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The Determination of Organochlorine Pesticides Residues in Chalus River Water by Multivariate Analysis

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Abstract: Numbers of chlorinated pesticides residues such as DDE, Kelthane, β-BHC and DDT were determined by those waters from paddy fields and rivers that discharged to Caspian Sea. The multivariate analysis of variance MANOVA was used to analyze the data obtained from this study. No significant difference was shown between the concentrations of all parameters during four seasons and all stations based on MANOVA test. The total percentage of DDE, Kelthane, β-BHC and DDT detected in stations were 63, 56, 50 and 69% over the year, respectively. The maximum concentrations of β-BHC (fall), kelthane (fall), DDE (spring) and DDT (summer) were 21.6, 15.4, 9.8 and 9.2μg/l, respectively. The minimum concentrations of kelthane, β-BHC, DDE and DDT were 3, 3.1, 1.9 and 3μg/l in stations 1 (summer), 2 (fall), 3 (summer) and 4 (summer), respectively. In agricultural periods, the most of chemicals compounds were found in spring and summer seasons. During four seasons, the most percentage of chemicals compounds such as DDT (summer), β-BHC (summer-fall), Kelthane (spring-summer) and DDE (spring) were 100, 75, 75 and 75%, respectively. According to the data, the amounts of β-BHC respect to the lethal concentration of β-BHC (LC_{50}) for fishes (50 through 200 μg/l) during 96 hours were less and not remarkable.

Key words: β-BHC · DDE · DDT · Kelthan · Environmental pollutions and Multivariate analysis

INTRODUCTION

In north of Iran, there are a lot agricultural lands, that their products are like as rice, oranges, wheat, cotton, bean,...and that their leaching water from those farms comes to different rivers and finally discharged to Caspian Sea. Chalus River is one of the rivers that discharged their POPs (Persistent Organic Pollutants) in Caspian Sea from Mazandaran province. Usually farmers, for protecting their products from pests and weedy in intensive cultivation use too much pesticides. The penetration of chlorinated pesticides on soil layer, freshwater resources, accumulation on fish tissues and organisms of other aquatics are harmful for human usage of fish and impact on environmental [1]. Organochlorine pesticide (OCPs) is ubiquitous anthropogenic environmental contaminants [2, 3]. Due to their lipophilicity and persistence, these types of pesticides are bio-accumulated in the food chain. Although the production and the use of organochlorine pesticides have been banned foe some decades in most countries, they are still used in Africa for agricultural and public health purposes [4, 5]. There are some of characteristics of Kelthane, β-BHC (benzenehexachloride) and DDT and their isomer such as DDE are described as follow:

The solubility of Kelthane or Dicofol in water is 0.8 mg/l, but in other chemicals such as acetone, methanol, hexane, isopropanol are 400, 36, 30 and 30, respectively (all in g/l 25°C). The toxicity classification of this chemical by WHO is third (III); and EPA is two or three (II or III) and non-systemic acaricide with contact action [6]. Kelthane are usable for many fruit, vegetable, ornamental, filed crops for various mite species and toxic for fishes. This chemical is compatible with many other pesticides but incompatible with highly alkaline materials. LD50 of this chemical for Pheasants and Japanese quail is 265 and 169 mg/kg daily, respectively [7].

1, 2, 3, 4, 5, 6-Hexachlorocyclohexane also is known a benzenehexachloride. Five isomers have been found in technical BHC, of which the γ- isomer is the only one having more than slight activity against insects. That grade of BHC obtained by extraction steps to produce the

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γ- isomer at least 99% pure is known as lindane. The γ-isomer does have some fumigant action; however, residual action is less than DDT since it is more volatile. Benzenhexachloride are useable for common bunt on wheat only and for wheat smut, in lowland rice, for pests of cereals, sugar beets, oilseed and also for fishes are toxic [7]. The toxicity classification of this chemical is II and insecticides. The α-isomer, poisoning may occurred by ingestion, inhalation, or percutaneous absorption. Tropical use caused local sensitivity reactions, vapor irritate eyes, nose and throat [6, 7].

Practically DDT [Dichlorodiphenyltrichloroethane] and their isomer such as DDE are insoluble in water. Readily is soluble in aromatic and chlorinated solvents; moderately soluble in polar organic solvents and petroleum oils. Action of DDT is persistent non-systemic insecticide with contact and stomach action. DDT used as a mosquito vector control for the eradiation of malaria. Usage on crops has generally been displaced by less persistent insecticides. DDT is phytotoxic to cucurbits, bean, young tomato plants and some varieties of barley. Also DDT are compatible with many other pesticides, but in incompatible with alkaline substances. The toxicity and classification of DDT by WHO and EPA are in class II and insecticides. DDT is toxic to fish and aquatic life and also accumulates in the fatty tissues of mammals and is excreted in milk [4, 5]. DDT may accumulate in the top soil layer where heavy applications are made annually to crops such apples and toxic to fish and aquatics life [6, 7].

MATERIALS AND METHODS

Chalous River is located in the southern part of Caspian Sea (Mazandaran province). The total length of the river from different branches and tributaries to the estuary is almost 80 km from mountainous station through estuary of the river). Longitudinal and latitudinal location of the sampling stations are 50°, 20′, 05″ E -36°, 31′, 28″ N (station 1), 51°, 24′, 28″ E -36°, 38′, 11″ N (station 2), 51°, 26′ 02″ E- 36°, 39′, 49″ N (station 3) and 51°, 27′ 31″ E- 36°, 40′ 50″ N in station 4, respectively (Figure 1). Four sampling stations were chosen from several branches and tributaries of the river. Sampling stations are located as follows: Station 1 is located in the mountain areas, station 2 is located on plain before declinatory dam, station 3 in plain part (around agricultural lands and station 4 in estuary of river. A total thirty samples were collected during four seasons and well-mixed, then separated into aqueous and organic phases. Samples were collected from spring through winter from four stations in Chalous River. In each station, the samples were collected almost with 200 meters from tow sides of river and then one litter of mixed water fixed by organic compound (n- hexane) and plus three times more for extraction. Finally, sample will be concentrate with KD flask (kedernian dainish) to reach 2cc and like as spike sample will be prepared and used for analysis with method of US-EPA (508) by Gas chromatograph (Shimadzu-14A, Japan) equipped with ^{63}Ni electron capture detector (ECD) was used. Detector temperature was set at 290°C. The GC capillary column

Fig. 1: Map of samples locations of Chalous River in eight stations by Google Earth (2010)

consisted of a CPB1 (non-polar), 0.25μmfilm thickness, length 25m and 0.22 mm internal diameter. The column temperature was initially maintained at 60°C for 1min, followed by the temperature programming with a rate of 20°C/min till it reached to 180°C. Then, the temperature was increased with a rate of 3°C/min till reached to 250°C. Helium and nitrogen was used with a flow rate of 50 mL/min. A 1μLin sample volume, spike and standard was injected into the column. The injection temperature was set at 235°C [8, 9].

RESULTS AND DISCUSSIONS

Kelthane: Figure 2 showed, the maximum concentration of kelthane between the four stations was 15.4µg/l in fall and this corresponds to the station 4. The reason for extra amount of kelthane only at this station (estuary) maybe related to influence of water current from neighbor river that discharged to Caspian Sea and effects on Chalous River estuary. During the spring, summer and winter seasons the concentration of pesticides residues in majority of stations are less than 10µg/l. The minimum amount of detectable concentration was 3µg/l in stations 1 (summer).

Generally in Figure 2, the concentration of Kelthane in different stations (more than 5µg/l) showed from maximum to minimum as follow [10]:

Kelthane; St. 4[fall]>St. 1[spring]> St. 3[summer]> St. 2[winter]> St. 4[spring]> St. 3 [winter]

The total percentage of Kelthane in samples were detected during one year sampling from spring, summer, fall and winter were 75, 75, 25 and 50%, respectively.

The maximum concentration of kelthan in this study was 15.4µg/l and this value was 3.5 times lower than that of Babolroud River, Iran (53.8µg/l) [11], 3 times lower than that of Tajan River, Iran (46.0µg/l) [12], 2 times lower than that of Shiroud River, Iran (29.70µg/l) [13] and 3 times more than that of Caspian Sea coastal water (54.2µg/l) [14].

DDT: Figure 3 showed, the maximum concentrations of DDT between the four stations were 9.2µg/l in summer and this corresponds to station 2. The reason for this maximum amount, maybe related to the situation of station that located before the dam and accumulation of water for specific time. The minimum detectable amount of DDT was found in stations 1 and 4 at the summer season.

In general at Figure 3, the concentration of DDT in different stations (more than 5µg/l) showed from maximum to minimum as follow [10]:

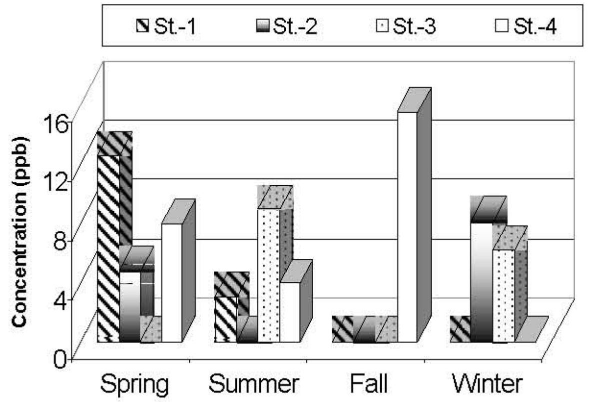

Fig. 2: Seasonal fluctuations of Kelthane (Dicofol) concentration in Chalous River

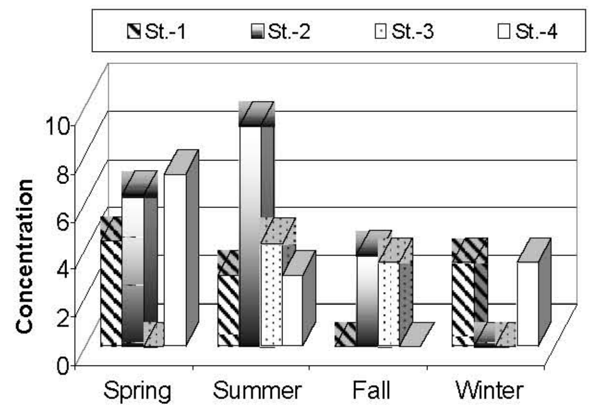

Fig. 3: Seasonal fluctuations of DDT concentration in Chalus River

DDT, St. 4 [summer] > St. 4 [spring] > St. 2 [spring]

The total percentage of DDT in samples were detected during one year sampling from spring, summer, fall and winter were 75, 100, 50 and 50%, respectively.

The maximum concentration of DDT in this study was 9.2µg/l and this value was 2 times less than that of Babolroud River, Iran (19.2µg/l) [11], almost 4 times less than that of Tajan River (42µg/l) [12], 6 times less than that of El-Haram Giza Canal, Egypt (61 µg/l) [15], almost 3 times less than that of Atoya River, Nicaragua (26.8µg/l) [16] and 6 times less than that of K.Menderes River, Turkey (58µg/l) [17].

β-BHC: Figure 4 shows, the maximum concentrations of β-BHC between the four stations was 21.6µg/l in fall and this corresponds to station 4. The reason for this extra amount in estuary maybe related to more influence water current from Neighbor Rivers flooding by rainfall that

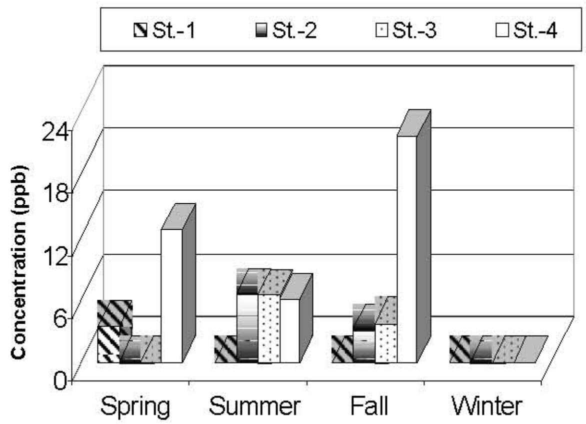

Fig. 4: Seasonal fluctuations of β-BHC concentration in Chalus River

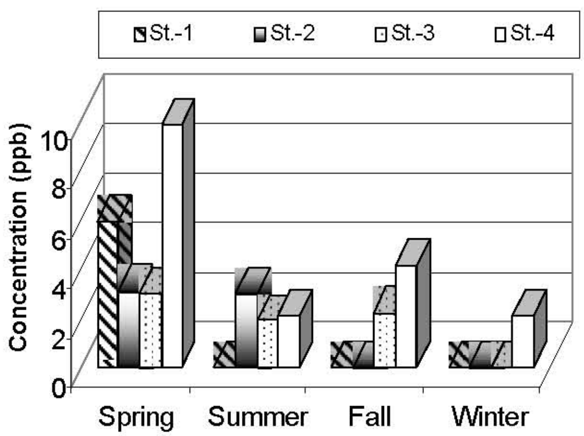

Fig. 5: Seasonal fluctuations of DDE concentration in Chalus River

discharged to Caspian Sea and effects on Chalus River estuary. During the spring, summer and fall seasons, the concentration of pesticides in majority of stations are less than 10μg/l.The minimum detectable amount of pesticide residue was 3.1 μg/L at station 2 (fall), but β-BHC in all stations during winter was not detected.

In general at Figure 4, the concentration of β-BHC in different stations (more than 5μg/l) showed from maximum to minimum as follow [10]:

β-BHC, St. 4 [fall] > St. 4 [spring] > St. 2 [summer] > St. 3[summer] > St. 4 [summer].

The total percentage of β-BHC in samples were detected during one year sampling from spring, summer, fall and winter 50, 75, 75 and 0.00%, respectively.

The maximum concentration of β-BHC in this survey was 21.6μg/l and this value was lower than that of Babolroud River and almost near to Tajan River, Iran (38.1 and 21.0μg/l) [11,12], 4 times lower than that of El-Haram Giza Canal, Egypt (86.2μg/l) [15], less than 2 times lower than that of Tajan River Estuary, Iran (31.8 μg/l)[18], a little more than that of Atoya River in Nicaragua (19 μg/l) [16] and a little lower than that of Caspian Sea coastal water (25 μg/l) [14].

DDE: Figure 5 showed that the maximum concentration of DDE in all stations was 9.8μg/l during summer time. The reason for this maximum amount, maybe related to the situation of station that located in estuary of the river and agricultural time. The minimum detectable amount of DDE was found in station 1.9μg/l in summer season. All of maximum concentrations of DDE occurred in agricultural months.

In general at Figure 5, the concentration of DDE in different stations (more than 4μg/l) showed from maximum to minimum as follow [10]:

DDE, St. 4 [spring] > St. 1 [spring] > St. 4 [fall]

The total percentage of DDE in samples were detected during one year sampling from spring, summer, fall and winter were 75, 100, 50 and 50%, respectively.

The maximum concentration of DDE in this research was 9.8μg/l and this value was 2times less than that of Babolroud River, Iran (19.2μg/l) [11], 9 times lower than that of Tonekabon River, Iran (88.6μg/l) [19], almost 4 times less than that of Tajan River (42μg/l) [20], 6 times less than that of El-Haram Giza Canal, Egypt (61 μg/l) [15], almost 3 times less than that of Atoya River, Nicaragua (26.8μg/l) [16] and 6 times less than that of K.Menderes River, Turkey (58.0μg/l) [17].

Statistics Analysis: Multivariate analysis of variance MANOVA showed that there is no significant difference between different seasons and also between all stations as shown in Table 1 and Table 2. The concentrations of DDT, β-BHC, DDE and Kelthane in all stations and during different seasons are the same, although there is a difference in records of these parameters but this difference is not real based on MANOVA test [21, 22].

The Pearson correlation of pesticides as shown in Table 3, that there was a strong correlation ($P<0.01$) between DDE, β-BHC and kelthane compounds. Also there was a very strong correlation ($P<0.05$) between β- BHC and kelthane compounds but DDT did not had any correction with other OCPs compounds.

Table 1: Multivariate Tests Effect for different Seasons

	Value	F	Sig.
Pillai's Trace	.472	.746	.665
Wilks' Lambda	.591	.656	.739
Hotelling's Trace	.589	.568	.811

Table 2: Multivariate Tests Effect for different Stations

	Value	F	Sig.
Pillai's Trace	.814	1.489	.190
Wilks' Lambda	.344	1.495	.205
Hotelling's Trace	1.472	1.417	.232

Table 3: Correlation coefficient matrix for OCPs residues in Chalus River

Pearson Correlation	DDE	DDT	b- BHC	Kelthane
DDE	1			
DDT	.467	1		
b- BHC	.537(*)	.158	1	
Kelthane	.507(*)	-.046	.655(**)	1

* Correlation is significant at the 0.05 level (2-tailed).

** Correlation is significant at the 0.01 level (2-tailed).

CONCLUSION

During agricultural time (spring and summer seasons), the concentration of these chemical were more than other seasons and this maybe comes from by washing paddy farms that accumulated in last decades. All four chemicals compounds (Kelthane, β-BHC, DDE and DDT) were determined in this study could be compared their distribution of concentration respect to each other in four seasons. During spring and summer seasons, at the most stations all compounds were detected but the component of kelthane among the other chemicals respect to other stations were higher.

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