World Journal of Fish and Marine Sciences 4 (2): 150-154, 2012
ISSN 2078-4589

DOI: 10.5829/idosi.wjfms.2012.04.02.56399

Determination of Organochlorine Pesticide Residues in Water, Sediments and Fish from Lake Parishan, Iran

[1]Farshid Kafilzadeh, [1]Amir Houshang Shiva,
[2]Rokhsareh Malekpour and [1]Hamid Noorani Azad

[1]Department of Biology, Jahrom Branch, Islamic Azad University, Jahrom, Iran
[2]Department of Biology, Kazeroun Branch, Islamic Azad University, Kazeroun, Iran

Abstract: In this study, the levels of organochlorine (OC) pesticide residues in Lake Parishan have been investigated using water, sediment and fish (*Barbus brachycephalus caspius*) samples as a case study to find out the extent of pesticide contamination and accumulation in the lake. Six OC pesticides namely DDT, DDE, Lindane, Endosulfan, Heptachlor and Chlordane were analyzed in four sites at four seasons. Water samples were processed using a liquid-liquid extraction technique and gas chromatograph equipped with electron capture detector (GC-ECD). Soxhlet extraction was used for fish and sediment samples followed by clean up and gas chromatograph. DDE was the predominant residue in all the samples analyzed, at the mean concentrations of 0.055 ppb, 9.84 ppb and 4.86 ppb in water, sediment and fish samples, respectively. The lowest levels of OC pesticides were related to Heptachlor and Chlordane which none of them were found in water samples. Pol-e-Abgineh and Midstream sites had the highest and the lowest concentrations of OC pesticides, respectively.

Key words: Organochlorine residues % DDT % Soxhlet % GC-ECD % Lake Parishan

INTRODUCTION

Organochlorine (OC) pesticides are among the agrochemicals that have been used extensively for long periods. They have been used widely in agriculture, as well as, in mosquito, termite and tsetse fly control programs [1]. OC pesticides are characterized by low polarity, low aqueous solubility and high lipid solubility (lipophilicity) and as a result they have a potential for bioaccumulation in the food chain posing a great threat to human health and the environment globally [2]. Residues and metabolites of many OC pesticides are very stable, with long half lives in the environment [3]. Studies have shown that DDT is still in its highest concentration in biota of some areas. It is a hydrophobic molecule which disrupts ionic channels like Na^+-K^+ pumps in nervous cell membrane leading to automatic stimulation of neurons and involuntary contraction of muscles [4].

Many other recent works have indicated the presence of OC residues in surface waters, sediments, biota and vegetations [2, 5-9]. The persistent nature of organochlorine residues in the environment may pose the problem of chronic toxicity to animals and humans via air, water and foods intake. Many of these OC pesticides and their metabolites have been implicated in a wide range of adverse human and environmental effects including reproduction and birth defects [10], immune system dysfunction, endocrine disruptions and cancer [11].

Fish are used extensively for environmental monitoring [12], because they uptake contaminants directly from water and diet. Generally the ability of fish to metabolize organochlorines is moderate; therefore, contaminant loading in fish is well reflective of the state of pollution in surrounding environments [1].

Parishan (Famour) wetland [29° 30' N, 51° 47' E, alt. 820 m] is located in 12 Km Southeast of Kazeroun, Southern Iran. It has around 1.6-2 m depth and the surface area is 10.8 Km^2. This lake is the only freshwater source in Iran with rare species of birds and aquatic organisms. Also it is one of the most important natural habitats for migrating birds which migrate from Siberia, Canada, Denmark and North Africa to Iran [13].

Corresponding Author: Farshid Kafilzadeh, Department of Biology, Jahrom Branch, Islamic Azad University, Jahrom, Iran.

The determination of OC residues in fish, sediments and water may give indication of the extent of aquatic contamination and accumulation characteristics of these compounds in the tropical aquatic biota that will help in understanding the behaviour and fate of these persistent chemicals [14]. This work, therefore, seeks to provide baseline information on levels of pesticide residues including DDT, DDE, Lindane, Endosulfan, Heptachlor and Chlordane in fish (*Barbus brachycephalus caspius*), sediments and surface waters of Parishan wetland through four seasons that will assist in a scientific assessment of the impact of pesticides on public health, agriculture and the environment in Iran.

MATERIALS AND METHODS

Fish, sediment and water samples were obtained from four various sites namely Gadarzavali, Hellak, Pol-e-Abgineh and Midstream in Lake Parishan. Samplings were conducted seasonally from winter 2010 to autumn 2010 following US-EPA [15]. Samples were collected from surface parts of the water and sediment. Also, each sampling was carried out in three replicates. A total of 48 samples each of sediments and water were collected randomly. However, fish samples were 14 because of little rainfall in recent years which has caused a decrease in water depth leading to limited dispersal of fish species. All samples collected (water, sediments and fish) were immediately stored in an ice-chest at 4°C and transported to the laboratory for analysis.

Extraction of OC Pesticides in Water Samples: In the laboratory, using liquid-liquid extraction (LLE) as described in APHA [16], the total amount of each surface water sample (800 ml) was filtered with Whatman filter paper (i.d. 70 mm) to remove debris and suspended materials and then poured into a 2 liter separatory funnel. For the first LLE, the mixture of 100 ml n-hexane and dichloromethane (1:1 v/v) was added and shaken vigorously for 2 min before two phase separation. The water-phase was drained from the separatory funnel into a 1000 ml beaker. The organic-phase was carefully poured into a glass funnel containing 20 g of anhydrous sodium sulfate through a 200 ml concentrator tube. Following the second and third LLE, the water-phase was poured back into the separatory funnel to re-extract with 50 ml of the same solvent mixture. The extract was concentrated to the volume of 2 ml under a gentle stream of nitrogen using rotary evaporator and then analyzed with Gas Chromatography with micro Electron Capture Detector (GC-ìECD) [17].

Extraction of OC Pesticides in Fish and Sediment Samples: The muscle tissues of the fish samples were ground in a blender to obtain a homogenous composite, while the sediments were air-dried. OC residues in sediments and fish samples were extracted using Soxhlet Extraction [18]. A 10 g sample was placed into a beaker containing 50 g anhydrous sodium sulfate and mixed thoroughly. The sample mixture was transferred to an extraction thimble and placed in a Soxhlet extractor. The mixture was extracted with 150 ml of acetone: n-hexane (20:80 v/v) at 50°C for 4 h. The extracts were filtered, concentrated to 1 ml using vacuum rotary evaporator. Each of the raw extracts was then dissolved in 10 ml hexane and passed through pre-conditioned octadecyl C-18 columns at a rate of 2 ml min^{-1} to clean up. The column was washed with 1 ml, 30% methanol followed by 1 ml ultrapure water and was allowed to dry. The sample (analyte) which was trapped in the column was eluted 5 times with 0.5 ml aliquots of hexane to recover the pesticide residues. Hexane in the sample was then allowed to evaporate off leaving the residue alone in the vial. Dried sample was dissolved in 1 ml portion of hexane, mixed thoroughly with a whirl mixer and then transferred to auto sampler vials ready for gas chromatography [5].

Statistical analyses were carried out by analysis of variance (ANOVA) using SPSS 15 software. Mean values were analyzed by the Duncan's test.

RESULTS AND DISCUSSION

Parishan wetland is surrounded by farm lands. A large amount of chemicals (fertilizers and pesticides) are used there by farmers which can enter the wetland through running waters and subterranean canals. Also, garbage and wastewaters are poured in the wetland by inhabitants. All of these factors may lead to the contamination of Parishan Lake.

Results from the study have been shown in tables 1, 2 and 3 which are related to the concentration of OC residues in water, sediment and fish samples, respectively. DDT was detected in 54% of water samples, 75% of sediments and 84% of fish samples. The associated figures for mean concentrations were 0.016 ppb, 4.980 ppb and 4.112 ppb. The ratios of incidence as well as the concentrations of DDE, a metabolite of DDT, in all the three sample types were higher than those recorded for DDT which was 84%, 96%, 94% in water, sediment and fish samples, respectively. This observed trend could be attributed to the decomposition and bioaccumulation of the DDT used in the past. DDE is more stable than DDT and decomposes more slowly by micro-organisms, heat and ultraviolet rays [4].

Table 1: Levels of organochlorine pesticide residues in water samples of Lake Parishan

Pesticide	Mean (ppb)	Standard Deviation (SD)	Range (ppb)	Percentage
DDT	0.016	0.003	0.12 - 0.24	54
DDE	0.055	0.008	0.05 - 0.14	84
Chlordane	-	-	-	-
Heptachlor	-	-	-	-
Lindane	0.058	0.012	0.45 - 1.50	68
Endosulfan	0.046	0.009	0.30 - 0.46	60

Table 2: Levels of organochlorine pesticide residues in sediment samples of Lake Parishan

Pesticide	Mean (ppb)	Standard Deviation (SD)	Range (ppb)	Percentage
DDT	4.980	1.66	4.21 - 6.18	75
DDE	9.840	2.85	12.27 - 30.43	96
Chlordane	0.074	0.03	0.28 - 0.42	24
Heptachlor	0.081	0.04	0.24 - 0.44	36
Lindane	6.920	1.18	3.06 - 14.21	72
Endosulfan	10.622	1.72	4.12 - 15.22	46

Table 3: Levels of organochlorine pesticide residues in fish muscle tissue samples of Lake Parishan

Pesticide	Mean (ppb)	Standard Deviation (SD)	Range (ppb)	Percentage
DDT	4.112	1.12	3.50 - 5.56	84
DDE	4.864	1.42	4.18 - 8.26	94
Chlordane	0.024	0.008	0.35 - 0.56	12
Heptachlor	0.041	0.01	0.28 - 0.58	34
Lindane	0.138	0.06	0.65 - 1.47	39
Endosulfan	0.816	0.12	0.94 - 2.14	33

Neither chlordane nor heptachlor was detected in the water samples showing that the farmers around the lake do not use them in their farming activities. However, these organochlorine pesticides were measured in fish and sediment samples, which is because they are less soluble in water. They, therefore, accumulate in fishes and sediments when they are discharged into water bodies. Frequency of detection (incidence) and concentration of chlordane and heptachlor measured in sediments were higher than those recorded for fish samples. Chlordane was detected in 24% of sediment samples at concentrations ranging from 0.28 to 0.42 ppb, while it was detected in 12% of the fish sample and their concentrations ranged between 0.35 and 0.56 ppb. Heptachlor was detected at an average concentration of 0.081 ppb and 0.041 ppb in sediments and fish, respectively.

Lindane was detected in 68% of water samples, 72% of sediment samples and 39% of fish samples analyzed with the highest concentration of 14.21 ppb occurring in sediments. This result suggests lindane is more prevalent and persistent in the sediments than in water and then in fish. The average concentration of lindane in sediments was about 50-folds the average concentration in fish and 120-folds the average concentration in water. It is therefore expected that lindane levels in fish will rise with time as they utilize the water and the sediments in the lake.

Endosulfan, a broad spectrum contact insecticide and acaricide, is another pesticide used by many farmers. The highest concentration of endosulfan (15.22 ppb) was detected in the sediment samples, however, the highest occurrence of detectable concentrations was found in water (60%). Endosulfan level in fish, on the average, is 16 times that found in water samples. This suggests that the residues in the water are accumulated and concentrated in the fish. Mean level of endosulfan in the sediments is about 13 times the levels measured in fish. Bioconcentration of endosulfan in fish could therefore arise.

In general, the concentration of OC pesticides in water was lower than sediments and fishes which was highly significant (P?0.05), because these pesticides are lipophilic and are not soluble in water. This fact can ease the accumulation of OC pesticides in micro-organism tissues.

The mean total concentration of organochlorine residues in water samples of Gadarzavali, Hellak, Pol-e-Abgineh and Midstream sites were 0.023 ppb, 0.030 ppb, 0.054 ppb and 0.010 ppb, respectively (Fig. 1).

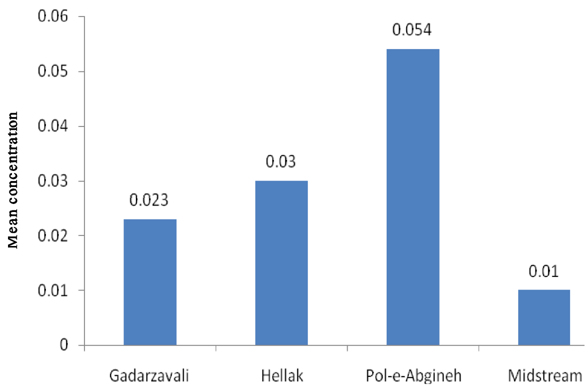

Fig. 1: Comparison among the mean total concentration of organochlorine pesticides in water samples of four sites

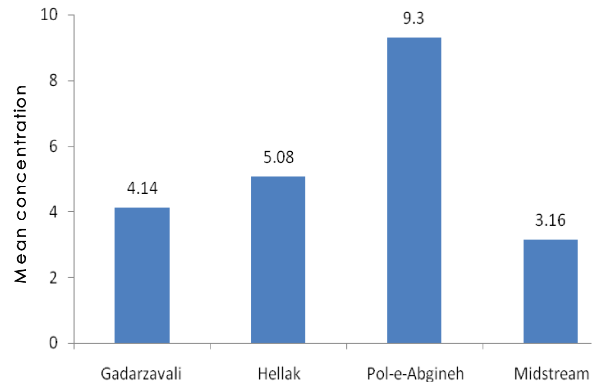

Fig. 2: Comparison among the mean total concentration of organochlorine pesticides in sediment samples of four sites

Based on ANOVA and Duncan tests, the mean concentrations of OC pesticides in water samples of Pol-e-Abgineh and Midstream sites showed significant differences (P?0.05). However, these differences were not significant between Gadarzavali and Hellak sites (P?0.05). In terms of the mean concentrations of OC residues in sediments, as fig. 2 illustrates, all four mentioned sites showed different levels which were highly significant (P?0.05). Generally, the highest concentration of OC pesticides was seen in Pol-e-Abgineh. It may be due to the abundance of farm lands around this site which have sharp slopes toward this part of the lake, so pesticides and other chemical materials can enter there more easily. However, the lowest concentration of organochlorine residues was related to Midstream site. Because there is a slow current toward this part and the contaminants cannot accumulate there.

Hardell *et al*. [19] reported the rate of chlorine pesticides in muscle tissue of fishes and DDE was the predominant target compound. The results obtained in this study generally agree with their findings.

The amount of OC pesticides in freshwater fishes of Punjab was measured in another study and showed the predominance of DDT, while other organochlorine pesticides such as lindane, alderine, dielderine, chlordane, endosulfan and heptachlor were found at lower levels [20]. These levels reported in India were extremely high compared to levels recorded in this work.

Some investigations have been done on OC residues in fish (*Tilapia*), sediment and water samples from Lake Bosomtwi in Ghana by Darko *et al*. [5]. The mean concentrations of DDT in water, sediment and fish were 0.012±0.62 nggG^{1}, 4.41±1.54 nggG^{1} and 3.64±1.81 nggG^{1}, respectively. In terms of DDE, the respective figures were 0.061±0.03 nggG^{1}, 8.34±2.96 nggG^{1} and 5.23±1.30 nggG^{1}. In this study, our results show that concentration of DDE is more than DDT.

According to Siriwong *et al*. [17] the rate of DDT and its derivatives in sediments was 12.05 nggG^{1} and in vertebrates was 4.16-57.66 nggG^{1} which were more than the results obtained in this investigation.

The levels of most of the residues in fish were higher than those found in water. Organochlorine pesticide residues in the lake are likely to originate from nonpoint sources via runoff, atmospheric deposition and leaching due to agricultural applications and vector control practices. The lake sediments act as a sink for the persistent contaminants, whose resuspension during the lake’s mixing may increase pesticide bioavailability and accumulation in the fish. Pesticide pollution to the lake is therefore, likely to pose a danger to both aquatic organisms and humans.

ACKNOWLEDGEMENTS

The authors would like to thank the Office of Vice Chancellor for Research of Islamic Azad University-Jahrom branch for collaboration in some parts of this study.

REFERENCES

1. Guo, Y., X.Z. Meng, H.L. Tang and E.Y. Zeng, 2008. Tissue distribution of organochlorine pesticides in fish collected from the Pearl River delta, China: Implications for fishery input source and bioaccumulation. Environ. Pollut., 155: 150-156.

2. Afful, S., A.K. Anim and Y. Serfor-Armah, 2010. Spectrum of organochlorine pesticide Residues in fish samples from the Densu Basin. Res. J. Environ. Earth Sci., 2(3): 133-138.
3. El-Mekkawi, H., M. Diab, M. Zaki and A. Hassan, 2009. Determination of chlorinated organic pesticide residues in water, sediments and fish from private fish farms at Abbassa and Sahl Al-Husainia, Sharkia Governorate. Aus. J. Basic Appl. Sci., 3(4): 4376-4383.
4. Esmaili Sari, A., 2002. Pollution, health and environmental standards. Naghsh Mehr Press. pp: 767.
5. Darko, G., O. Akoto and C. Oppong, 2008. Persistent organochlorine pesticide residues in fish, sediment and water from lake Bosomtwi, Ghana. Chemo., 72(1): 21-24.
6. Dem, S.B., J.M. Cobb and D.E. Mullins, 2007. Pesticide residues in soil and water from four cotton growing areas of Mali, West Africa. J. Food Environ. Sci., 1: 1-12.
7. Haozheng, W., H. Mengchang, L. Chunye, Q. Xiangchun, G. Wei and Y. Zhifeng, 2007. Monitoring and assessment of persistent organochlorine residues in sediments from Daliaohe River watershed, Northeast of China. J. Environ. Monitor., 133: 231-242.
8. Imo, T.S., M.A. E. Sheikh, T. Oomori and F. Tamaki, 2007. Contamination by organochlorine pesticides from rivers. Int. J. Environ. Sci. Tech., 4: 1-9.
9. Ize-Iyamu, OK., I.O. Asia and P.A. Egwakhide, 2007. Concentrations of residues from organochlorine pesticide in water and fish from some rivers in Edo State Nigeria. Int. J. Phys. Sci., 2: 237-241.
10. Edwards., C.A., 1987. The environmental impact of pesticides. Parasitis. 86: 309-329.
11. Adeyemi, D., G. Ukpo, C. Anyakora and J.P. Unyimadu, 2008. Organochlorine pesticide Residues in fish samples from Lagos Lagoon, Nigeria. Am. J. Environ. Sci., 4(6): 649-653.
12. Lanfranchi, A.L., M.L. Miglioranza, K.S.B. Menone, L.J. Janiot, J.E. Aizpùn and V.J. Moreno, 2006. Striped weakfish (*Cynoscion guatucupa*): a biomonitor of organochlorine pesticides in estuarine and near-coastal zones. Mar. Pollut. Bull., 52: 74-80.
13. Ostovan, H. and J. Niakan, 2005. Faunistic and biocenotic studies on aquatic beetles in Eastern and Western shores of Parishan Lake. J. Agri. Sci., 11(3): 5-18.
14. Kannan, K., S. Tanabe and R. Tatsukawa, 1995. Geographic distribution and accumulation features of organochlorine residues in fish in tropical Asia and Oceania. Environ. Sci. Tech., 29: 2673-2683
15. US-EPA, 2000. Guidance for assessing chemical contaminant data for use in fish advisories. Volume 1: Fish Sampling and Analysis.3. US-EPA, Washington, DC.
16. APHA, 1975. Standard methods for examination of water and wastewater. AWWA/WPCE.14.Washington, DC.
17. Siriwong, W., K. Thirakhupt, D. Siticharoenchai, J. Rohitrattana, P. Thongkongown, M. Borjan and M. Robson, 2009. DDT and derivatives in indicator species of the aquatic food web of Rang sit agricultural area, Central Thailand. Ecol. Indic. 9(5): 878-882.
18. Therdteppitak, A. and K. Yammeng, 2003. Determination of organochlorine pesticides in commercial fish by gas chromatography with electron capture detector and confirmation by gas chromatography - mass spectrometry. Sci. Asia. 29: 127-134.
19. Hardell, S., H. Tilander, G. Welfinger-Smith, J. Burger and D.O. Carpenter, 2010. Levels of polychlorinated biphenyls (PCB_5) and three organochlorine pesticides in fish from the Aleutian Islands of Alaska. PLoS ONE. 5(8): 87-92.
20. Kaur, M., J.K. Sharma, J.P. Gill, R.S. Aulakh, J.S. Bedi and B.S. Joia, 2008. Determination of organochlorine pesticides residues in freshwater fish species in Punjab, India. Bull. Environ. Contam. Tox., 80(2): 154-157.