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Investigation on the Fate Pesticides in Water and Sediments Iraqi Marshland

Abdal-Kader Saeed Latif, Reyam Naji Ajmi, Huda Farooq Zeki, Wathiq Abaas Hatit

***Abstract*—**These studies have been carried out on the behavior of pesticides in aquatic environments of marshes to monitoring water and sediment. A total of 25 water and 25 sediment samples were collected at five sampling station during April, June and September. 2013 the levels of organochlorine (OCP) pesticide as a case study to find out the extent of pesticide contamination and accumulation, in water was the concentration of OCPs (0.02, 0.066, 0.7, 0.8, 0.072, 0.058) ppb. In sediment was the concentration of OCPs (5.897, 10.987, 0.089, 0.096, 7.897, and 12.389) ppb respectively in DDT, DDE, Chlordane, Heptachlor, Lindane, and Endosulfan. There is a relationship between pesticides and sediment and water with physical properties because the concentrations of pesticide in water and sediment are not always in equilibrium Furthermore, when sediments are smaller, the rate of deposition is slower. There the wetlands of pesticides due to factors of high temperature and evaporation but used in the control of pesticides in water and sediment also there still exist a variety of organochlorine pesticide residues in water and sediments of wetlands.

***Keywords*—**Bioindicators, Iraqi marshes, Pesticides, Sediment, Water.

I. Introduction

PESTICIDES have the potential to prevent and control harmful organisms. Some pesticides can be toxic to humans and animals and their continuous application is causing serious problems of environmental and water contamination. The existing standards for the analysis of some priority substances, where some pesticides are included, are not sensitive enough to conduct the actual compliance monitoring [1]-[3].

Marshes in southern Iraq derive most of their water from upstream streams and rivers and the surrounding watershed. Water entering the wetlands contains high suspended sediment loads and organochlorine pesticides. Among such pesticides, Benlate, Diazinon, Dursban, Malathion, Propanil, Permethrin, Methiocarb, Ridomil, Triosulfuron add to DDT dichlorodiphenyltrichloroethane, was one of the most predominantly used pesticides in the watershed. Marshes were nearly completely dried during the 1990s as a result of large-scale water diversions. Consequently, the wetlands changed from serving as important biogeochemical sinks to becoming sources of sediments through wind erosion and remobilization of biogeochemical elements that previously would have been held in the accumulated sediments [4]. Those pesticides which are likely to be present in given water supply. The limits set for both type of waters are 0.5 µg/L for the sum of all pesticides and 0.1 µg/L for each compound [5], [6].

The Mesopotamian marshlands are located mostly in south-eastern Iraq but also extend across the border into Iran. They once covered an area (20,000 Km^2) between the three Iraqi cities of Amarah in the north, Basra in the south, Naseriyah in the west [7]. The sources of marshland water were of multi origin namely rivers, precipitations and groundwater. The marshlands constitute the largest wetland ecosystem in the Middle East. These wetlands are located at the confluence of Tigris and Euphrates rivers in southern Iraq. This area supported a marsh Arab population of 500,000 as well as numerous endemic species of birds, mammals, amphibians, reptiles, fish and invertebrates [7]. OCPs possess a cumulative capacity, slow degradation rate, and their residues are present in water and sediment even several years after their application [8]-[10] because of a number of disadvantages including environmental persistence, bioaccumulation and contamination by OCPs such as DDT, HCHs, HCB has been reported in water, sediment and aquatic birds [11], foodstuffs [12], wildlife [13], drinking water [14], human adipose tissue [15], and human milk [16], [17].

A. Aim of Study

Owing to the greater environmental significance of OCP in marshes, the study envisages having a proper assessment of OCP in water and sediment. Thus, the objective of the present study was:

1) To determine the concentration levels of OCP in pesticides in surface sediment of marshes.
2) To obtain trends in spatial and temporal variation of organochlorine pesticides concentration and Correlation with the physical properties [Temperature (C) water, PH and EC (ls/cm)].

The results obtained may be made use of as a baseline data in developing effective remedial measures to improve the water quality status of marshes.

II. Materials and Methods

The present study was conducted to investigate the levels of pesticides in flooded marshes. This information an important baseline for monitoring the impacts of pesticides on the

Dr. Wathiq Abaas Hatit is with the Baghdad University, Genetic Engineering and Biotechnology Institute, Baghdad 496, Iraq (e-mail: wathiqaldrghi@yahoo.com).

Dr. Reyam Naji Ajmi is post doctorate, main research field: environmental water quality (e-mail: reyam80a@yahoo.com).

Dr. Huda Farooq Zeki is with the Department of Environmental Science, AL-Mustansaryah University, and Baghdad 496. Iraq (e-mail: zekihuda@ yahoo.com).

Dr. Abdal-Kader Saeed Latif is with the Medical City Hospital in Baghdad, Iraqi Ministry of Health /Baghdad 496, Iraq (e-mail abdalkader@ yahoo.com).

restored wetlands and the quality of the environment in marshes, the work steps as follows:

A. Site Description

The study areas are points along the major marshes (Hawizeh, Hammer and The Central Marsh) in southeast Iraq. Hawizeh marsh is located to the east of the Tigris River in Missan Governorate. Depending on the time of the season, Hawizeh marsh could cover about 3,000 km^2. Al-Hammar Marsh is situated almost entirely south of the Euphrates, extending from near Al-Nasiriyah in the west to the outskirts of Basra on Shatt al-Arab in the east. Al-Hammar Marshes are bordered by a sand dune belt of the Southern Desert. Estimates of this marsh area range from 2800 km^2, extending to a total area of over 4500 km^2 during periods of seasonal and temporary inundation. Al-Hammar dominates the marshes is the largest water body in the lower Euphrates. Maximum depth at low water levels is 1.8m. The triple-quad LVI/GC/MS/MS provides excellent selectivity in complex matrices by generating unique spectral fingerprints. These provide identification producing increased data. This enhancement is essential in further accuracy in measuring the concentration of the pesticides.

B. Sample Collection and Preparation

We collected 25 samples of water and 25 samples of sediment was based on points along the five major marshes five replicates for each (AL-Hammar in June, Cross of Al Fuhod Al Tar, Downstream of AL-Mashab & AL-Salal, Hawizeh, and AL-Chebayesh) in Southern Iraq during three months: April, June and September. Collection of five replicates of each site within three months distributed within the entire marsh. One liter of station water from 20 to 30cm below the water surface was locations near the site of sediment sampling. The upper 15cm of the surface sediments that each station to avoid site deviations in each sampling, were chosen based on their distinguishable locations and were positioned by a Global Positioning System (GPS) based on the main entrance in marshes. At each sampling site, the samples were collected and transferred into polythene bags and transported to laboratory. After drying, the samples were mixed thoroughly then sieved through a 2mm sieve. The sediment samples were extracted by Soxhlet extraction method [26]. Then, the cleanup was carried out by Silica Gel (Silica gel 60, particle size 0.0630-0.200mm, 70-230 mesh ASTM purchased from Merck, Darmstadt, Germany) Clean-up Method, USEPA Method [18], [19]. Standard mixture containing twenty-two OCPs (22 compounds specified in EPA method 8081B) was purchased (Sigma Aldrich, USA).

C. Analysis

All the samples were analyzed on Gas Chromatograph (Perkin Elmer Instruments, Auto System XL GC), equipped with ECD (Electron Capture Detector) and a Perkin- Elmer wide-bore capillary column (PE-5 column) with the dimensions 30m × 0.53mm i.d. × 1.5µm. Scheirer–Ray–Hare extension of the Kruskal–Wallis test was used to determine differences in some OCP residues in water and sediment samples and sampling station and seasons [20]. The 0.05 level of significance for probability was used as the criterion of statistical significance.

1. Extraction of OC Pesticides in Water Samples

In the laboratory, using liquid-liquid extraction (LLE), the total amount of each surface water sample (800ml) was filtered with Whitman filter paper (i.d. 70mm) to remove debris and suspended materials and then poured into a 2 liter separatory funnel. For the first LLE, the mixture of 100ml n-hexane and dichloromethane (1:1 v/v) was added and shaken vigorously for 2min before two phase separation. The water-phase was drained from the separator funnel into a 1000ml beaker. The organic-phase was carefully poured into a glass funnel containing 20g of anhydrous sodium sulfate through a 200ml concentrator tube. Following the second and third LLE, the water-phase was poured back into the separator funnel to re-extract with 50ml of the same solvent mixture. The extract was concentrated to the volume of 2ml under a gentle stream of nitrogen using rotary evaporator and then analyzed with Gas Chromatography with micro Electron Capture Detector (GC-IECD) [21], [22].

2. Extraction of OC Pesticides in Sediment Samples

OCP in sediments samples were extracted using Soxhlet Extraction. A 10g sample was placed into a beaker containing 50g 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 150ml of acetone: n-hexane (20:80 v/v) at 50°C for 4h. The extracts were filtered, concentrated to 1ml using vacuum rotary evaporator. Each of the raw extracts was then dissolved in 10ml hexane and passed through pre-conditioned octadecyl C-18 columns at a rate of 2ml minG1 to clean up. The column was washed with 1ml, 30% methanol followed by 1ml ultrapure water and was allowed to dry. The sample which was trapped in the column was eluted 5 times with 0.5ml 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 1ml portion of hexane, mixed thoroughly with a whirl mixer and then transferred to auto sampler vials ready for gas chromatography [22], [23].

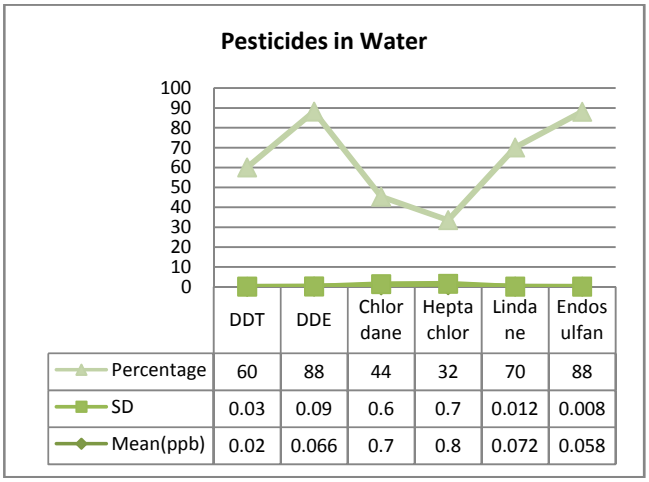
III. Results And Discussion

This study indicates the levels of organic contaminants represent an attempt to understand the effects of the pollution and current contamination status in this area. As a result, the following interpretation and discussion will be focused on the nine organochlorine pesticides (lindane, heptachlorepoxide, chlordane, endosulfan I, endosulfan II, die ldrin, endrin, DDT, heaxachlorobenzene) in water and sediment.

A. OCP in Water

The total OCP concentrations in water of marshes ranged (0.018-0.020), (0.05-0.014), (0.02-0.06), (0.03-0.06), (0.050-1.20), (0.040-0.078) ppb, respectively DDT, DDE, Chlordane,

Heptachlor, Lindane, Endosulfan recorded a high concentration in some locations a close to a source input flow. The high concentrations at these sites might be associated with the input of pollutants from the marshes. The concentrations of pollutants were diluted when they discharged from the marshes water may be influenced by the balance of sorption and partitioning between sediments and pour water [17], [21], [23], [25]. The concentration OCP compound showed that no significant differences can be seen among seasons unless for lindane. We notice this difference between April and June and according to mean value of lindane, which can be related to time of sampling. Fig. 1 shows the total results from concentration of OCP residues in water during three seasons.

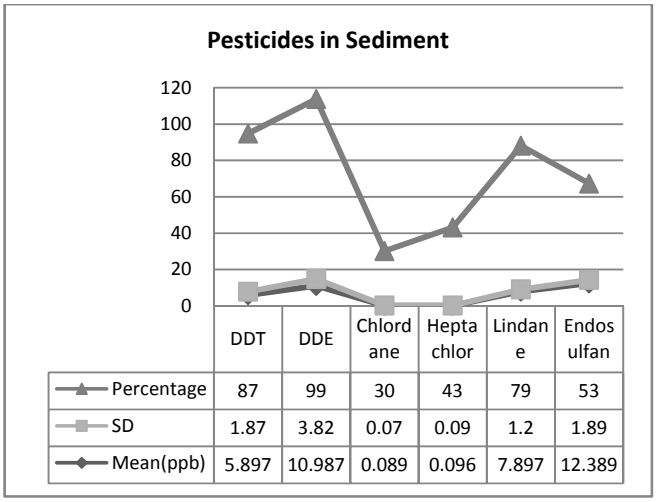


	DDT	DDE	Chlordane	Heptachlor	Lindane	Endosulfan
Percentage	60	88	44	32	70	88
SD	0.03	0.09	0.6	0.7	0.012	0.008
Mean(ppb)	0.02	0.066	0.7	0.8	0.072	0.058

Fig. 1 The total results from concentration of OCP residues in water

B. OCP in Sediments

The total OCP concentrations in sediment of marshes ranged (5.34-7.13), (13.37-33.43), (0.34-0.45), (0.25-0.59), (3.98-4.36), (6.45-7.89) ppb, Respectively DDT, DDE, Chlordane, Heptachlor, Lindane, Endosulfan. Fig. 2 shows the concentrations of pesticides in Sediments in marshes during three seasons. The concentrations of OCPs are at a relatively less to medium level and significant effect of season on OCP compound concentrations for chlordane (p\0.05) between April and June. According to mean value of chlordane, it was more in June than September. There wasn't significant differences in OCP compound concentrations among stations in each season. The patterns of change in pesticide concentrations relatively a few high in the sediment than the water because the concentrations of pesticide are not always in equilibrium. Furthermore, when sediments are smaller, the rate of deposition is slower in almost an exponential manner; however, the sedimentation rate of sediments with pesticides and the characteristics as an adsorbent of pesticides. Sediments as a carrier of pesticides are necessary in the field. Also, garbage and wastewaters are poured in the wetland by inhabitants. All of these factors may lead to the contamination of marshes [11], [17], [24], [25].



	DDT	DDE	Chlordane	Heptachlor	Lindane	Endosulfan
Percentage	87	99	30	43	79	53
SD	1.87	3.82	0.07	0.09	1.2	1.89
Mean(ppb)	5.897	10.987	0.089	0.096	7.897	12.389

Fig. 2 The concentrations of pesticides in Pesticides in marshes

C. Correlation of OCPs with the Physicochemical Parameter of Samples

Organochlorine pesticides are derived from anthropogenic inputs, their levels in water are therefore determined by a number of closely related factors such as the nature of the transport processes, reactions in the sediment, and reactions across the sediment/water interface [18], [25], [26] Results in water less than in sediments reflecting possible long term deposition and accumulation in marshes.. Table I percentage concentrations of organochlorines in water (ng/l) and sediment (ng/g dry wt.) with Parameters. These correlations reflect the fact that many factors contributed to the OCP residues in water. Also, it exhibited good correlation between OCP in Sediments with parameters. It depicted that the relationship between total OCPs of sediment was only significant for contaminated sites. This depicts that partitioning of OCPs; they may not have reached equilibrium, resulting in low correlations between OCP in sediments and water. For this can see the high temperatures in the months April and June is a major cause to evaporation and this reduces the possibility of increased deposition pesticides with a convergence in pH and EC through the season statistical analysis and the percentage between the concentration of pesticides in water, sediment and its relationship with parameters explains that there is a positive correlation between high temperature and electrical conductivity with equal pH in most seasons of the year that the marsh region in winter the temperature range 10-15°C and 40-50°C in the summer and this increases the possibility of evaporation and deposition of organic pesticides long term. This is a good percentage not more than permissible limits with the WHO [22].

IV. Conclusion

Pesticides are present in everyday life of any community. Depending on their toxicity it might also be expected that the newly flooded wetlands are almost pesticides-free. Where a few percentages present and possible are the future contamination and accumulation in the marshes and increase the concentration levels of organochlorine (OCP) pesticide,

this is an indicator of pollution. This hypothesis is based upon the following assumptions: (1) exposure to high temperature (i.e., in excess of 50C in summer) and solar radiation for more than 10 years could have activated bacterial degradation of organochlorine residues under aerobic conditions, and (2) obliteration of the river water inflows to the wetland would have limited upstream pesticide inputs via drainage from the surrounding watershed to the new flooded wetlands. As a consequence of exposure and drying out of the wetlands, pesticide residues in the wetland sediments were subjected to harsh weathering processes. The concentration range was less in comparison to other studies [26].

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APPENDIX

TABLE I
PERCENTAGE CONCENTRATIONS OF ORGANOCHLORINES IN WATER (NG/L) AND SEDIMENT (NG/G DRY WT) WITH PARAMETERS

Parameters	Station 1		Station 2		Station 3		Station 4		Station 5	
	Water	Sediments	Water	Sediments	Water	Sediments	Water	Sediments	Water	Sediments
Temperature April	40%	0.80%	43%	0.74%	49%	0.64%	33%	0.76%	49%	0.75%
Temperature June	33%	0.73%	39%	0.85%	32%	0.68%	42%	0.88%	33%	0.54%
Temperature September	42%	0.63%	41%	0.96%	40%	0.60%	29%	0.75%	41%	0.64%
PH April	5.60%	5.60%	5.60%	6.80%	5.60%	6.60%	5.60%	7.60%	4.56%	6.30%
PH June	5.80%	5.70%	5.80%	7.40%	5.80%	5.90%	5.80%	8.10%	5.28%	6.90%
PHSeptember	5.10%	6.10%	5.10%	6.60%	5.10%	6.10%	5.10%	7.10%	5.90%	6.20%
EC(ls/cm) April	0.06%	10.80%	0.08%	5.10%	0.09%	7.80%	0.04%	5.50%	0.07%	4.30%
EC(ls/cm)June	0.15%	15.12%	0.19%	14.10%	0.18%	12.30%	0.11%	10.20%	0.15%	18.60%
EC(ls/cm) September	0.19%	17.40%	0.22%	14.10%	0.29%	10.20%	0.18%	10.90%	0.20%	20.23%

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