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Full Length Research Paper

Residual levels of the organophosphate malathion in water, sediment and a threatened fish from Ethiope River, Delta State, Nigeria

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Abstract

The organophosphate pesticide malathion, was observed and measured in water, sediment and fish (*Tilapia mariae*) from Ethiope River. This study was made from three stations, Amukpe, Igun watershed and Owah-Abe, all along the River during the dry (January-April) and wet seasons (May-August). The physicochemical and microbiological characteristics of surface water were also taken on a monthly basis. Analysis of the pesticide was done using High Performance Liquid Chromatography (HPLC model CECIL 1010) to elucidate its distribution in the different environmental compartments. The concentration of the pesticide residue in the matrices ranged from 0.01µg/l – 2.24µg/l (water), 0.03ug/gdw – 2.46ug/gdw (sediment) and 0.16ug/gdw – 5.10ug/gdw (*Tilapia mariae*) during the dry and wet seasons. Results from the study showed that sediment and *Tilapia mariae* were higher in malathion residue than water, that is, concentrations of malathion increased in the order of water, sediment, fish samples. Spatial variations occurred with downstream stations having statistically higher concentrations in all matrices at $p < 0.05$. There was seasonal variation with higher concentrations of malathion residues observed in the dry season for water, while sediment and fish had higher concentrations during the wet season. The physicochemical parameters analysed were within the recommended limit accepted by the regulatory body in Nigeria. The observed residual levels of malathion were above the ecological bench mark (0.01ug/l) stipulated by the Federal Ministry of Environment, an observation that calls for proper monitoring of the Niger Delta water bodies in Nigeria so as to prevent contamination that could be detrimental to human health.

Keywords: Surface water; Sediment; Ethiope River; Amukpe; Igun ; Owah Abe

INTRODUCTION

Malathion is a non systemic, wide-spectrum organophosphate insecticide. It was one of the earliest organophosphate insecticides developed (introduced in 1950). It is widely used in agriculture, residential landscaping, public recreation areas, and in public health pest control programs such as mosquito eradication. In the US, it is the most commonly used organophosphate insecticide (Bonner et al., 2007). It is available in emulsifiable concentrate, wettable powder, dustable powder, and ultra low volume liquid formulations. It may also be found in formulations with many other pesticides.

Malathion may enter the aquatic habitat either from direct use in insect control and in the suppression of pests or from indirect sources. Indirect sources of hydrosphere contamination include residue transfer through spray drifts, aerial application, wash-off from the atmosphere by precipitation, erosion and run-off from agricultural lands, and discharge of industrial and sewage affluents (Premazzi, 1984). Malathion is also used as a grain protectant to control insects attacking stored grains and grain products in many countries of the world (Tagatz et al., 1974). Transport of malathion residues in air may follow aerial applications or result from spray drift or post application volatilization. Data indicate that malathion may be transported in the air following application to either agricultural or urban/residential areas, (Le Noir et al., 1999). Malathion has been observed in fogwater collected from pristine remote areas, indicating that it may be transported away from locations of use. The water solubility of malathion is relatively high from an environmental fate perspective, at 145 mg/l (25 EC), leading to a high potential for its transport in surface water and groundwater (Mulla and Mian, 1981). Additionally, malathion generally does not adsorb significantly to soils, leading to a high potential for its leaching through soils and into groundwater. Data from several studies summarized in a review paper indicate that malathion has been detected in both surface water and groundwater, and that its presence may be attributed to either direct application or contamination from indirect sources (Mulla and Mian, 1981).

The physio-biological effect of malathion on different species of fish have been given by various workers (Ahirwar et al., 2012; Leight and van Dolah, 1999; Lal B et al., 2003; Naosekpam and Gupta, 2013),who reported on the sublethal and lethal effect of this pesticide.

MATERIALS AND METHODS

Description of study area

The Ethiope River is situated in the North Central part of Delta State between (Latitudes 05º 52.390´ – 05º 51. 592´ N and Longitude 006º 10.675´- 005º 43.863´E), with sampling stations at Amukpe, Igun watershed and Owah-Abe (Figure 1). Amukpe and Igun stations were selected for this study as a result of the widespread use of pesticides in these regions while Owah-Abe served as a reference station, an upstream station without agricultural activities. The Ethiope River meets several socio-economic needs (aquaculture, fishing, sand dredging and drainage) of the various towns and villages bordering it. The geology of the study area is of the sedimentary type with a lithology of top layer (4- 6m) of silty clay and sand followed by a thick (up to 17m) sand layer, silty at the top but becoming coarse and pebbly with depth (Okoye *et al.,* 1987). The study area is located within the equatorial region, having two climatic regimes: the wet season, which begins in April and lasts till October and the dry season from November to March. With the incidence of climate change, the timing of the seasons fluctuate from year to year. The mean annual rainfall is 2800mm with temperatures varying between 23^0C and 37^0C in the afternoon and dropping to between 18^0C and 22^0C at night.

Sampling plan

The stations from which samples were taken were visited monthly to collect surface water, sediment and fish samples, *Tilapia mariae* for pesticide residue analysis. Analysis of physicochemical and microbiological characteristics of surface water was also carried out from each of the sampling stations monthly. The parameters measured are; Temperature, pH, Turbidity, Total Dissolved solids, Dissolved Oxygen, Biological Oxygen Demand, Nitrate, Phosphate and Faecal coliform from each of the sampling stations and was done monthly.

Sample collection

One Liter surface water grab samples from each station was collected monthly and kept refrigerated at 4ºC until analysis for pesticide residues. The upper 2 cm of the bed sediment at each site was taken from where fine-texture substrates accumulated with a Teflon coated spoon and wrapped in aluminium foil. Samples were immediately placed on ice during transport (< 6 h)) and then stored at - 20ºC in the laboratory until analysis. Fish samples (*Tilapia mariae*), caught from each sampling station was kept in plastic bag, labeled and kept at -20ºC in the laboratory until analysis.

Chemical analysis

Malathion (98.5% purity) and methanol for High-Performance Liquid Chromatography (HPLC) were obtained from Chemical Service (West Chester, PA, USA). High purity pesticide grade solvents (hexane, dichloromethane and surrogate standard solution) were obtained from Merck (Darmstadt, Germany). Na_2SO4 (99% purity), petroleum ether (analytical grade) were supplied by Sigma –Aldrich (USA) and helium (purity 99.99%) by Messer Technogas (Czech Republic). Equipment included glassware, Cecil HPLC system comprised of CE 1200 high performance variable wavelength monitor and CE 1100 liquid chromatography pump, UV detector with variable wavelength and stainless steel column (C18 Reverse phase) packed with Octasilica, vacuum pump and ultrasonic check.

Sample Extraction

Water

One liter water sample was extracted by Pure Solvent Extraction. 150ml of Petroleum ether and 100g anhydrous sodium sulphate (Na_2SO_4) was added to the water sample. Petroleum ether supernatant was decanted into a glass funnel fitted with filter paper and collected as petroleum ether extract. The above extract was concentrated on a rotary vacuum evaporator and eluted with methanol.

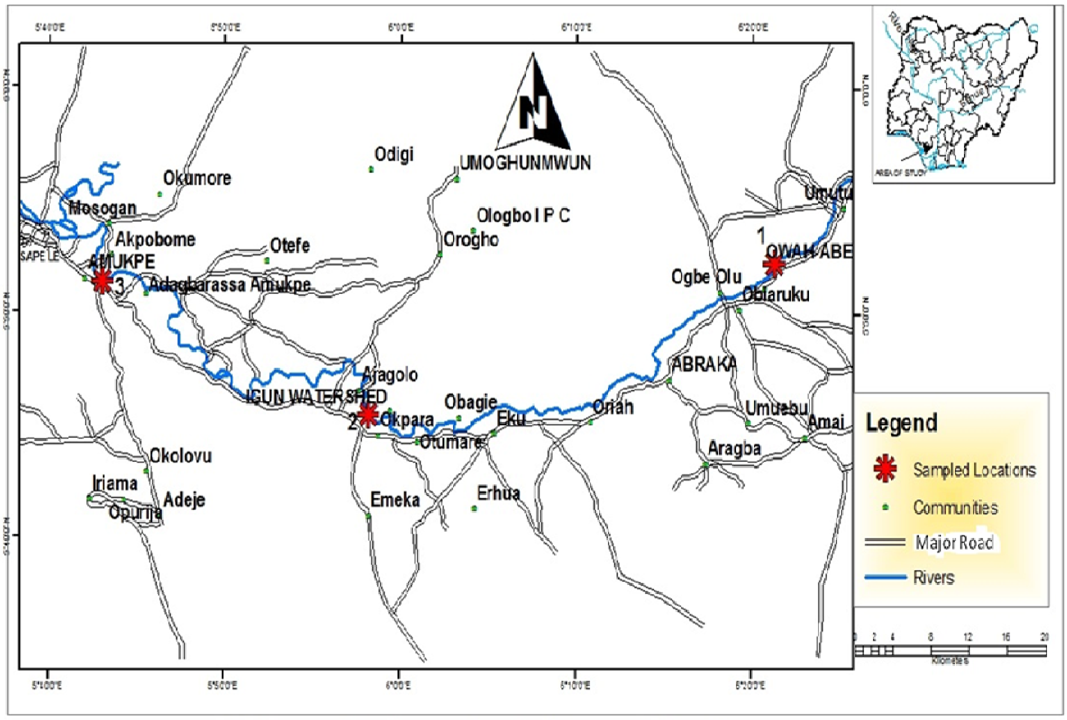

Figure 1: Map of study area showing the sampled locations

Sediment

Wet sediment samples were homogenized, air dried and extracted using Solid Phase Extraction (International Sorbent Technology, 1995). The samples were passed through a no. 32 mesh sieve. 15 gram of dried sample was thoroughly homogenized in 150ml of petroleum ether in a metallic blender at high speed until thoroughly mixed and 100g anhydrous sodium sulphate (Na_2SO_4) was added. Petroleum ether supernatant was filtered into a 500ml flask fitted with a suction apparatus. The residue in the blender cup was re-extracted with two 100ml portions of petroleum ether, blended for 2 minutes each time, filtered and combined with the first extract. The combined extract was passed through column (25mm x 50mm long) of anhydrous Na_2SO_4 and collected as petroleum ether extract. The above extract was concentrated on a rotary vacuum evaporator at steam bath temperature and eluted with methanol.

Fish

One gram of dried fish tissue was weighed into a clean extraction bottle. Malathion was extracted using acetone, water and dichloromethane, having been subjected to vigorous shaking in a sonication bath for 5hrs.The solvent was separated and concentrated in a rotary vacuum evaporator and eluted using HPLC methanol.

Pesticide Analysis

Each sample residue was dissolved in 1ml HPLC methanol. The extracted residues were then injected into the valve of the chromatograph system. The resulting chromatogram for each sample was printed out. The retention times noted, concentrations determined and recorded.

Data Analysis

The data were summarized separately for each sampled station using Description Statistics (means, range, standard deviation, standard error). Statistical differences between the seasons were analysed using Student's t-test, while the differences between the polluted and reference stations were analysed using one-way analysis of variance with confidence range of $p < 0.05$ with SPSS (16.0 version), SPSS Inc, USA. Multiple bar graphs were used for pictorial representation.

RESULTS

The concentration of the physicochemical characteristics of the study river is within the water quality standard range recommended for domestic water by the Nigerian Federal Ministry of Environment (Table 1). The results of

Table 1: Range of the concentrations of the physicochemical parameters of Surface Water at three stations along the Ethiope River, sampled monthly from January to August.

Parameters	Amukpe	Igun watershed	Owah-Abbe	DPR/FMEnv Recommendation
Temperature (ºC)	24.00-27.00	22.00-26.00	22.60-26.00	40 ± 5
pH	5.08-7.03	5.60-6.80	4.95-6.95	6.5-9.2
Turbidity (NTU)	0.50-18.33	0.40-18.00	0.40-14.00	10
Total Dissolved Solids (mg/l)	84.00-151.00	74.00-143.00	52.00-162.00	300
Dissolved Oxygen (mg/l)	4.48-8.20	5.03-7.90	4.94-7.30	6
Biological Oxygen Demand (mg/l)	3.32-5.00	4.00-5.08	3.38-4.64	4
Nitrate (mg/l)	0.70-7.00	2.75-4.80	2.58-5.01	10
Phosphate (mg/l)	0.01-2.90	0.01-1.98	0.00-2.40	5
Faeca6+l coliform (CFU/100ml)				

DPR: Department of Petroleum Resources, FMEnv: Federal Ministry of Environment

Table 2: *Malathion* concentrations during the dry season in surface water, bottom sediments and fish at three sites along the Ethiope River, sampled monthly from January to April. The means are based on monthly measurements, ND = Not detectable

Stations	Surface water			Sediment			Fish		
	Mean ± SD	SE	Range	Mean ± SD	SE	Range	Mean ± SD	SE	Range
Amukpe	1.93 ± 0.36	0.18	1.42-2.24	0.36 ± 0.44	0.22	0.03-1.00	1.62 ± 0.60	0.30	1.20-2.50
Igun watershed	0.83 ± 0.56	0.28	1.00-1.23	0.20 ± 0.22	0.11	0.03-0.52	0.73 ± 0.41	0.21	0.20-1.20
Owah-Abbe	0.02 ± 0.03	0.01	0.01-0.06	0.06 ± 0.03	0.02	0.03-0.10	0.59 ± 0.35	0.17	0.16-0.98

Table 3: *Malathion* concentrations during the wet season in surface water, bottom sediments and fish at three sites along the Ethiope River, sampled monthly from May to August. The means are based on 6+monthly measurements, ND = Not detectable

Stations	Surface water			Sediment			Fish		
	Mean ± SD	SE	Range	Mean ± SD	SE	Range	Mean ± SD	SE	Range
Amukpe	0.21 ± 0.39	0.20	0.04-0.80	2.07 ± 0.73	0.37	1.00-2.60	3.52 ± 1.12	0.56	2.72-5.10
Igun watershed	ND	0	ND	0.96 ± 0.40	0.20	0.64-1.50	1.85 ± 0.18	0.09	1.72-2.10
Owah-Abbe	ND	0	ND	0.73 ± 0.61	0.30	0.20-1.50	1.30 ± 0.54	0.27	0.98-2.10

seasonal and spatial variations in concentrations of Malathion in surface water, bottom sediments and fish tissue from the Ethiope River are shown in Tables 2, 3 and 4 with further illustrations in Figures 2, 3 and 4.

Malathion concentrations in surface water

The mean concentrations of malathion residues in surface water after eight months of sampling in the three selected stations along the Ethiope River were 1.07μg L^{-1}, Amukpe, 0.41 μg L^{-1}, Igun water shed, and 0.01 μg L^{-1} at Owah Abe (figure 2). The respective mean values for dry and wet seasons were 1.93 μg L^{-1} and 0.21 μL^{-1} at Amukpe, 0.83 μg L^{-1} and 0.00 μg L^{-1} at Igun water shed, 0.02 and 0.00 μg L^{-1} at Owah-Abe (Table 2and 3). Limit of detection is 0.01 μg L^{-1}.

Malathion concentrations in sediment

Figure 3 shows the concentrations of malathion residues in the sediment samples from the Ethiope River. Comparing the three sampling sites, the highest concentrations of 2.60μg gdw^{-1} was recorded at Amukpe in the month of August and 1.50 μg gdw^{-1} at Igun water shed and Owah-Abe also in the month of August. The respective means for dry and wet season were 0.36 μg

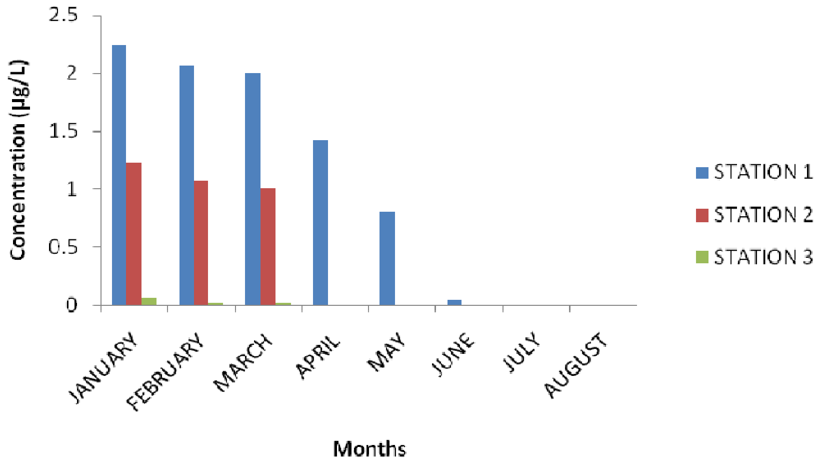

Figure 2: Malathion concentration *in* surface water of the Ethiope River, Niger Delta, Nigeria. Data are presented as monthly + concentrations standard error

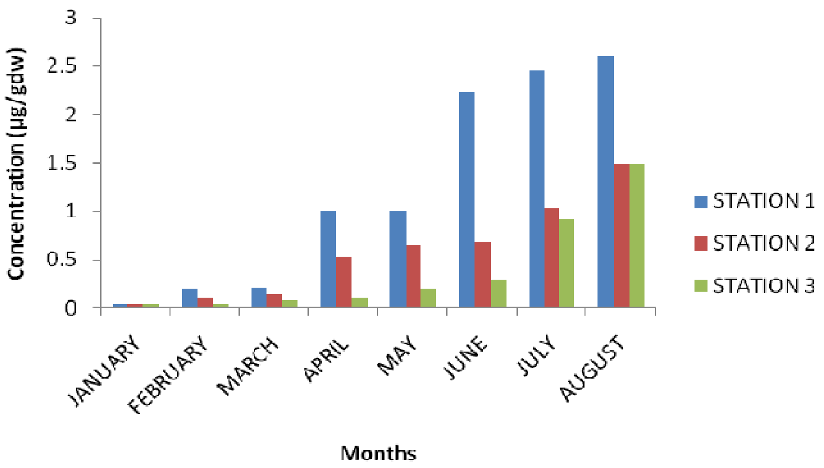

Figure 3: Malathion concentration in sediment of the Ethiope River, Niger Delta, Nigeria. Data are presented as monthly + concentrations standard error

gdw^{-1} and 2.07 µg gdw^{-1}, Amukpe, 0.20µg gdw^{-1}, and 0.96 µg gdw^{-1}, Igun water shed, and 0.06 µg gdw^{-1} and 0.73 µg gdw^{-1} at Owah Abe (Table 2 and 3). Limit of detection is 0.01 µg gdw^{-1}.

Malathion concentrations in Fish

Figure 4 shows the concentrations of malathion residues in the fish samples from the Ethiope River. Comparing the three sampling sites, the highest concentrations of 5.10µg gdw^{-1} was recorded at Amukpe in the month of August, followed by 2.10 µg gdw^{-1} at Igun water shed and Owah Abe in the same month. The respective means for dry and wet season were 1.62 µg gdw^{-1} and 3.52 µg gdw^{-1}, Amukpe, 0.73 µg gdw^{-1} and 1.85 µg gdw^{-1}, Igun water shed, and 0.59 µg gdw^{-1} and 1.30 µg gdw^{-1} at Owah Abe (Table 2 and 3). Limit of detection is 0.01 µg gdw^{-1}.

DISCUSSION

From this study, the occurrence and distribution pattern of the pesticide malathion was observed in varying

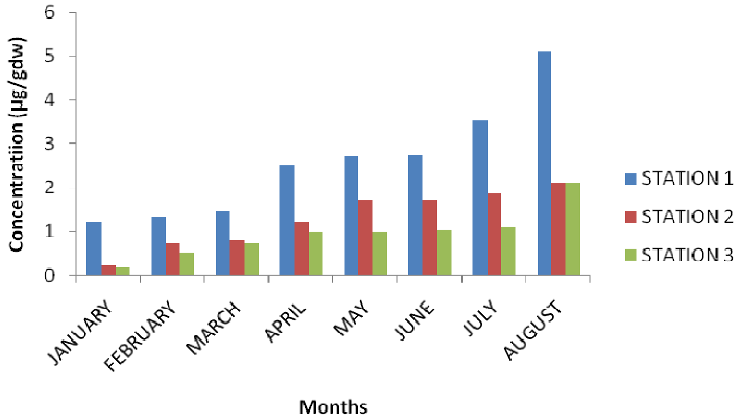

Figure 4: Malathion concentration in fish from the Ethiope River, Niger Delta, Nigeria. Data are presented as monthly + concentrations standard error

concentrations spatial-temporally in the different matrix studied. The occurrence of malathion residues may be as a result of the high use of this pesticide in the region. Of all the matrices sampled, water had the least concentration of pesticide residues. Lower concentration of pesticide residues in water according to Osibanjo et al., (1994) could be due to the hydrophobic nature of pesticides that make their presence in water to be at ultra-trace level and their accurate determination difficult. The adsorption of these compounds to particulate matter and sediment is also an important mechanism for their removal from the water column, consequently the sediment component of aquatic ecosystems can be the ultimate sink of this pesticide. In aquatic ecosystems, pesticides may rapidly be absorbed by organisms and sediments or volatilized, so that less pesticide is dissolved in water (Sara Yulia and Katharina, 2009). This could also be the reason why the concentration of malathion residues in water was lower than in fish and sediment.

The concentration of malathion residues observed in this study were higher in sediment when compared with the concentration in water. This corroborates the findings of Voss and Embrey (2000), where they reported higher concentrations of dichlorvos and malathion in bottom sediment of small streams toxicity/pesticide study in selected small streams in King and Snohomish Counties, Washington. Ezemonye (2005) reported that sediments are known to act as a sink for pollutants and therefore have the tendency of accumulating pesticide residues. In his work he observed higher PCB values in the sediment of the Ethiope and Benin Rivers of the Niger Delta Region, Nigeria.

The concentration of malathion residues in fish observed in this study was higher than the concentration in water and sediment. Ezemonye et al., (2008, 2009 and 2010) recorded higher concentrations of diazinon, propoxur and endosulphan in fish than in sediment from the Warri River also of the Niger Delta Region, indicating possible bioaccumulation. Wilfred (1995), reported higher levels of diazinon in fish than in sediment, stating a possible poor elimination in the fish.

There was a significant variation in the level of malathion residues spatially. The concentrations of malathion increased towards the downstream direction, with the station at Amukpe having highest concentrations. Pesticide contamination was comparatively low at Owah-Abe, the station upstream: this condition may be due to very low to absence of agricultural activities in the area.

The residual levels of malathion during dry season was significantly different from the levels during the wet season. Higher concentration of malathion was observed in water during the dry season compared with the wet season. Similar reports were made by Osibanjo and Jenson (1980); Ezemonye et al., (2008 and 2009) who recorded higher concentrations of pesticide residues in water during the dry season. In contrast to this, higher levels of the pesticide were observed in sediment and fish during the wet season compared with the dry season.

CONCLUSION

This stu6+6+dy reports that water, sediment and fish samples collected from Amukpe, Igun watershed and Owah-Abe stations of the Ethiope River are polluted with malathion residues. The presence of this pesticide residue may be attributed to its use by the farmers living in these areas. Therefore, proper handling of pesticides should be ensured to avoid direct or indirect exposure. Also, new and strict enforcement should be implemented by the authorities as soon as possible to control the indiscriminate use of pesticides so as to safeguard the environment and human health.

REFERENCES

Ahirwa MK, Shammi QJ, Chalko SR, Nabi Lone G (2012). Effect of Malathion on physio-biological aspects of *Notopterus notopterus* (Pallas). *Asian J. Biological and Life Sci.* 1:159-163.

Bonner MR, Coble J, Blair A (2007). "Malathion Exposure and the Incidence of Cancer in the Agricultural Health Study." *American J. Epidemiology* 166 (9): 1023–1034.

Ezemonye LI, Ikpesu TO, Tongo I (2010). Distribution of endosulfan in water, sediment and fish from Warri river, Niger delta, Nigeria. *African J. Ecology*, *48*(1), 248-254.

Ezemonye LIN (2005). Polychlorinated biphenyls (PCBs) levels and distribution in Surface water and Sediment of Ethiope and Benin Rivers of the Niger Delta, *Intern.j. Env. Studies* 65:491-504.

Ezemonye LIN, Ikepsu TO, Ilechie I (2008). Distribution of diazinon in water, sediment and fish from Warri River, Niger Delta, Nigeria. *Jordan J. Biol. Sci.* 1:31-7.

Ezemonye LIN, Ikpesu TO, Tongo I (2009). Distribution of Propoxur in Water, Sediment and Fish From Warri River, Niger Delta, Nigeria. *Turkish J. Biochemistry*. 34 (3):121–127.

Lal B, Singh A, Kumari A, Sinha A (2003). Biochemical and Haematological changes following malathion treatment in the 6+`freshwater catfish *Heteropneustes fossilis* (Bloch). *Environmental Pollution Series A, Ecological and Biological.* 42(2):151-156.

Le Noir SH, Kobayashi N (1999). Effects of aerial spraying of insecticides on non target macrobenthos in a mountain stream. *Ecotoxicol. Environ. Saf*. 19:254-270.

Leight AE, Van Dolah RF (1999). Acute toxicity of the insecticide endosulphan, chlorphyirifos and malathion to the epibenthic estuarine amphipod *Gammarus palustrid* (Bousfield). *Environ. Toxicol.Chem.* 18(50):958-964.

Mulla, M. and Mian, L. (1981). Biological and environmental impacts of the insecticides malathion and parathion on non-target biota in aquatic ecosystem. *Resver.* 78:35-101

Naosekpam S, Gupta A (2013). Acute Toxicity of Endosulfan, Malathion and Carbaryl, and their Sublethal Effects on Growth of *Channa punctatus* bloch in Cachar District, Assam, India. *Intl. Res. J. Environ. Sci*. 2(10): 39-43.

Okoye NV, Schoutan J, O'sullivan AJ (1987). "Monitoring and Evaluation of Oil Related Pollution in NNPC operation" in proceedings of the 1987 seminar on the Petroleum Industry and the Nigeria Environment held at Imo Concorde Hotel Owerri.

Osibanjo O, Biney C, Calamari D, Kaba N, Mbome IL, Naeve H (1994). Chlorinated hydrocarbon substances. In: Calamari D, Naeve H. (ed.) Review of pollution in the African aquatic environment. CIFA Technical Paper Rome: Food and Agricultural Organization of the United Nations, FAO.

Osibanjo O, Jensen S (1980). Ecological and environmental perspectives pollution. Proceeding of first national conference on water pollution and pesticide residues in food. University of Ibadan press, Nigeria. pp 206-220.

Premazzi G (1984). Evaluation of the impact of malathion on the aquatic environment. *European Appi. Res. Rept.-Environ. and Nat. Res. Sect.* 2(2):221-292.

Sara Yulia P, Katharina, O. (2009). Influence of Seasonal Changes toward Organochlorine Insecticide Residues in Fish, Water and Sediment from Upper Citarum Watershed Segment, Cisanti To N6+`5anjung, West Java. Environmental Engineering Study Program, Bandung Institute of Technology. Pp: 1-11.

Tagatz UE, Borthwick PW, Cook GH, Coppage DL (1974). Effects of ground applications of malathion on salt-marsh environments in north-western Florida. *Mosq. News* 34:309.

Voss FD, Embrey SS (2000). Pesticides detected in urban streams during rain storms in King and Snohomish Counties, Washington,1988:United State Geological Survey Water Resources Investigations Report 00-4098, 22pp.

Wilfred OB (1995). Pesticides in surface water. Distribution trends and governing factors. *Pesticides in the Hydorologic System*. S. Ann Arbor Press, Chelsea, M. I., USA.