.64±0.01	0.31±0.04
Min	0.36	0.48	0.27	0.23	0	0.55	0	0.44	0
Max	0.72	0.91	0.73	0.55	0.31	0.82	0.65	0.68	0.65
Mean	0.56	0.69	0.50	0.38	0.13	0.67	0.25	0.60	0.42
Std. Dev	0.12	0.13	0.13	0.12	0.13	0.07	0.21	0.07	0.18

Spatial distribution of pesticides at Karachi coast

The application of GIS allowed us to interpolate the spatial distribution of pesticide pollution along the Karachi coast where minimum levels were found at S-1, S-2, S-3, S-5 and S-7 (Fig.2). These sites show less contamination from obsolete pesticides in two-year average recorded in 2017 and 2018. The highest concentration was observed to be from Creek Avenue site (S-10), where mean Endosulfan levels were found as 0.82 µg/L. The same site reported higher levels of DDT and transchlordane. This location is at Malir River which carries most of the agricultural run-off containing pesticides, also confirmed by Rahman *et al*. (2018). HCH and Methoxychlor were detected to be the highest average from Channa Creek while Heptachlor near Manora. Channa creek is observed to be a site near many chemical plants including pest control chemicals so it could be one reason of contamination at this site but effluent from Liyari River must be considered as the other source of pollution. Aldrin, Dieldrin and Endrin were found in a concentration of 0.53 (S-6), 0.52 (S-9) and 0.46 (S-4). The samples get from Manora (S-4) is nearby many industries that discharge their effluent directly into the sea and agricultural discharge as well from Liyari River whereas Karachi Fish Harbor (S-6) is reportedly the highly polluted area that shows all types of physicochemical pollution in the past years.

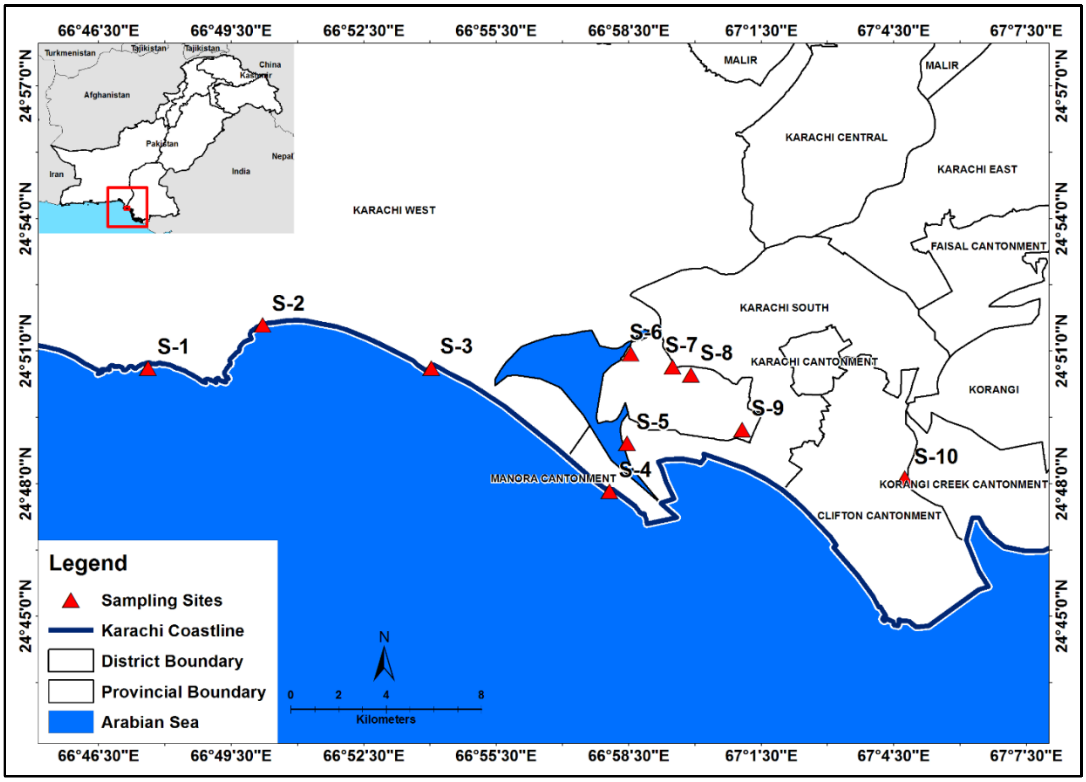

Fig. 1. Study area map of Karachi coast.

Impacts of OCPs in living organisms

Living organisms can get the entry of OCPs from skin, lungs and absorption through gut wall depending on the pesticide. For instance, few OCPs like HCH, Endosulfan, Lindane can pass through the skin but DDT, Methoxychlor, Mirex, etc have less absorption (Subramaniam and Solomon, 2006; Costa, 2008). It has also been reported that the gastrointestinal tract can also absorb lipophilic OCPs mainly due to the consumption of vegetable oils and fats. The organisms at higher trophic levels such as mammals have a greater chance of increased accumulation of OCs in their bodies because of more consumption through the food chain (Dierauf, 2001). These compounds are reported to interact with endocrine hormones i.e. estrogen and androgen and disturb them. The poisoning may produce symptoms like nausea, vomit, headache, dizziness, tremors, mental inability and confusion (Dierauf, 2001). Geric *et al*., (2012) is reported to do cytogenetic investigations for exposure to DDT in humans. Organochlorine compounds not only affect the central nervous system but also cancer is observed to be associated with the human exposure of OCPs such as DDT, HCH and Dieldrin (Xu *et al*., 2010). Different studies conducted to demonstrate the exposure of DDT and associated health risks including cancers and malignancies (Wong *et al*., 2015; Han *et al*., 2010; Diel *et al*., 2002).

Remedial options

Humans and natural environments are adversely disturbed by pesticide release in the water bodies (Zhou *et al*., 2015). The entrance of pesticide in aquatic ecosystem can be through spray, run off, leaching and subsurface drainage (Cosgrove *et al*., 2019). However, worldwide attention is towards the safe removal of pesticides from environment. There present physical and chemical options of pesticide treatment from water bodies that include adsorption, membrane filtration and advance oxidation process while biological removal involves the process of bioremediation, phytoremediation and activated sludge system and many others (Mojiri *et al*., 2019). Adsorption is, however, a good option if a low coast material is used for pesticide removal from an aqueous solution specifically for industrial wastewater to lessen the persistent organic and inorganic contaminants (Yagub *et al*., 2014). But these technologies have some constrains in terms of flexibility, time consumption, cost, efficacy and waste or by-products (Shamsollahi and Partovinia, 2019).

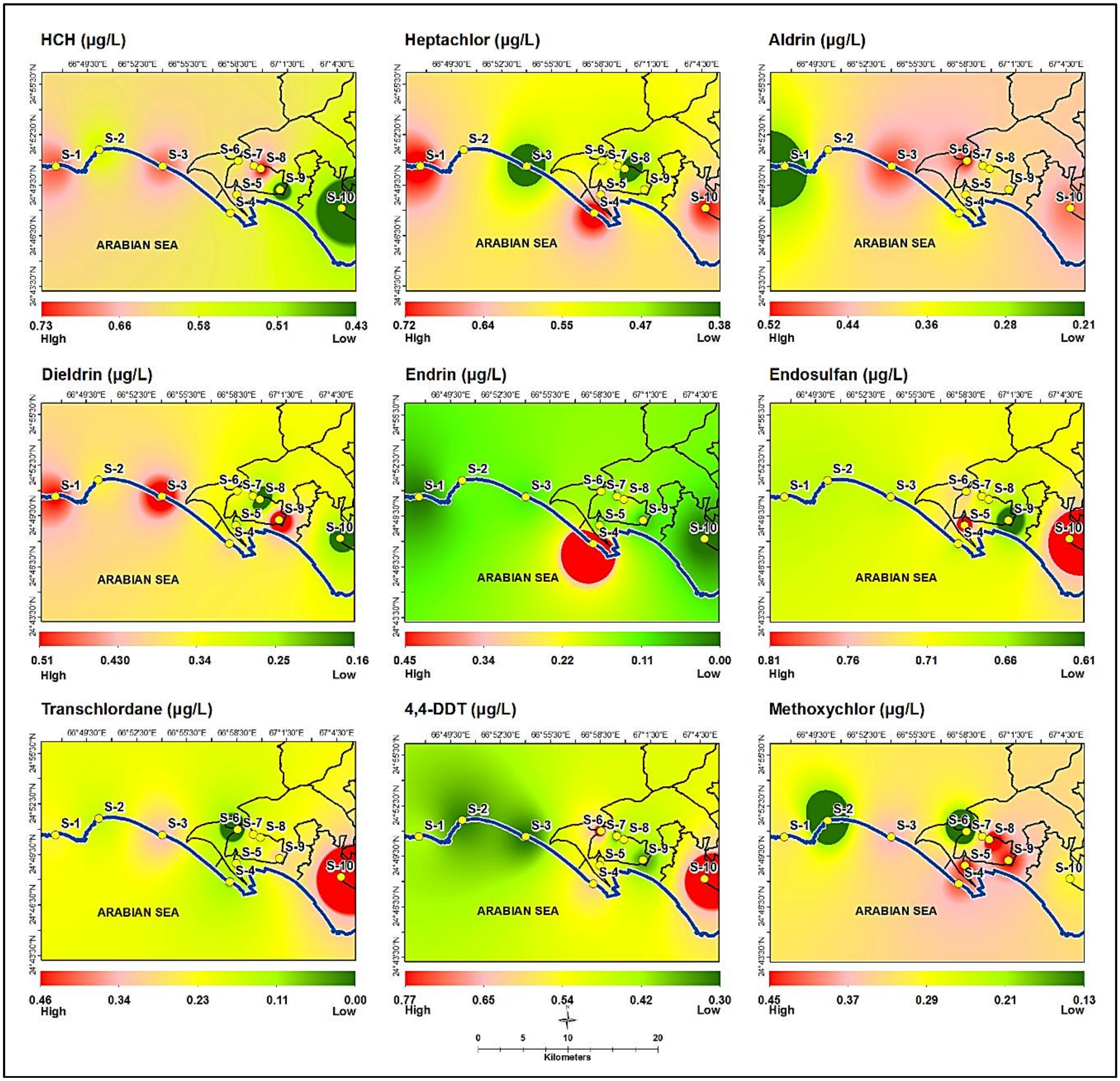

Fig.2. Spatial distribution of pesticides along Karachi coast, an average of 2017-18 in µg/L.

Conclusion

The presence of banned organochlorine pesticides in sea water indicates towards illegal usage of such compounds for agricultural purposes. The contamination is mainly from agricultural lands that discharge the effluents directly into sea. The OCPs are usually applied on vegetable crops hence threatening the public health quality. Strict regulations are required to stop trading and usage of banned pesticides in Pakistan to avoid vegetable contamination with these highly toxic persistent compounds.

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