INNSPUB

Journal of Biodiversity and Environmental Sciences (JBES)
ISSN: 2220-6663 (Print) 2222-3045 (Online)
Vol. 9, No. 4, p. 50-60, 2016
http://www.innspub.net

RESEARCH PAPER OPEN ACCESS

Synoptic survey of organochlorine pesticides in coastal waters of Sindh and Balochistan, Pakistan

Monawwar Saleem*[1], Arshad Ali Khan[1], Muhammad Qammaruddin[2], Syed Waseem Haider[1], Sanober Kahkashan[1], Syed Imran Hasany[1], Javed Aftab[1], Mohsin Muzaffar[1]

[1]*National Institute of Oceanography, Clifton, Karachi, Pakistan*

[2]*Center of Excellence in Nanotechnology (CENT),*

King Fahd University of Petroleum and Minerals (KFUPM), Dhahran, Saudi Arabia

Article published on October 30, 2016

Key words: Organochlorine pesticides, Karachi coast, Balochistan coast, Korangi, Gharo and Gizri creek.

Abstract

A survey of sixteen organochlorine pesticides (OCP's) was conducted for their contamination status and spatial distributions in coastal waters of Karachi and four cities of Balochistan. Thirty nine surface seawater samples were collected from the Karachi coast (Karachi west coast and off-Clifton), creeks of Karachi (Gizri, Korangi and Gharo creeks) and four Balochistan coastal cities (Jiwani, Gwadar, Pasni and Ormara). DDT, HCH and its metabolites were found most dominating while Endrin, Dieldrin and Aldrin aldehyde were recorded higher among the 16 monitored pesticides in Karachi and Balochistan coastal waters. The present results were compared with water quality criteria as set by USA-EPA, which shows that OCPsin Balochistan and Karachi coastal waters were found under the limits. Results of some of these pesticide concentrations (i.e. Heptachlor epoxide, Endrin, Dieldrin and Endosulfan I & II) from the Karachi coast are found close to chronic levels for marine organisms when compared to marine water quality criteria set by New-Jersey State, USA. The diagnostic ratio of DDT and HCH metabolites shows that HCH is still being used around the study area, while DDT is currently used in Jiwani, Gwadar and Pasni coastal areas. A survey indicates that the chlorinated pesticides in the studied coastal areas are still very low except in the Off-Clifton coast and western coastal waters of Karachi, which is mostly domestic and industrial originated.

***Corresponding Author:** Monawwar Saleem ✉ monawwars@gmail.com

Introduction

Organochlorine pesticides are synthetic chemicals with persistent, bio-accumulative and toxic characteristics. As these pesticides are most toxic and harmful, even in a very small quantity to humans and animals, production and application of these chemicals were banned during 1960s and 1970s in developing countries. The Government of Pakistan banned these pesticides in the early 1990s; however, these chemicals are still being used for agricultural and health control programs in many countries, including Pakistan (Daily DAWN, 2007; Ali *et. al*., 2014). Most common of these are DDT, Aldrin, Chlordane, Dieldrin, Endrin, Heptachlor and Toxaphene. These hydrophobic compounds are mainly stored in fat tissues of organisms and when fats are mobilized, the toxic substances enter into the circulatory system, causing disturbance in the organism's normal body physiology (Winter *et al*., 1992). Generally, organochlorine pesticides have caused extensive concerns for a long time due to their strong lipophilic properties, persistent in the environment due to slow degradation process which leads to accumulating in the food chain (Yang *et al*., 2013) and sediments Yang *et al*., 2005. Organochlorine pesticides are persistent and semi-volatile with a low vapor pressure, and soluble in water. Therefore, they get transported easily and deposited over long distances (Weber *et al*., 1990). DDT can be found everywhere. Organochlorine pesticides are detected in almost all of the environmental components, i.e., air, water, sediments, soil, fruits, vegetables, animals and humans. Organochlorine pesticide residue was found in the sediments, in the Antarctic lakes (Sarkar *et al*., 1994) and Li and Xiao observed it in Mount Everest (Himalayas) air and ice core samples (Li *et al*., 2006, Xiao *et al*., 2008). Recently, Devi observed organochlorine pesticide residue in the soil samples in the Indian Himalayan Region (Devi *et al*., 2015).

Chlorinated pesticides had been extensively used in Pakistan for protection of cotton crops till 1993, when the government of Pakistan imposed ban over it.

After banning these obsolete pesticides about 2016 tons of these were stored in different places of Sindh province. The biggest dump was stored in Malir, Karachi that contained about 400 tons of obsolete pesticides. The half quantity of these obsolete pesticides has been stolen from the Malir store (Khan, 2001). These pesticides are still illegallybeing used by farmers in remote areas for the eradication of insects due to their low prices and effectiveness (Altaf*et al*., 2015). Aijaz reported that Pakistan imported 78,133Metric tons (MT) of pesticides in 2003 and these pesticides belong to organophosphate, organochlorine and pyrethroid groups, while in the same year sales of Endosulfan were 117.98 MT in Pakistan (Aijaz *et al*., 2008). According to GEF and UNDP project, 2015, the Government of Pakistan POPs inventory report, till 2005 in Balochistan, a large quantity of the POPs pesticides (obsolete) have been reported in the stores of the public sector departments in Quetta (49 MT), Pangur (102 MT) and Turbat (94 MT).

The Karachi coastal area receives more than 550 million gallons per day (MGD) of domestic and industrial wastewater primarily through the Lyari and Malir Rivers, and a small amount through streams and small drainages around the coastal areas. According to Karachi Water and Sewerage Board (KWSB) only 5-8% of waste water is being treated from two treatment plants located on Malir and Lyari Rivers (KWSB, 2014). The populations of the four studied coastal cities of Balochistan were less than 100 thousand each and all of the domestic wastes were being dumped without treatment in the related coastal areas.

Only few studies have been conducted regarding the chlorinated pesticides in surface seawater in Sonmiani Damb, Balochistan and the Karachi Harbour (Saleem *et al.,* 2013, 2014). Traces of these pesticides were found in human foods and marine biota of Karachi coast (Munshi *et al*., 2004, Hina *et al*., 2013 and Sanpra *et al*., 2003).

The objective of the present work is to study the contamination status of chlorinated pesticides in coastal surface water for assessing the environmental and ecological risk as a contribution to the knowledge and rational management of the Karachi coastal area and its surrounding regions in the future.

Materials and methods

Sample collection

Surface seawater samples were collected (in precleaned four liter amber glass bottles) from sixteen stations in four coastal cities (Jiwani, Gwadar, Pasni and Ormara) of Balochistan coast (Fig. 1). The samples from Jiwani, Gwadar, Pasni and Ormara were collected from 3, 6, 3 and 5 sampling sites, respectively. All samples were collected during 16-22 June, 2007 using a fisherman boat. Samples could not be collected from off-shore Gwadar stations by boat due to bad weather condition, therefore; collection was made along the coast. The sampling bottles were stored in an icebox at 4°C, reaching the laboratory on the same day, and were normally extracted on the next day of sampling. Twenty three surface seawater samples were collected from Karachi coast using a fisherman boat. Ten samples were taken on 25thSeptember 2007 from Gizri, Korangi and Gharo creeks from 2, 3,and 5 stations, while from eight stations of Karachi west coast and five stations fromOff-Clifton coast on 12th and 14th February, 2008 respectively.

Chemicals

Solid Phase Micro extraction (SPME) holder and fiber assemblies for manual sampling were provided by Supelco (Germany) and used without modification. The fiber coating assayed was polydimethylsiloxane (PDMS, 100 µm). A pesticide calibration mix (10 to 60µg/ml in methanol) was purchased from Supelco (Germany). Individual pesticides for peak identification were also acquired: p, p-DDE,p, p-DDD Endrin, Endosulfan-I Endosulfan-II, Endosulfan sulfate, α-BHC), β-HCH, γ-HCH, δ-HCH, Endrin aldehyde, Aldrin, Dieldrin, DDT, Heptachlor, Heptachlor epoxide (all 20 µg/ml in methanol) were purchased from Supelco (Germany).

Solvents used were methanol, acetone (Absol grade, Tedia USA) and water (HPLC grade, Tedia chemical). The high purity nitrogen gas (99.999%) for the GC carrier was obtained from a local supplier (BOC, Pakistan).

Extraction of seawater samples

There were two different techniques of extraction used, liquid-liquid extraction (Sepratory funnel) and solid phase micro-extraction (SPME). All samples from Balochistan coastal cities and from creeks of the Karachi coast were used by liquid-liquid extraction USA-EPA method 3510. Extracted samples were dried with anhydrous sodium sulphate and concentrated through vacuum rotary evaporation and followed by cleanup USA-EPA method 3620C. Finally extracted solvent was dried to evaporate by the stream of nitrogen gas (N-5 grade) and concentrate to 2 ml. Duplicate samples were analyzed in each case. SPME techniques were used only for the samples of Karachi west coast and Off-Clifton coast.

SPME techniques

The analysis of pesticides was based on the SPME procedures described in Saleem *et al*., 2013. Before measurements the PDMS fiber was conditioned in the injection port for 1 h at 260^0 C, with the split vent open to fully remove any contaminant that might have caused very high baseline noise and large ghost peaks. The fiber was then repeatedly injected into the GC system until interfering peaks disappeared. Samples and standard were extracted on fiber which were absorbed as per instrument oven and injector programmed described below.

GC analysis

A Gas Chromatograph Agilent model 6890N with a micro-cell electron capture detector (µECD) and Chemstation software was used for the analysis of organochlorine pesticides in seawater samples. The capillary column used for the analyses was an Altech AT™-5(30 m × 0.25 mm id × 0.25 µm film thickness).

The oven temperature was programmed from 120 °C for 1 min, then heated to 180°C at 30°C min⁻¹, then heated to 290°C at 10°C min⁻¹ and held at 290°C for 7 min. The carrier gas was Nitrogen (1.4 ml min⁻¹). The injector temperatures were 260°C.

Quantification of the samples was carried out by peak area using the external standard calibration. A calibration curve was obtained with pesticide standards in the range from 5 to 10ng/ml, extracted under the same conditions as the real samples. The concentrations of the detected pesticides were the average values of three measurements.

Results and discussion

Spatial distribution of chlorinated pesticides in Karachi and Balochistan coastal waters

The results of the thirty nine stations, samples of chlorinated pesticides means, ranges and spatial distribution in four Balochistan coastal cities (Jiwani, Gwadar, Pasni and Ormara), Karachi west coast, Off-Clifton coast and Karachi creeks' water are given in Table1, 2, 3 respectively. Averages of each site are given in Table 4. The results of the organochlorine pesticides in Off-Clifton coast (β-HCH, and δ-HCH),

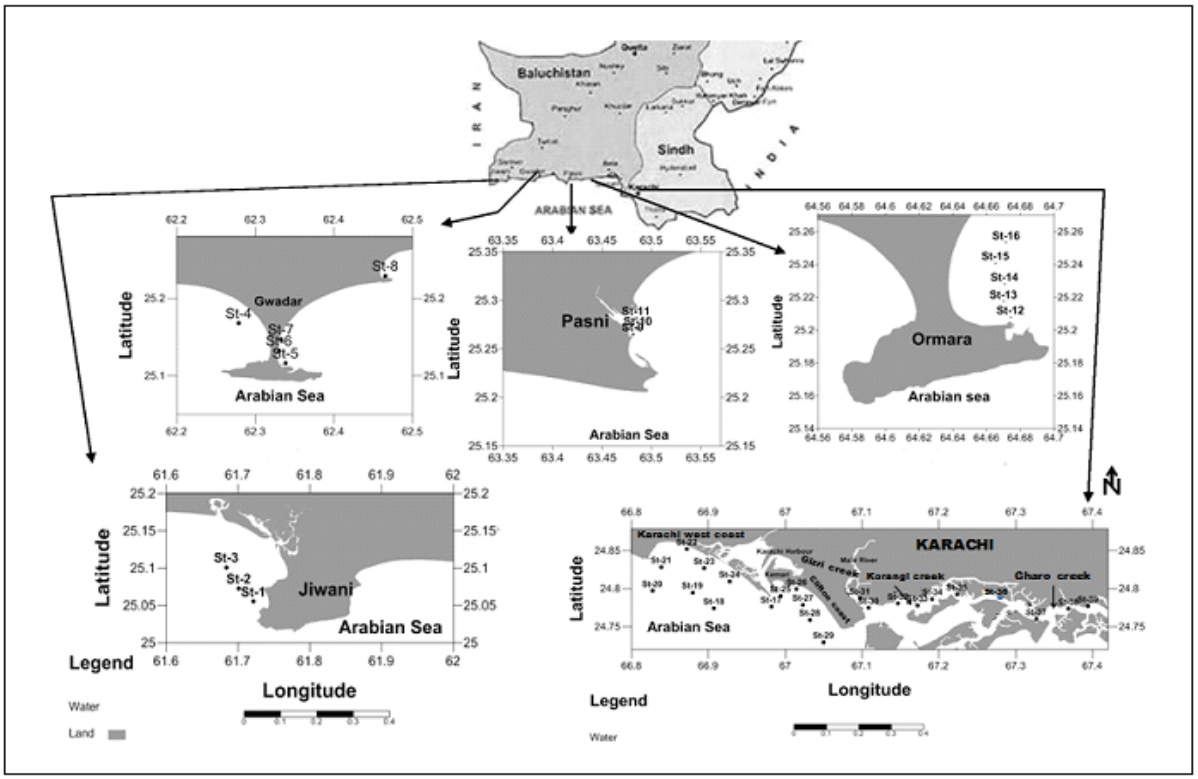

Fig. 1. Map of study area and shown the location of sampling sites.

Cyclodiene (including Endrin, Endrin aldehyde, Endosulfan-1, and Endosulfan sulphate) and DDT, its residue (p,p-DDE, p,p-DDD) was found highest in studied coastal area, while α-HCH, γ-HCH, Heptachlor, Heptachlor epoxide, dieldrin, Aldrin and Endosulfan-II were found highest in Karachi west coast.

The concentrations and averages of ΣHCH (including α-HCH, β-HCH, γ-HCH, δ-HCH), ΣDDT (including p,p-DDE, p,p-DDD) and Σ Cyclodiene (including Heptachlor, Heptachlor epoxide, Aldrin, Dieldrin, Endrin, Endrin aldehyde Endosulfan-1, Endosulfan-II, Endosulfan sulphate), in each site of seawater are given in Table-4. Ranges of ΣHCH, ΣDDT and ΣCyclodienein Balochistan coastal cities, Karachi west coast, Off-Clifton coast, and Creeks of Karachi were 1.4–140.43, 1.59–105.24 and 1.8–195.68 mg/l, respectively (Table4).

The contamination levels of ΣHCH and Σ Cyclodiene in seawater samples in present studied sites were found in the following order: Karachi West coast>Off-Clifton coast>Balochistan coastal cities>Karachi creeks. The contamination levels of ΣDDT were found in the following order Off-Clifton coast>Karachi West coast> Balochistan coastal cities>Karachi creeks (Table4).

The results indicate that the HCH's and DDT's were predominant contaminants in the surface seawater samples.

Table 1. Concentration and distribution of chlorinated pesticides in seawater (ng/L) of Balochistan coastal cities.

	Jiwani			Gwadar					Pasni			Ormara				
Chlorinated pesticides	St-1	St-2	St-3	St-4	St-5	St-6	St-7	St-8	St-9	St-10	St-11	St-12	St-13	St-14	St-15	St-16
Alpha-HCH	1.90	0.06	0.04	1.00	0.07	2.19	0.59	1.11	0.03	ND	0.04	0.14	0.09	0.05	0.04	0.06
Beta-HCH	1.60	0.38	0.45	2.41	0.73	4.68	5.01	6.52	0.30	1.79	0.26	0.39	0.26	0.06	0.15	0.28
Gamma-HCH	1.53	0.84	1.08	0.31	0.36	ND	0.34	ND	0.78	1.50	0.99	0.68	1.55	0.40	0.99	1.15
Delta-HCH	0.32	0.29	0.27	1.01	1.38	2.24	2.16	2.05	0.16	0.17	ND	0.20	0.16	ND	ND	0.36
Heptachlor	0.83	0.73	0.79	1.43	1.31	2.15	1.19	1.67	0.73	0.89	0.56	0.67	2.18	1.26	0.88	1.00
Heptachlor Epoxide	ND	ND	ND	0.12	ND	ND	0.12	0.55	ND	ND	ND	ND	ND	ND	ND	0.38
Aldrin	0.15	0.08	0.06	0.09	0.19	0.22	0.24	0.11	0.05	ND	0.05	0.05	0.20	0.06	0.16	0.07
Dieldrin	1.46	1.73	1.68	0.87	1.81	3.18	1.62	2.05	1.02	1.01	1.15	0.93	0.82	0.38	1.03	2.13
Endrin	ND	0.61	0.63	1.03	1.15	1.35	0.67	0.64	0.57	0.65	0.58	0.68	0.59	0.61	0.54	0.67
Endrin aldehyde	9.57	4.61	8.77	1.19	1.16	5.75	5.90	4.94	0.76	0.89	3.26	ND	ND	ND	ND	0.55
Endosulfan-I	1.03	0.13	0.15	ND	0.21	ND	N.D	ND	0.12	0.19	ND	ND	0.20	ND	0.15	0.20
Endosulfan-II	2.19	ND	ND	ND	0.74	ND	1.64	ND	ND	ND	ND	ND	ND	ND	ND	ND
Endosulfan sulfate	5.44	ND	ND	2.13	0.42	10.44	6.40	2.50	ND	3.46	ND	ND	ND	ND	ND	ND
4,4-DDE	1.22	1.73	1.75	2.93	2.91	4.01	2.51	3.00	1.68	2.00	1.28	1.63	5.62	3.06	3.52	1.82
4,4-DDD	0.84	ND	ND	ND	ND	ND	N.D	ND	ND	ND	0.04	ND	ND	ND	ND	ND
4,4-DDT	6.97	5.50	4.70	2.09	11.73	5.22	4.01	7.66	7.94	7.11	4.56	0.79	1.80	0.51	1.52	2.06

ND* # not detected.

The β-HCH, δ-HCH were found in most of the sampling sites, followed by DDT and 4, 4-DDE. The highest mean concentrations of β-HCH, δ-HCH, and 4,4 DDT, 4,4-DDE were 59.01, 55.57 and 41.30, 30.25 ng/lrespectively in Off-Clifton coast, most probably because this area receives massive amounts of partially treated waste water (about 350 million gallons per day Lyari River via Karachi Harbour) including sewage and industrial boat and shipping wastes. Wastewater from city includes persistent insecticides which may bestolenobsolete pesticides which are being used illegally in Karachi as domestic insecticides (Ahmer, 2001).

Table 2. Concentration and distribution of chlorinated pesticides in coastal water (ng/L) Off-Karachi west coast and Off-Clifton Coast.

	Off-Karachi West Coast								Off-Clifton Coast				
Organochlorine pesticides	St-17	St-18	St-19	St-20	St-21	St-22	St-23	St-24	St-25	St-26	St-27	St-28	St-29
Alpha-HCH	43.8	43.9	33.7	34.7	61.7	8.5	64.3	20.1	ND	ND	ND	ND	ND
Beta-HCH	6.3	3.4	ND	ND	25.0	ND	32.8	ND	55.2	62.2	66.3	56.0	55.3
Gamma-HCH	ND	21.6	36.2	49.3	75.4	34.1	68.9	19.2	ND	20.4	51.7	38.4	4.1
Delta-HCH	47.1	39.9	54.2	76.0	50.5	52.4	72.8	47.7	55.9	52.1	60.2	44.3	65.4
Heptachlor	ND	2.0	1.7	4.6	18.6	4.0	9.3	4.9	5.5	ND	ND	ND	ND
Heptachlor epoxide	ND	ND	6.1	21.5	ND	ND	32.9	ND	21.3	ND	ND	ND	ND
Aldrin	ND	ND	4.8	3.8	8.5	ND	28.9	2.8	21.3	6.5	5.5	ND	ND
Dieldrin	57.8	76.5	86.6	61.2	6.5	ND	33.2	ND	26.6	16.9	ND	ND	ND
Endrin	ND	ND	ND	ND	30.6	ND	ND	ND	32.4	26.2	26.0	ND	22.1
Endrin aldehyde	ND	ND	18.9	33.0	35.9	33.2	ND	ND	ND	ND	ND	ND	ND
Endosulfan-I	ND	ND	ND	ND	34.0	19.8	29.5	ND	37.9	40.7	49.8	7.1	36.9
Endosulfan-II	53.5	76.8	66.8	55.0	50.2	65.2	42.8	63.3	ND	ND	ND	ND	ND
Endosulfan sulfate	87.2	66.6	64.6	ND	79.2	ND	ND	83.6	98.9	66.2	77.4	73.6	74.3
4,4-DDE	ND	ND	ND	ND	56.1	52.3	32.8	35.8	32.2	20.6	34.9	37.2	26.4
4,4-DDD	ND	15.1	47.0	37.3	46.0	42.6	ND	39.9	40.6	54.8	29.6	18.5	25.0
4,4-DDT	ND	ND	ND	ND	ND	ND	22.0	ND	45.9	55.2	34.4	18.3	52.7

ND # Not Detected.

Table 3. Concentration and distribution of chlorinated pesticides in Karachi Creeks water (ng/L).

	Gizri Creek		Korangi Creek			Gharo Creek				
Organochlorine pesticides	S-30	St-31	St-32	St-33	St-34	St-35	St-36	St-37	St-38	St-39
Alpha-HCH	0.05	0.10	0.08	ND*	ND	0.16	ND	ND	0.45	0.14
Beta-HCH	0.06	1.34	0.67	0.33	ND	0.06	ND	0.16	0.77	0.44
Gamma-HCH	0.67	0.52	0.78	1.21	0.98	0.83	0.76	0.60	1.48	0.76
Delta-HCH	ND	0.37	0.18	0.28	0.22	0.44	0.09	0.64	0.21	0.49
Heptachlor	1.76	4.16	0.37	0.67	0.40	0.08	0.06	0.22	0.17	0.33
Heptachlor Epoxide	0.21	ND	0.15	0.09	ND	ND	ND	ND	ND	ND
Aldrin	0.30	0.13	0.05	0.10	0.09	ND	ND	ND	0.15	0.07
Dieldrin	0.63	0.90	0.60	0.66	0.48	0.24	0.16	ND	ND	0.35
Endrin	0.33	0.31	0.46	0.32	ND	1.33	0.36	ND	ND	ND
Endrin aldehyde	ND	5.79	0.21	ND	ND	ND	ND	ND	5.25	0.57
Endosulfan-I	ND	0.05	0.34	0.06	0.10	0.07	ND	ND	0.12	0.04
Endosulfan-II	ND	0.61	0.11	ND	ND	ND	ND	ND	ND	ND
Endosulfan sulfate	ND	ND	ND	0.16	ND	ND	ND	ND	ND	ND
4,4-DDE	4.90	2.39	3.32	2.03	0.86	0.78	0.78	0.45	1.12	0.92
4,4-DDD	2.20	ND	ND	ND	ND	ND	ND	ND	ND	ND
4,4-DDT	0.20	1.05	0.81	0.81	0.98	0.69	0.67	ND	1.47	1.10

ND* # not detected.

Organochlorine pesticide was found highest in Gwadar coastal water among the four studied coastal cities of Balochistan, whereas Endrin aldehyde, Endosulfan-I & II and Endosulfan-sulphate were found highest in the Jiwani coastal waters (Table1). All of these organochlorine pesticides were found under the limit of the US-EPA water quality criteria (US-EPA, 2006).

Table 4. Average concentration of organochlorine pesticides in seawater (ng/L) of Balochistan Coastal cities, Creeks of Karachi and Karachi coast.

	Balochistan Coastal cities				Creeks of Karachi			Karachi coast	
Chlorinated Pesticide	Jiwani	Gwadar	Pasni	Ormara	Gizri Creek	Korangi Creek	Gharo Creek	Karachi West coast	Off-Clifton coast
Alpha-HCH	1.33	1.39	0.02	0.08	0.08	0.03	0.15	38.85	ND
Beta-HCH	0.81	3.87	0.78	0.23	0.70	0.33	0.29	8.44	59.01
Gamma-HCH	1.15	0.20	1.09	0.95	0.60	0.99	0.89	38.08	22.92
Delta-HCH	0.29	1.77	0.11	0.14	0.19	0.23	0.37	55.07	55.57
ΣHCH	3.59	7.23	2.01	1.40	1.56	1.58	1.69	140.43	137.50
Heptachlor	0.78	1.55	0.73	1.20	2.96	0.48	0.17	5.63	1.09
Heptachlor Epoxide	ND	0.16	ND	0.08	0.11	0.08	ND	7.55	4.26
Endrin	0.41	0.97	0.60	0.62	0.22	0.08	0.04	6.09	6.64
Dieldrin	1.62	1.91	1.06	1.06	0.77	0.58	0.15	40.21	8.69
Endrin aldehyde	7.65	3.79	1.64	0.11	0.32	0.26	0.34	3.83	21.32
Aldrin	0.10	0.17	0.03	0.11	2.90	0.07	1.16	15.13	ND
Endosulfan-I	0.44	0.05	0.10	0.11	0.03	0.17	0.05	10.40	34.47
Endosulfan-II	0.73	0.48	ND	ND	0.31	0.04	ND	59.20	ND
Endosulfan sulfate	1.81	4.38	1.15	ND	ND	0.05	ND	47.64	78.08
ΣCyclodien	13.55	13.44	5.31	3.28	7.59	1.80	1.91	195.68	154.56
4,4-DDE	1.57	3.07	1.65	3.13	3.65	2.07	0.81	22.11	30.25
4,4-DDD	0.28	ND	0.01	ND	1.10	ND	ND	28.48	33.69
4,4-DDT	5.72	6.14	6.54	1.34	0.63	0.87	0.79	2.76	41.30
ΣDDT	7.57	9.21	8.20	4.47	5.37	2.94	1.59	53.35	105.24

ND* # not detected.

The concentration of these studied pesticides, were mostly below the limit of chronic or acute level for marine organisms except DDT as per water quality standard by New Jersey State, USA (Table5).

Concentration of studied organochlorine pesticides was found low in creeks water of Karachi (Gizri, Korangi and Gharo Creek), Balochistan coastal cities, Karachi west coast and Off-Clifton coast waters (Table5).Amongst all studied creeks, the highest concentration of organochlorine pesticides was recorded in Gizricreek; however the values are far below the US-EPA water quality criteria or chronic or acute levels for marine organisms as per New Jersey State(Surface Water Quality Standards New Jersey, 2011).

Table 5. Comparisons of average concentration of organochlorine pesticides of Karachi and Balochistan coastal water (ng/L) with US-EPA marine water-quality criteria, chronic and acute marine water concentration for organisms for New Jersey.

Organochlorine Pesticides	Average Conc. in Karachi area	Average Conc. Korangi, Gizri &Gharo Creeks seawater	Average Conc. of Balochistan coastal cities seawater	US-EPA* Marine Water quality criteria	Chronic For Marine organisms NJ**	Acute for Marine organisms NJ**
Alpha-HCH	19.42	0.08	0.71	NE	NE	NE
Beta-HCH	33.76	0.44	2.17	NE	NE	NE
Gamma-HCH	30.5	0.82	0.85	160	NE	160
Delta-HCH	55.32	0.26	0.58	NE	NE	NE
Heptachlor	3.36	1.2	1.06	53	5.6	53
Heptachlor epoxide	5.91	0.06	0.06	53	5.6	53
Aldrin	40.89	0.11	0.1	37	2.3	37
Dieldrin	34.81	0.08	0.18	71	1.9	710
Endrin	45.91	0.11	0.3	NE	NE	NE
Endrin aldehyde	109.78	0.02	1.84	1300	NE	1300
Endosulfan-I	22.43	0.31	0.65	710	8.7	34
Endosulfan-II	29.6	0.5	1.41	37	8.7	34
Endosulfan sulfate	62.86	1.38	3.3	NE	NE	NE
4,4'-DDE	26.18	2.17	2.36	NE	NE	NE
4,4'-DDD	29.09	0.37	0.07	NE	NE	NE
4,4'-DDT	18.03	0.73	7.65	130	1	130

The highest concentration in the Gizri creek is most probably because this area is directly connected to the Malir River and is receiving about 100 MGD mostly untreated waste water from the eastern part of the Karachi city.

Diagnostic ratio (DR) for the inference of sources

According to the Wurl *et al*., 2006, sources of HCH in the environment can be diagnosed with the ratio of its metabolite α-HCH/γ-HCH, if the value of ratio is < 1, HCH application is recent around the environment, if ratio is > 1,it indicates that this pesticide was applied in the past.

Diagnostic ratio (DR) of DDT and its main metabolites 4,4-DDD, 4,4-DDE are used to identify the possible pollution source, and their ratio is used to investigate the extent of DDT degradation in the environment (Eqani *et al*., 2011; Sarkar *et al*., 2008).

If the DR of 4,4-DDT/(4,4-DDD+4,4-DDE) is>1 it indicates fresh application, while ratio <1 suggests historical use.

In the present study diagnostic ratios of HCH and DDT metabolites are shown in figure 2 and 3. The diagnostic ratio of α-HCH/γ-HCH values are found <1 in the study area which indicates that HCH is recently being used.

Diagnostic ratios of 4,4-DDT/(4,4-DDD+4,4-DDE) values found <1 in the study area (Karachi west coast, off- Clifton coast, creeks of Karachi and Ormara coast) indicates historical input of DDT, while ratio >1 observed in the Jiwani, Gwadar and Pasni coastal are as suggests current discharge of DDT.

Comparisons of ΣHCH and ΣDDT studied values with different world waters

The present results of ΣHCH and ΣDDT have been compared with those reported from coastal waters, harbours and estuary areas around the world (Table 6).

The level of ΣHCH in the Balochistan coastal city waters and creeks of Karachi water (0.45–15.21 ng/l) was lower than that in the Pearl River Estuary (Cai *et al*., 1998) in China, Jiulong River Estuary (Zhang *et al*., 2002) in China, Mumbai Coast, India (Pandit *et al*., 2002), Daya Bay, China (Zhou*et al*., 2001) and Karachi Harbour, Pakistan (Monawwar *et al*., 2008) except reported in the Damietta Harbour, Egypt (Tarek and Hamed 2006) and Singapore Coastal water (Wurl and Obbard, 2005) (Table 6).

Table 6. Comparisons of average ΣHCHs and ΣDDTs of Pakistani coastal seawater with different world coastal waters.

Sites	ΣHCHs (ng/L)	Range (ng/L)	ΣDDTs (ng/L)	Range (ng/L)	References
Pearl River Estuary (China)	45	21 - 84	41	ND - 86	Cai *et al.,* 1998
Jiulong River Estuary, (China)	62.5	32.0-129.8	48.7	19.2-96.6	Zhang *et al.,* 2002
Minjiang River Estuary (China)	205.5	52.09–515.0	142	40.61–233.5	Zhang *et al.,* 2003
Mumbai coast, (India)	5.42	0.16–15.92	12.45	3.01–33.21	Pandit *et al.,* 2002
Singapore Coastal Water	9.9	0.6 - 64.6	0.2	0.01 - 0.7	Wurl and Obbard, 2005
Damietta Harbour (Egypt)	0.48	0.08 - 1.41	50.29	0.75 - 148.7	Tarek and Hamed 2006
Xiamen Harbour (China)	8.57	3.51 - 27.8	1.45	0.95 - 3.25	Zhang *et al.,*2000
Tianjin Harbour (China)	272	225-330	ND	ND	Zhang *et al.,* 1998
Daya Bay (China)	264.64	35.5-589	188.4	26.8-975.9	Zhou *et al.,* 2001
West coast of Arabian sea (India)	2.7	0.26–9.4	115.2	N.D-444	Sarkar and Sen Gupta 1989
Karachi Harbour (Pakistan)	259.8	BDL – 1001	41.8	BDL – 304.8	Monawwar *et al.,* 2008
Off-Clifton Beach, Karachi (5 samples)	138.63	116.7-178.2	93.24	74.01-118.6	Present Study
Off-Karachi west coast (8 samples)	140.43	86.9-212.6	53.35	<0.1-102.02	Present Study
Coastal cities of Balochistan* (16 samples.)	4.3	2.0-3.58	10.1	5.66-15.21	Present Study
Creeks of Karachi** (10 samples)	1.6	0.78-2.91	3.3	0.45-7.1	Present Study

ND # Not detected, BDL # Below detection limit

* Cities of Balochistan # Gwadar, Jiwani, Pasni, Ormara.

** Creeks of Karachi # Gizri, Korangi and Gharo Creek.

The values of ΣHCH were also compared with the Karachi West coast and Off-Clifton coastal waters. The value of ΣHCH was found lower than the Minjiang River Estuary, China (Zhang *et al* 2003), Tianjin Harbour, (Zhang *et al*., 1998) and Karachi Harbour, Pakistan (Zhang *et al*., 1998), but higher than the Pearl River Estuary, Jiulong River Estuary, China, Mumbai Coast, Singapore Coastal water, Damietta Harbour, Egypt and Xiamen Harbour.

The result of ΣDDT in the surface seawater of the study area was quite similar to ΣHCH as shown in (Table6). The compared levels of ΣDDT in the Off-Clifton coast and Off-Karachi west coast (55.3-92.24 ng/l) were lower than that in the Minjiang River Estuary (Zhang *et al*., 2003), Daya Bay, China (Zhou *et al*., 2001) and West coast of the Arabian sea, India (Sarkar and Sen Gupta 1989) while, present study result iscomparativewith Damietta Harbour, (Tarek and Hamed, 2006) in Egypt.

Conclusion

The results obtained in this study document the first known analyses of OCP's distributions in surface seawater collected from Balochistan coastal cities, Karachi west coast and creeks of Karachi. The values of DDT, HCH and its metabolites were found most dominating while Endrin, Dieldrin and Aldrin aldehyde were recorded higher among the sixteen monitored pesticides in Karachi and coastal waters of Balochistan cities. OCP's in surface seawater collected from Balochistan coastal cities and Karachi creeks were found under the US-EPA guideline limit and also under the limit of chronic level and acute level, however, DDTs' values are observed above the chronic level in Balochistan coastal cities.

Concentration of OCP's in Karachi west coast and off-Clifton coast is found at least ten times higher than the Balochistan coastal cities and Karachi creeks. The concentration levels of Karachi west coast and off-Clifton coast are under the US-EPA guideline limit except Aldrin, however, some pesticides (Aldrin, Dieldrin, Endosulfan-I, Endosulfan-II and 4,4-DDT) are above chronic level as described by New Jersey state, USA. Higher values of OCP's in the seawater samples from Clifton and off-Karachi west coast may be harmful for ecology of this area.

Acknowledgment

The Present study was a part of the project "Pak-EPA marine water pollution monitoring center at the National Institute of Oceanography" funded by Ministry of Environment Government.

References

Aatif HM, Hassan Z, Hassan N. 2105. Imprudent Practice of Pesticides (Chemicals): A Growing Menace to Human and Environment. The Patriot, June 9, 2015.
www.dailythepatriot.com/imprudent-practice-of-pesticides-chemicals-a-growing-menace-to-human-and-environment/

Ahmar MK. 2001. Pakistan's Malir Dump. www.albionmonitor.com/0102a/malir.

Ahsan H, Karim N, Ali S.S, Munshi AB, Shaukat S. 2013.Impact of Pesticides Contamination on Nutritional Values of Marine fishery from Karachi Coast of Arabian Sea. Food and Nutrition Sciences **4,** 924-932.
www.dx.dor.org/10.4236/fns.2013.49120

Aijaz Ali Khooharo, Rajab Ali Memon, Muhammad Umar Mallah. 2008. An empirical analysis of pesticide marketing in Pakistan. Pakistan Economic and Social Review, 46, (1), 57-74.

Cai FL, Lin ZF, Cheng Y. 1998.The study on the behavior character of HCB and DDT in the tropical marine environment. The content and distribution of BHC and DDT in the rain season in the Zhujiang Estuary. Marine Environmental Science, **17**, 1-7.

Daly DAWN, Mar 26, 2007. Pesticides, health and environment.
www.dawn.com/news/239206/pesticides-health-and-environment

Eqani SAMAS, Malik RN, Mohammad A. 2011. The level and distribution of selected organochlorine pesticides in sediments from River Chenab, Pakistan. Environmental Geochemistry and Health,**33**:33–47.

GEF and UNDP project, comprehensive reduction and elimination of POPs in Pakistan 2015.
https://info.undp.org/docs/pdc/Documents/PAK/ProDoc%20%20POPs%20Full%20Phase%20Signed.pdf

Karachi coastal Recreation Development Plan 1990-2000. Karachi DevelopmentAuthority Master Plan& Environmental Control Department. UNDP United Nation Center for Human Settlement. Doxiadis Associate International Group S A Consultant on Development and Ekistics & Osmani and Company (Pvt.) Limited. 104.

Karachi water Sewerage Board. KWSB. 2014. Webpage http://www.kwsb.gos.pk/view.aspx?Page=32

Li J, Zhu T, Wang F,Qiu XH, Lin WL. 2006. Observation of organochlorine pesticides in the air of the Mt. Everest region. Ecotoxicology and Environmental Safety, **63,** 33–41.

Munshi AB, Detlef SB, Schneider R, Zuberi R. 2004.Organochlorine concentrations in various fish from different locations at Karachi Coast. Marine Pollution Bulletin, **49,** 597–601.

Devi NL, Yadav IC, RahaP, Shihua Qi, Yang Dan. 2015. Spatial distribution, source apportionment and ecological risk assessment of residual organochlorine pesticides (OCP's) in the Himalayas. Environmental Science Pollution Research, **22,** 20154. www.dx.doi.org/10.1007/s11356-015-5237-5.

Pandit G.G, Sahu SK and Sadasivan S. 2002.Distribution of HCH and DDT in the coastal marine environment of Mumbai, India. Journal of Environmental Monitoring, **4**, 431-434. www.dx.doi.org/10.1039/b202598a.

Pandit G.G,Sahu SK, Sharma S, Puranik VD. 2006. Distribution and fate of persistent organochlorine pesticides in coastal marine environment of Mumbai. Environment International, **32(2),** 240-243.

Yang Rui-qiang, Jiang Gui-bin, Zhou Qun-fang, Yuan Chun-gang Jian-bo Shi. 2005. Occurrence and distribution of organochlorine pesticides (HCH and DDT) in sediments collected from East China Sea. Environment International **31**, 799–804.

Saleem M, Rizvi SHN, Aftab J, Kahkashan S, Khan AA, Qammaruddin M. 2013.Short Assessment Survey of Organochlorine Pesticides in Marine Environment of Damb (Sonmiani) Balochistan. Pakistan Journal of Chemistry **3(3),** 107-115.

Saleem M, Rizvi SHN, Khan AA, Qammaruddin M, Kahkashan S, Aftab J. 2014. Distribution of organochlorine pesticides in the seawater of Karachi Harbour (Pakistan) using SPME techniques. Pakistan Journal of Oceanography, **7(1),** 21-31.

Sanpera C, Ruiz X, Llorente GA, Jover L, Jabeen R. 2002. Persistent Organochlorine compound in sediment and biota from the Haleji Lake: a wildlife sanctuary in south Pakistan. Bulletin of Environmental Contamination and Toxicology, **68 (2),** 237-44.

Sarkar A, Nagarajan R, Chaphadkar S, Pal S, Singbal SYS. 1997. Contamination of oraganochlorine pesticides in sediments from the Arabian Sea along the west coast of India. Water Research, **31**, 195–200.

Sarkar SK, Bhattacharya BD, Bhattacharya A, Chatterjee M, Alam A, Satpathy KK, Jonathan MP. 2008. Occurrence, distribution and possible sources of organochlorine pesticide residues in tropical coastal environment of India: An overview. Environment International, **34**, 1062–1071.

Sarkar A, Sen Gupta R. 1989. Determination of organochlorine pesticides in Indian coastal waters using a moored in situ sample. Water Research, **23,** 975–8.

Surface Water Quality Standards New Jersey. April 4 (2011) (43 N.J.R. 833(a). www.nj.gov/dep/rules/rules/njac7_9b.pdf

Tarek Said O, Hamed MAF. 2006. Determination of persistent organic pollutants in water of new Damitta Harbour, Egypt. Egyptian Journal of Aquatic Research **32(1),** 235-245.

UNEP. 2003. Global report on regionally based assessment of persistent toxic substances. UNEP chemicals, Geneva, Switzerland; cited in K.P. Singh, A. Malik, D. Mohan and S. Sinha. 2005. Persistent organochlorine pesticide residues in alluvial groundwater aquifers of Gangetic plains, India. Bulletin of Environmental Contamination and Toxicology **74,** 162-169.

USEPA. 2006. National Recommended Water Quality Criteria 25. www.epa.gov/waterscience/criteria/wqctable/nrwqc-2006.pdf

Weber RR, Montone RC. 1990. Distribution of Organochlorine in the atmosphere of the South Atlantic and Antarctic Oceans. In: Kurtz, D.A. (Ed.), Long Range Transport of Pesticides. Lewis Publishers, 185–197.

Winter S, Streit B. 1992. Organochlorine compounds in a three-step terrestrial food chain. Chemosphere **24,** 1765-1774.

Wurl O, Obbard JP. 2005. Chlorinated pesticides and PCBs in the sea-surface microlayer and seawater samples of Singapore. Marine Pollution Bulletin **50**, 1233–1243.

Xiao ping Wang, Bai Qing Xu, Shi Chang Kang, Zhiyuan Cong, Tan Dong Yao. 2008. The historical residue trends of DDT, hexachlorocyclohexanes and polycyclic aromatic hydrocarbons in an ice core from Mt. Everest, central Himalayas, China. Atmospheric Environment **42,** 6699–6709.

Yuling Wu, Xinhong Wang, Yongyu Li, MiaoleiYa, Hui Luo, Huasheng Hong. 2015. Polybrominated diphenyl ethers, organochlorine pesticides, and polycyclic aromatic hydrocarbons in water from the Jiulong River Estuary, China: levels, distributions, influencing factors, and risk assessment. Environmental Science and Pollution Research. **14**. www.dx.doi.org/10.1007/s11356-015-4782-2.

Zhang ZC, Dai SG, Zhu CS, Wu SH. 1998. Enantioselective breakdown of α hexachlorocyclohexane (HCH) and concentrations of α β, γ δ-HCH isomers in Xingang harbour marine water and Haihe River estuary water at Tianjin. China Environmental Science **18(3),** 197-201.

Zhang ZL, Hong HS, Zhou, JL Huang J, Yu G. 2003. Fate and assessment of persistent organic pollutants in water and sediment from Minjiang River Estuary, Southeast China. Chemosphere **52,** 1423–1430.

Zhang ZL, Hong HS, Maskaoui K. 2000. Study on organochlorine pesticide and PCBs at surface water in Xiamen harbour. Marine Environmental Science **19**, 48-51.

Zhang Z, Hong H, Wang X, Lin J, Chen W, Xu L. 2002. Determination and load of organophosphorus and organochlorine pesticides at water from Jiulong River Estuary, China. Marine Pollution Bulletin **45,** 397–402.

Zhou JL, Maskaoui K, Qiu, YW, Hong HS, Wang ZD. 2001. Polychlorinated biphenyl congeners and organochlorine insecticides in the water column and sediments of Daya Bay, China. Environmental Pollution, **113,** 373–384. www.dx.doi.org/10.1016/S0269-7491(00)00180-9