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Original Article

The level and distribution of selected organochlorine pesticides in water of River Satluj Pakistan

Nível e distribuição de pesticidas organoclorados selecionados na água do Rio Satluj Paquistão

A. A. Qazi[a*], M. Ali[b], M. Latif[c], S. A. A. Naqvi[d], S. Jalbani[e], F. Jabeen[f], R. Iqbal[g], Z. Farooq[a], Hamidullah[h], K. Malik[i], A. Naz[j], S. Hussain[f], M. A. Iqbal[k], A. Hakim[l] N. Tariq[m] and T. Kausar[n]

[a]Cholistan University of Veterinary and Animal Sciences, Department of Zoology, Bahawalpur, Pakistan
[b]Quaid e Azam University, Islamabad, Pakistan
[c]University of Education, Division of Science & Technology, Lahore, Pakistan
[d]Government College University, Department of Geography, Faisalabad, Pakistan
[e]Shaheed Benazir Bhutto University of Veterinary & Animal Sciences, Department of Fisheries & Aquaculture, Sakrand, Pakistan
[f]Government College University, Department of Zoology, Faisalabad, Pakistan
[g]Bahuddin Zakariya University, Institute of Pure and Applied Biology, Multan, Pakistan
[h]The Islamia University of Bahawalpur, Department of Zoology, Bahawalnagar, Pakistan
[i]Punjab University, Centre of Excellence in Molecular Biology, Lahore, Pakistan
[j]Children Hospital and Institute of Child Health, Department of Pathology, Multan, Pakistan
[k]Gomal University, Department of Zoology, Dera Ismail Khan, Pakistan
[l]Muhammad Nawaz Shareef University of Agriculture, Department of Computer Science, Multan, Pakistan
[m]Sardar Bahadur Khan Women University, Department of Zoology, Quetta, Pakistan
[n]Government Sadiq College Women University, Department of Zoology, Bahawalpur, Pakistan

Abstract

The study was aimed to identify different environmental factors (selected organochlorine pesticides) affecting the river water of Satluj. River Sutlej is about 1400 kilometers long and its water is extensively used for irrigation in Punjab, located both in India and Pakistan, which was also a reason of dispute between both countries for its water share. The study area was divided into four zones, Sulemanki Zone, Islam Zone, Mailsi Syphone Zone and Panjnad Zone. Liquid Liquid Extraction (LLE) technique was used for the collected water samples followed by high performance liquid chromatography (HPLC) UV-Visible detector The current finding revealed that aldrin was not detected during summer period in water samples of SZ-1 (Sulemanki Barrage), SZ-2 and SZ-3 (Maisli Siphon) of the study area. Lindane and DDE were found more in the samples of sediments from the study area at SZ-4 ranging from 2.238-8.226 ppb and 4.234-6.876 ppb, respectively. Heaptachlor (in sediments) was found to be0.032-234 ppb only at SZ-4.Endosulfan concentrations in water (winter) at SZ-3 was 0.06 ppb and at SZ-4,it was 0.05 ppb; dieldrin in water (winter) at SZ-4 was 0.0314 ppb and heptachlor was detected at SZ-1 (0.0315 ppb) and SZ-2 (0.0310 ppb) in water during winter season, were reaching to the Maximum Concentrations Limits (MCL), while all other residues investigated were found below the MCLin all the compartments of the study area set by various agencies like WHO/FAO- Codex Alimenterious. Present findings revealed that although the organochlorine pesticides are banned for agricultural use in many countries, including Pakistan, their presence in various samples might be due to illegal use of these pesticides in the study area and its neighboring regions. The overall study area comprises of mainly urban, suburban and agricultural land being the largest cotton growing area of the country. There is a need to take serious steps to minimize water pollution caused by pesticides to achieve a healthy lifestyle.

Keywords: water pollution, pesticides, freshwater management, River Satluj.

Resumo

O estudo teve como objetivo identificar diferentes fatores ambientais (pesticidas organoclorados selecionados) que afetam a água do rio Satluj. O rio Sutlej tem cerca de 1.400 quilômetros de extensão e sua água é amplamente utilizada para irrigação no Punjab, localizado tanto na Índia quanto no Paquistão, o que também foi motivo de disputa entre os dois países por sua cota de água. A área de estudo foi dividida em quatro zonas, Zona Sulemanki, Zona Islam, Zona Mailsi Syphone e Zona Panjnad. A técnica de extração líquida líquida (LLE) foi usada para as amostras de água coletadas seguida de cromatografia líquida de alta eficiência (HPLC) Detector UV-Visível, SZ-2 e SZ-3 (Sifão Maisli) da área de estudo. Lindano e DDE foram mais encontrados nas amostras de sedimentos da área

*e-mail: qaziadnanahmad@cuvas.edu.pk
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de estudo na SZ-4 variando de 2.238-8.226 ppb e 4.234-6.876 ppb, respectivamente. O heptacloro (em sedimentos) foi encontrado em 0,032-234 ppb apenas em SZ-4. As concentrações de endosulfan na água (inverno) em SZ-3 foram de 0,06 ppb, e em SZ-4, de 0,05 ppb; dieldrin em água (inverno) em SZ-4 foi de 0,0314 ppb e heptacloro foi detectado em SZ-1 (0,0315 ppb) e SZ-2 (0,0310 ppb) em água durante o inverno, atingindo os Limites Máximos de Concentrações (LCM), enquanto todos os demais resíduos investigados foram encontrados abaixo do MCL em todos os compartimentos da área de estudo definidos por diversos órgãos, como OMS/FAO – Codex Alimenterious. Os resultados atuais revelaram que, embora os pesticidas organoclorados sejam proibidos para uso agrícola em muitos países, incluindo o Paquistão, sua presença em várias amostras pode ser devido ao uso ilegal desses pesticidas na área de estudo e regiões vizinhas. A área total de estudo compreende principalmente áreas urbanas, suburbanas e agrícolas, sendo a maior área de cultivo de algodão do país. Há uma necessidade de tomar medidas sérias para minimizar a poluição da água causada por pesticidas para alcançar um estilo de vida saudável.

Palavras-chave: poluição da água, pesticidas, gestão de água doce, Rio Satluj.

1. Introduction

The Satluj ascends from the north slant of the Greater Himalaya in Lake RakshasTal in South West Tibet, at a height over 15,000 ft (4.6 km). Streaming towards North West and after that west-south-west from the Himalaya canyons, it goes through and passes Himachal Pradesh, just prior starting its course during the Punjab (India) land. Proceeding with southwestward in a wide channel, it is joined by the Beas waterway for 105 kilometers, at the Indian-Pakistani boundary ahead of inflowing to Pakistan and streaming a further 350 kilometer, to meet the River Chenab, west of Bahawalpur District and start of Muzaffargarh District (PWP, 2011; Encyclopedia Britiannica Online, 2017; Sharma and Walia, 2017).

Water flow in Sutlej River is controlled by the snow which fall on Himalayas and melt in summer, along with South Asian Monsoon rainfall. Sometime heavy monsoon rains caused huge flooding in downstream. In historical records, maximum flood discharge occurred in 1955, which was about 600000 cubic feet per second. In winter water flow is minimum due to low rain and ice melt from glaciers. River Sutlej is about 1400 kilometers long and its water is extensively used for irrigation in Punjab, located both in India and Pakistan, which was also a reason of dispute between both countries for its water share. However, in 1960 through Indus Water Treaty Sutlej water was allocated to India, while Pakistan got right on the Indus and its three western tributaries (PWP, 2011; Encyclopedia Britiannica Online, 2017).

Recently in agriculture, chemicals are utilized to increase the productivity of crops and fertilizers are used to enhance the growth. Similarly, pesticides are normally practiced to protect various types of crops against pests. Because of the increasing concentration of these chemicals in the environment, million cases of pesticide poisoning are noted every year. Pesticides comprised of every substance that is used to restrain weeds, insects and fungi. Classification of these substances is done on the basis of organisms, i.e., the specific pesticide targets as herbicides, fumigants, insecticides, fungicides, etc., few of these pesticides are further classified into sub-categories. This is done on the basis of their active agents as insecticides are further sub-classified as organochlorines, pyrethroids, organophosphates (OPs) and carbamates (Eqani, 2011; Eqani et al., 2012; Byer et al., 2013; Asghar et al., 2016; Battaglin et al., 2016).

2. Materials and Methods

2.1. Study area

Length of Sutlej River in Pakistan is 329 miles. Out of these 231 miles (372 km) of River stretch was selected for this study purpose. There are four major Sulemanki Barrage, Islam Barrage, Mailsi Syphon and Panjnad Barrage. The study area was divided into four zones, Sulemanki Zone, Islam Zone, Mailsi Syphone Zone and Panjnad Zone. Each study zone was further divided into three sub-sampling stations.

2.2. Study zone 1: Sulemanki Barrage

Sulemanki Barrage located on the River Satluj in Punjab province of Pakistan, is used for irrigation and flood control. Various industries are also situated in the region including sugar mill, oil mill, and paper mill (Irrigation and Power Department, 2004).

2.3. Study zone 2: Islam Barrage

It is present in Bahawalpur District, 12 km ahead from the Tehsil of Hasilpur (Figure 1). This water reservoir is the habitat of wintering water fowls along the other resident and passage migrants.

2.4. Study zone 3: Mailsi Siphon

This sampling zone; Mailsi Siphon is located at River Satluj, 18 km downstream of Islam Barrage, which is one of the main tributaries of River Indus. Nevertheless, the site is being situated in the rural part of Mailsi Tehsil, Vehari District, and considered one of high yielding of cash crops,including wheat, cotton, sunflower, and maize.

2.5. Study zone 4: Panjand Headworks

Panjand Head-works is present near the city of Alipur Tehsil, District Muzaffargarh and Uch, Tehsil Ahmadpur East, Bahawalpur (Figure 1). This barrage was also constructed in 1925-1930. River Satluj joins the River Chenab slightly before the upstream side.

2.6. Collection of water samples

Samples were collected seasonally (June 2015 to May 2017) from different sites of River Satluj along the river stretch of approximately 372 km in Punjab province.

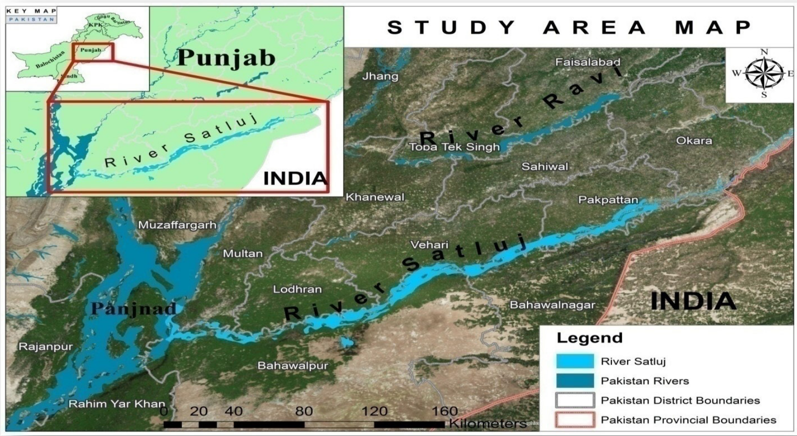

Figure 1. Map of study area.

The study area was divided into four zones, Sulemanki Zone, Islam Zone, Mailsi Syphone Zone and Panjnad Zone. Each zone was further divided into three sub sampling points; making total 12 sampling sites. The water was collected in glass bottles of 1 L capacity.

2.7. Extraction of organo chlorine pesticides in water samples

For water, Liquid Liquid Extraction (LLE) technique was used as mentioned in APHA (1975), briefly the water sample of 1000 ml was filtered to eliminate residues (FP ID 70 mm). After that, it was poured into a separating funnel (2 L). To get two phase separation, a mixture of 100 ml n-hexane and DCM (Dichloromethane) 1:1 v/v, was transferred and mix thoroughly.

For the first Liquid Liquid Extraction (LLE), water phase was poured into 1 L beaker from separating funnel. By using a concentrator tube (200 ml), one phase (organic) was transferred into a glass funnel that already contained sodium sulphate (anhydrous). The water phase was empty back into the funnel (separating) to re-extract with the same solvent mixture of 50 ml in the 2^{nd} and 3^{rd} LLE.

By using rotary evaporator with the help of nitrogen the final extract was obtained about 2 ml which was further analyzed through chromatographic analyses.

2.8. Instrumental analysis

The collected water samples were employed through high performance liquid chromatography (HPLC) UV-Visible detector.

2.9. HPLC analysis of water samples

High performance liquid chromatography (HPLC) reverse phase (Shimadzu, Japan) and UV-Visible detector were employed to examine the standards, spiked specimens in water specimens (Paranthaman and Kumaravel, 2013; Ismail et al., 2014). The parameters for the analyses during this study; included oven temperature of 30°C, 20 µl injection loop, flow rate of 1 ml/min and column C-18 (250 mm × 4.6 mm, 5 µl). Whereas, the parameters that vary for different pesticide examination, included wave length, pressure and mobile phase.

Prior to HPLC analysis, the samples of water (collected during this study) were gone through 0.45 µm of nylon (Altech Assocites, int., USA).Each time. The samples were injected manually, with the help of syringe. The identification of the suspected pesticide was done, relative to the retention time of the pure analytical standard.

2.10. Data handling

Statistical analyses were carried out by applying Analysis of Variance ANOVA (one-way) by using SPSS-17 software, with significance level ($P< 0.05$); and by MS-Excel -2010 to residues of pesticides while various diversity indices for avifauna and ichthyofauna were calculated through SPSS and MS-Excel- 2010.

3. Results

Lindane in water samples was observed during the winter at SZ-4(0.031 ppb), SZ-1 (0.022ppb), SZ-3 (0.055 ppb) and SZ-2(0.088 ppb) (Tables 1 and 2). In summer season the values of Lindane were observed in decreasing order as SZ-4 (0.013 ppb) <SZ-3 (0.028 ppb) <SZ-2(0.049 ppb) <SZ-1(0.072 ppb) (Tables 1 and 2). DDT was found highest in samples of the sediments SZ-2 while lowest in SZ-3 with average concentration of 4.03(ppb) and 2.19 (ppb) respectively. DDT was also observed in the samples of water in both seasons (Tables 1 and 2 and Figures 1-3). It was found in high concentration in water samples of SZ-2 (0.0481 ppb) during winter while low in summer at SZ-1 (0.013 ppb).

DDE concentration in water varied asSZ-3 (0.017 ppb)<SZ-1 (0.022 ppb) <SZ-2 (0.033 ppb)<SZ-4 (0.046 ppb) during winter (Tables 1 and 2). During summer the average concentration of DDE in water samples was noted

Table 1. Mean±SE of pesticide residues in water for winter season (µg/l).

Pesticides	Zone			
	SZ-1	SZ-2	SZ-3	SZ-4
Lindane	0.0219±0.0020^{bC}	0.0882±0.0023^{bA}	0.0558±0.0087^{aB}	0.0319±0.0051^{bcC}
DDT	0.0180±0.0032^{bcB}	0.0481±0.0044^{cA}	0.0381±0.0058^{bcA}	0.0430±0.0050^{abA}
DDE	0.0225±0.0032^{bB}	0.0336±0.0020^{dAB}	0.0171±0.0022^{dB}	0.0468±0.0107^{aA}
Aldrin	0.0129±0.0006^{cA}	0.0166±0.0024^{eA}	0.0173±0.0023^{dA}	0.0149±0.0019^{dA}
Dielderin	0.0231±0.0017^{bB}	0.0154±0.0013^{eC}	0.0274±0.0020^{cdAB}	0.0314±0.0025^{bcA}
Endosulfan	0.0217±0.0031^{bB}	0.0612±0.0080^{bA}	0.0480±0.0055^{abA}	0.0518±0.0029^{aA}
Heptachlor	0.0315±0.0021^{aA}	0.0310±0.0035^{dA}	0.0193±0.0027^{dB}	0.0221±0.0024^{cdA}

Means sharing similar letter in a row (upper case) or in a column (lower case) are statistically non-significant (P>0.05). Upper case letters are used for comparison among fish means and lower case letters are for comparison among different pesticides.

Table 2. Mean±SE of pesticide residues in water for summer season.

Pesticides	Zone			
	SZ-1	SZ-2	SZ-3	SZ-4
Lindane	0.072±0.001^{aA}	0.050±0.006^{aB}	0.028±0.003^{aC}	0.013±0.002^{cdD}
DDT	0.013±0.000^{dB}	0.059±0.004^{aA}	0.019±0.004^{aB}	0.023±0.005^{bcB}
DDE	0.055±0.001^{bA}	0.049±0.002^{aA}	0.021±0.004^{aC}	0.037±0.002^{aB}
Aldrin	BDL	BDL	BDL	0.012±0.000^{d}
Dielderin	BDL	0.023±0.003^{bA}	0.020±0.002^{aA}	0.025±0.002^{bA}
Endosulfan	0.043±0.001^{cB}	0.054±0.003^{aA}	0.022±0.004^{aC}	0.022±0.004^{bcC}
Heptachlor	BDL	0.021±0.002^{aB}	0.281±0.084^{aA}	BDL

Means sharing similar letter in a row (upper case) or in a column (lower case) are statistically non-significant (P>0.05). Upper case letters are used for comparison among fish means and lower case letters are for comparison among different pesticides. BDL: below detection limit;

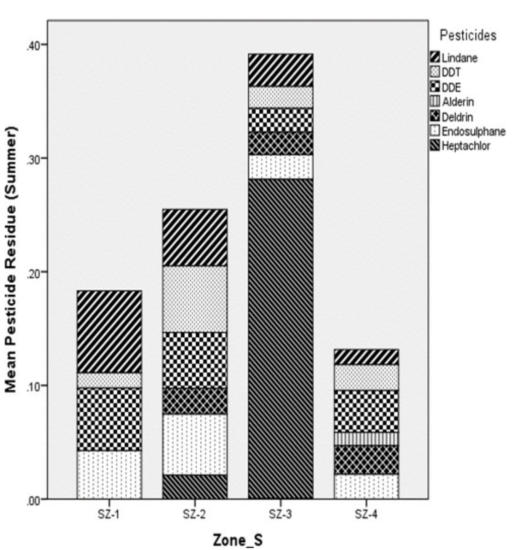

Figure 2. Mean pesticide residues (µg/l) zone wise during winter seasons.

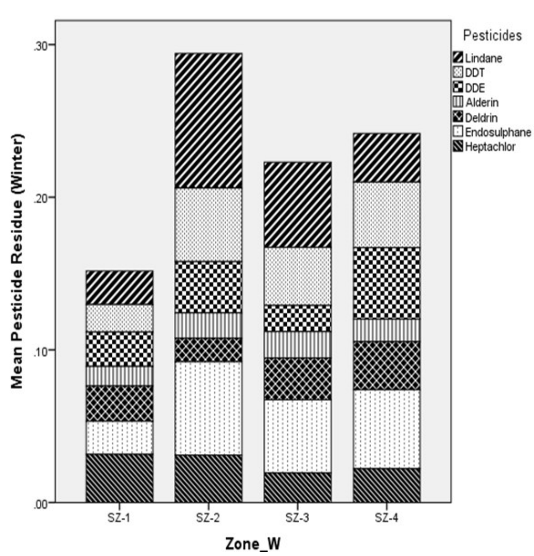

Figure 3. Mean pesticide residues (µg/l) zone wise during summer season.

high at SZ-1 (0.055 ppb) while low at SZ-3 (0.021 ppb) Tables 1 and 2.Aldrin concentrations in water during the winter season varied as SZ-1 (0.0129 ppb) < SZ-4 (0.0149 ppb)<SZ-2 (0.0166 ppb)< SZ-3 (0.0173 ppb) for selected study zones (Tables 1 and 2). During summer the average concentration of Aldrin in water samples was noted only at SZ-4 with (0.012 ppb) while at other study zones of the study area it was not detected (Tables 1 and 2).

Dieldrin, a broad spectrum insecticide is another pesticide used by many farmers. The highest concentration of Dieldrin (1.34 ppb) was detected in the sediment samples of SZ-4. The lowest level of Dieldrin in the sediments of SZ-2 remained with average of (0.78 ppb, Tables 1 and 2). Endosulfan, a broad spectrum insecticide and acaricide is another pesticide used by many farmers. The highest concentration of Endosulfan (4.39 ppb) was detected in the sediment samples of SZ-1. The lowest level of Endusufan in the sediments of SZ-3 remained with average of 3.14 (ppb).Heptachlor was observed high in water samples during winter season atSZ-1 (0.315 ppb), while lowest in SZ-3 (0.022 ppb) Tables 1 and 2. In summer season it was observed in only two zone in increasing order as SZ-3 (0.281 ppb) > SZ-2 (0.021 ppb) Tables 1 and 2.

4. Discussion

A great quantity of agrochemicals are in the use of farmers. These chemicals can move into the wetlands via running waters as well as subterranean canals. Garbage and wasted waters are added into the wetland by the residents. It is estimated that approximately 0.1% of agrochemicals used affect the target ones while leftover 99.9% scatter through different ways including air, sediments and through other means like water, thus bringing about in contamination of natural resources and disturbing human being's health in addition to other biotic life (Carvalho et al., 2009; Chopra et al., 2011; Krief et al., 2017; Migheli, 2017; Le et al., 2017).

Organochlorine pesticides have constantly proved their importance in agriculture. However, a number of studies have demonstrated that they have negative effects on human's health.The organochlorine pesticides are more accumulated in the fat. They tend to stay until the fat is broken down for energy. The chlorinated organic pesticides can pass through the mother placenta to the unborn child. They lead to many harmful effects such as abnormal development of the immune system, birth defects and fetal death. This is why organochlorine pesticides are considered as one of the main environmental and human health problems in the world (Akhtar, 2013; Lai, 2017).

Present work revealed that during winter season, DDT and Lindane in water samples remained predominantly high at SZ-2 (Islam Barrage) and SZ-4 (Panjnad Barrage). While DDT was found more in the samples of water (summer) from study at SZ-2 (Islam Barrage). In the current study aldrin was not found during summer period in water samples of SZ-1 (Sulemanki Barrage), SZ-2 (Islam Barrage) and SZ-3 (Maisli Siphon) of the study area.

In the developed countries, the use of OCPs has been banned (Byer et al., 2013; Buah-Kwofie and Humphries, 2017). However, in South Asia several of them are in use even now. For example in Pakistan and India a constant addition of DDTs into the atmosphere has been indicated (Syed et al., 2014). The use of POPs in the developing nations of South Asia may result in the contamination in other regions of the world too, as they have the potential of reaching the distant places. This contamination may occur even in the pristine regions like Arctic and Antarctic. Moreover, the process of POPs recycling from contaminated soils to the atmosphere is another source to environmental pollution round the world (Mendes et al., 2016). The discussed facts support the supposition that in the developing nations of south Asia, POPS contamination is still a grave environmental issue (Eqani, 2011; Ali et al., 2016).

Pesticides go through water reservoirs via diffuse input ways together with surface leaching and runoff, where the quantity distributed to surface waters relies upon many features, including soil characteristics, landscape, climate, crop type and their characteristics (Battaglin et al., 2016). Pesticide pollution of wastewater can be attributed to careless disposal of pesticide-containers and equipment washing and urban use such as gardening, vector control and biocidal use, e.g., in paints (Helbling, 2015; Camenzuli et al., 2016).

In current study, maximum concentration of pesticides' residues in river and its tributaries were found during the period of low water availability (dry season) of the year particularly (October to April) when minimum water was moving in the Satluj River and its tributaries. During the period (months) of low water availability; pesticides and its residues are being concentrated in the water and maximum chances for the increase in their concentration (Akhtar, 2013), also coupled the use of more agrochemicals in the fields during the seasoned crops (cotton crop, the area is being considered as highest cotton growing of the country).

The results of the study are generally in line with previous literature (Akhtar et al., 2014). High levels of OCP residue concentarions during the dry season were also documented in the study of another researcher (Jabber et al., 2001). The lowest concentrations of pesticide were found in the summer months, particularly during the rainy season months i.e., July to September. During the months of monsoon or rainy period, water supply reaches maximum in the water bodies due to heavy rains and also with the process of snow melting on mountains. The increased water in the river, tributaries and drains dilute the concentrations of pesticides and the minimum levels of residues (pesticide) concentration were identified (Akhtar et al., 2014).

5. Conclusions

The current study revealed that water contamination of the selected study area was due to the various anthropogenic activities. Therefore, prompt and relevant actions are required for properly management of wastes in the cities and long term measure and control of human activities in order to ensure lessened effects of these parameters on the River Satluj. Ever increasing anthropogenic activities are severely affecting and degrading river habitats. This habitat degradation combined with changes in natural flows of rivers is changing the patterns of distribution of the fish fauna in these water bodies.

Endosulfan concentration in water (winter) at SZ-3 was (0.06 ppb) and at SZ-4, it was (0.05 ppb); dieldrin in water (winter) at SZ-4 was (0.0314 ppb) and heptachlor findings obtained from the current study at SZ-1 (0.0315 ppb) and at SZ-2 (0.0310 ppb) in water during winter season, were reaching to the Maximum Concentration Limits (MCL) while all the other findings of residues investigated were found below in all the compartments of the study area to the MCL set by various agencies like WHO/FAO- Codex Alimenterious.

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