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PESTICIDE RESIDUE ANALYSES IN FRESHWATER FISH OF MAIN LAKE, IITA, IBADAN, NIGERIA

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Matthew Zabik
Major professor

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PESTICIDE RESIDUE ANALYSES IN FRESWATER FISH OF MAIN LAKE, IITA, IBADAN, NIGERIA

By

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ABSTRACT

PESTICIDE RESIDUE ANALYSES IN FRESHWATER FISH
OF MAIN LAKE, IITA, IBADAN, NIGERIA

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Some organochlorine and organophosphorus pesticides were monitered in fish originated from Nigeria. Samples for organochlorine pesticides were mixed with Sodium Sulfate and blended with petroleum ether. A portion of the blend was placed on a Florisil column and compounds were eluted with mixtures containing 6 and 15% ethyl ether in petroleum ether. Gas-liquid chromatography with electron capture detection was used for determination of residues. DDT, Lindane, Aldrin, Endosulfan, and Methoxychlor were found in all samples at concentrations ranging from trace to 0.593 ppm. Samples for organophosphorus (OP) residues were blended with acetonitrile in lieu of petroleum ether. The blend was cleaned up through hexane/acetonitrile partitioning. Gas-liquid chromatography with flame photometric detection was used for residue analyses. Only trace to 0.220 ppm of Malaoxon was found in some samples. No other OP residues were detected. Data are intended to provide an entry point for future assessment of any change in pesticide exposure levels in this lake.

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I. INTRODUCTION

Agriculture has evolved throughout the world, especially in developed nations, as a result of innovative developments of many types. For instances, diverse and specialized machinery, development of productive varieties of plants, development and use of chemical fertilizers, and discovery and use of pesticides, to mention just a few, have helped to maintain adequate food supplies in many parts of the globe. In contrast to the developed nations, many developing countries still suffer from low productivity. In the same countries, excessive loss of food crops to insects and other destructive pests leads obviously to starvation. In all these countries use of pesticides remains one of the most powerful and dependable tools available for controlling these pests. These chemicals are more effective, economical, and adaptable for use in a variety of situations than any other proved tools for controlling pest populations at sub-economical levels (Newson et al.,1976).

As man has developed machinery and pesticides to sustain and increase productivity he has, at the same time, developed source of environmental pollution that has had adverse effects on nontarget plants and animals, including humans, our waterways (Stickel,1968) beside other related problems such as increasing number of resistant pest species (Smith,1976; Brown,1977,1978; Croft,1978). On the other hand, intensive use of pesticides in agriculture today has

led to increasing awareness of the problem of safeguarding the consumer and the environment.

Upon release in the environment a chemical may be metabolized by living organisms, be transformed through chemical or photochemical reactions, or persists unaltered. In some instances degradation or transformation results in toxic products (Menzie,1972; Crosby,1973; Goring et al., 1975). There are several properties of pesticides that contribute to their behavior as pollutants. Among these are toxicity, stability, solubility, and adsorptivity.

Different types of pesticides vary greatly in their toxicity to animals and plants. Insecticides, for example, are selected for their toxicity to insects whereas herbicides are selected for their toxicity to weeds.

Stability or persistence implies a chemical characteristic giving the products long live in soil and aquatic environments, and animal and plant tissues. They are not readily broken down by microorganisms, enzymes, heat or ultraviolet light. From the insecticidal viewpoint these are good characteristics. From the environmental viewpoint they are not. DDT and other chlorinated hydrocarbons are among the most noteworthy examples for their persistence. Their stability combined with their solubility in lipids account for their bioaccumulation and biomagnification. In contrast to the lipid-soluble chemicals, the water-soluble or polar compounds generally are excreted by animals and tend to

remain in the aqueous medium where they are readily available to attack by microorganisms.

Adsorption or binding of a chemical to soil colloids or other micellar components in the environment tends to decrease its availability to plants and animals, including microorganisms and to subsequently reduce it decomposition.

In view of the importance of the environmental quality control many countries have introduced rigid legislation requiring detailed examination of all kinds of potential hazards before a new agrochemical can be approved for specific usage. In the United States, for example, the Environmental Protection Agency (EPA) is basically the primary regulatory institution to take such measures.

Residues, hazards, and legal problems are all functions of the overall pesticide load placed on the agroecosystem. The significance of these problems is at best poorly understood on a worldwide basis because developing countries do not have qualified personel and the technological systems necessary to monitor pesticide residue levels, distribution, and degradation in the environment.

The aquatic environment in particular serves as a reservoir for tremendous quantities of foreign organic chemicals, or xenobiotics. These compounds, many of which are toxic to both aquatic and mammalian species (Matsumura, 1975; Cin et al.,1982), enter our waterways through various routes. Aquatic organisms may be exposed to xenobiotics, including pesticides by intentional contamination as in the

case of sewage effluents, hydrocarbons, lampricides, molluscides, and mosquitoe larvicides (Manda et al.,1974; Cooper,1978; Argaman,1978). Unintentional contamination may result from run-off of pesticides, industrial effluents, hydrocarbons, and other waste substances into the aquatic habitat (Keith,1974,1975; Kanazawa,1975; Carter,1978; Haller,1978).

Cases of water contamination with organochlorine pesticides or industrial chemicals were much in the news during the 1960's and 1970's. The result has often been an appearence of persistent contaminants in the exposed aquatic life. Such cases of alleged environmental pollution include PCBs in the Hudson River and the Great Lakes, Mirex in the Great Lakes, and Kepone in the James River. The direct consequences that one can infer from this type of pollution are: 1) that exposed aquatic organisms (e.g., fish) may express adverse biological effects which can bring about death (Sheila et al.,1982) and 2) when some of these substances (e.g., organochlorine insecticides) are incorporated by fish (or plant or animal) into the food chain they pass along it and accumulate in the highest predator in the chain, so that a lethal concentration may be obtained at a level several thousand times that found in the actual water (Young et al.,1979; Fry and Toone,1981). Therefore, aquatic animals consumed as foodstuff may represent a potential source of human exposure to toxic xenobiotics, including carcinogens and mutagens.

Since man heavily depends on animal proteins (e.g., fish) fate of these xenobiotics in aquatic species is of importance. Hence the concern about Main Lake at the International Institute of Tropical Agriculture (IITA) at Ibadan, Nigeria. IITA is one of the major links in a worldwide network of agricultural research and training centers (IITA Research Highlights,1983).

The importance of Main Lake for fish production, water supplies for both human needs and agricultural purposes (e.g., irrigation) has greatly increased over the years with growing populations. In addition, since outflow of this lake is limited (surrounded by agricultural lands) chemical discharges can be very persistent.

Currently there is much concern over the environmental quality of this lake with regard to its fish proteins and drinking water along with general public health. Consequently IITA has requested an evaluation on how much Main Lake is "polluted" through biological matrices (fish) after several years of expanding use of pesticides on nearby farmlands.

Organochlorine (OC) insecticides were given priority in our study because of their well known environmental persistence and high toxicity to marine organisms (Goldberg,1975; Portmann,1975). Moreover, OC pesticides, even though discontinued in use in some nations (e.g., DDT banned in the USA), are still being used and will probably continue to be used for some time in developing countries, further increase the need to study these chemicals.

Of equal importance to this investigation were the organophosphorus (OP) insecticides, most of which are known to be more toxic and less persistent than the OCs (Kanazawa,1975; Matsumura,1975), for they have also been used among other classes of chemicals at the IITA.

The purpose of this investigation was :

1. to determine the presence and magnitude of pesticide residues in fish of Main Lake;
2. to subsequently measure regional pollution believed to be caused by agricultural discharges into this lake; and,
3. to establish an initial baseline for comparison with future work for this region of Nigeria.

Our initial studies, which are reported here, describe the concentration levels and significance of nine selected pesticides in twelve fish species of Main Lake. At present, no comprehensive trace study in fish has been conducted at the IITA.

II. ANALYTICAL METHODS

A. Materials

1. Collection methods

Details on methods for fish collection are lacking. However, whole fish belonging to twelve different species (Table 1) were brought to our laboratory for trace analyses following capture. The original samples were then kept frozen (-20 ^{o}C) until analysis.

2. Sample preparation

In the laboratory each whole fish was considered as one sample. Each fish was allowed to thaw, rinsed with tap water, shaken dry, scaled off, and weighted. Then, fish was individually ground in an industrial type blendor (Model CB-5, Waring Blendor, Waring Products Co., Winted, Conn.) until a homogenous puree was obtained. The finely ground sample was subsampled into widemouth-screw-cap bottles with aluminum foil-lined caps. Every subsample was properly labelled and stored in freezer at -20 ^{o}C until analysis.

3. Glassware preparation

All glassware (separatory funnels, beakers, flasks, funnels, Teflon seals, and chromatographic tubes) were thoroughly washed sudy in hot water, rinsed out several times with tap water, then distilled water and, finally, with acetone (plus an additional appropriate solvent if necessary, for used glassware only -"like dissolves like")

Table 1 - Fish from Main Lake (IITA) sampled for residue analysis

No.	English Name	Scientific Name	Family	No. of Specimens	Wet Weight (kg)	Note
1	Nile Tilapia	Oreochromis niloticus	Cichlidae	2	1.32/0.49	A
2	Guinee Tilapia	Tilapia guineensis	Cichlidae	2	0.76/0.60	A
3	Zil's Tilapia	Tilapia zillii	Cichlidae	2	0.14/0.05	B
4	Galilee Tilapia	Sarotherodon galilaeus	Cichlidae	2	0.99/1.30	B
5	Niger Perch*	Lates niloticus	Centropomidae	2	2.83/0.29	A
6	-	Chromidotilapia guntheri	Cichlidae	2	0.05/0.04	B
7	African Pike*	Hepsetus odoe	Hepsetidae	10	0.30-0.33	B
8	Snake Head	Channa obscura	Channidae	2	0.73/0.55	B
9	-*	Mormygrops delicious	Mormyridae	1	2.63	C
10	African Mudfish	Clarias lazera	Clariidae	2	1.70/2.34	B
11	Yellow Catfish	Auchenoglanis occidentalis	Bagridae	1	1.05	C
12	Stone Head	Heterotis niloticus	Osteoglossidae	1**	2.91	A

Notes ; * - Carnivorous
** - Received with half portion (tail) chopped off
A - Introduced in 1981
C - Introduced in 1983
B - Indigenous

to get rid of any interfering contaminants. The glassware was then heated overnight in a furnacle at 450 ^{o}C before usage. Teflon seals, on the other hand, were dried out in an oven at less than 100 ^{o}C to prevent degradation of the layers.

4. Reagents

   a. Solvents

      i) All solvents; petroleum ether(PE), ethyl ether(EE), hexane, acetone, and acetonitrile were pesticide grade, glass distilled, and used as received.

      ii) Solvent mixtures

         * Mixture A : 94% PE - 6% EE

         * Mixture B : 85% PE - 15% EE

   b. Chemicals

      i) Sodium Sulfate - Na_2SO_4 (ACS) granular, anhydrous, reagent grade, and free of interference with the electron capture detector.

      ii) Florisil - PR grade, 60-100 mesh, activated in oven at 135 ^{o}C for 48 hrs. After cooling in a dessicator at room temperature, the activated Florisil was stored in glass containers with foil-lined screw caps. Enough Florisil from the same batch was submitted to the same treatment for use during the entire work.

c. Miscellaneous items

i) Glass wool (Pyrex) - free of interference with the electron capture detector (ECD).

ii) Glass filter 17G3 or equivalent was used.

iii) Reference chemical standards - all pesticides (Table 2) were obtained from EPA, Research Triangle Park, N.C..

B. Analytical Procedures

1. Organochlorine (OC) pesticides

a. Extraction

Fish sample (thoroughly ground and mixed) (10g) was mixed with Na_2SO_4 (10g) and blended, for 1-2 minutes, with petroleum ether (PE) (50 ml) in Sorvall Omni-Mixer. Following centrifugation at ca 2000 rpm for 1-2 minutes, the PE extract was decanted through a Na_2SO_4 layer (in order to remove the excess water) into a 125 ml volumetric flask. Two additional extractions were carried out as in above using 50 ml and 35 ml of PE, respectively. The total blend volume was diluted to 125 ml with a portion of PE before proceeding to the clean-up step. A 25 ml aliquot of the blend was removed for gravimetric determination of per cent fat. Another 25 ml aliquot was concentrated to approximately 2-3 ml on a rotary film evaporator for introduction onto a clean-up column.

b. Florisil chromatographic column preparation and clean-up

Pyrex columns (10 cm internal diameter(i.d.) x 51 cm length (l) with Teflon stopcocks) were packed with

Table 2 - List of selected pesticides studied

Class/Common Name	Molecular Formula
Organochlorine pesticides	
Lindane, BHC-gamma isomer	$C_6H_6Cl_6$
Aldrin (HNDN)	$C_{12}H_8Cl_6$
Endosulfan I	$C_9H_6Cl_6O_3S$
Endosulfan II	$C_9H_6Cl_6O_3S$
p,p'-DDT	$C_{14}H_9Cl_5$
Methoxychlor-p,p'	$C_{16}H_{15}Cl_3O_2$
Organophosphate pesticides	
Malathion	$C_{10}H_{19}O_6PS$
Malaoxon (Malathion oxygen analog)	$C_{10}H_{19}O_7PS$
Monocrotophos	$C_7H_{14}NO_5P$

4g of activated Florisil topped with a 2 cm Na_2SO_4 layer. This was achieved by gently taping the chromatographic tube. Each tube or column was washed with 20-25 ml of PE. The column was not allowed to dry at any time in the procedure.

The concentrate (residues) was transfered into the column using disposable Pasteur pipets. Then, the container was washed out with 1 ml of PE and wash was added to the column. Compounds were eluted with Mixture A (35 ml of 94% PE - 6% EE) for very non-polar pesticides such as Aldrin, Lindane, DDT and analogs, and PCBs if any. Relatively polar compounds like Dieldrin and Methoxychlor were eluted with Mixture B (35 ml of 85% PE - 15% EE). All eluted fractions were concentrated on a rotary film evaporator (or under liquid Nitrogen) to appropriate volume for gas-liquid chromatography (GLC) determination.

At this juncture it is essential to point out some aspects on the variability in Florisil activity. Florisil is a polar adsorbent known to have a large surface area, which is the basis of its adsorption properties. Paul A. Mills (1968) reported that the adsorption capacity of Florisil varied from one batch to another due to varying Sodium Sulfate content. Since then, several methods had been assessed to rule out this constraint. Lauric acid method is one commonly used example among major breakthroughs. In our study, however, we bipassed this problem by simply standardizing the chromatographic column with 15 ml of PE containing 10 ppm of the chemicals studied. Care was taken to keep the

Florisil activity rather constant by avoiding long exposure of the treated Florisil to humidity.

These extraction and clean-up procedures generally follow those set up by Ronald D. Erney (1983) but with slight modifications. His methodology was developed as a rapid and reliable screening procedure for pesticides and PCBs in fish (collaborative study) and was proven to be efficient, less time-consuming, economic, and comparable to the official methods for determination of residues (Erney, 1983).

Figures 1 & 2 summarize the experimental section as described above.

c. Quantitation

A standard curve was constructed for each pesticide from different concentration levels of standard solutions following injections of appropriate volume into the GLC-ECD.

A Tracor 560 Gas Chromatograph equipped with a discharge ^{63}Ni electron capture detector was used for the analyses. It was fitted with a DB1 fused Silica capillary column (30 m l. x 0.25 mm i.d.) with 25 micron liquid phase thickness and was operated at a column (oven) temperature of 270 ^{o}C and a 30 ml/min. Nitrogen (99.995% purity) flow rate. The injection port temperature was 285 ^{o}C and the detector temperature 275 ^{o}C. A SP4270 Spectra Physics Integrator was used for recording.

Figure 1 - Extraction scheme for organochlorine pesticides

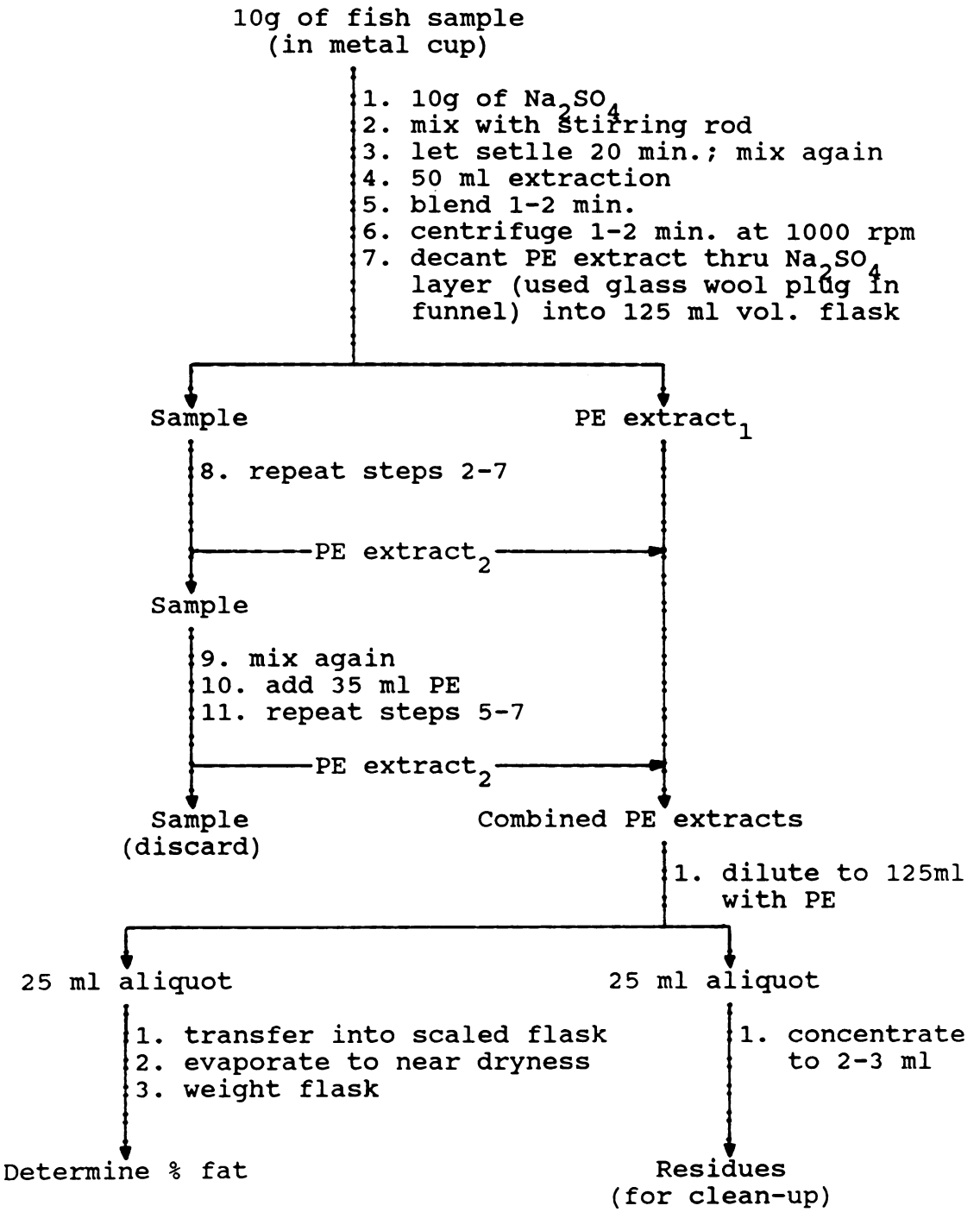
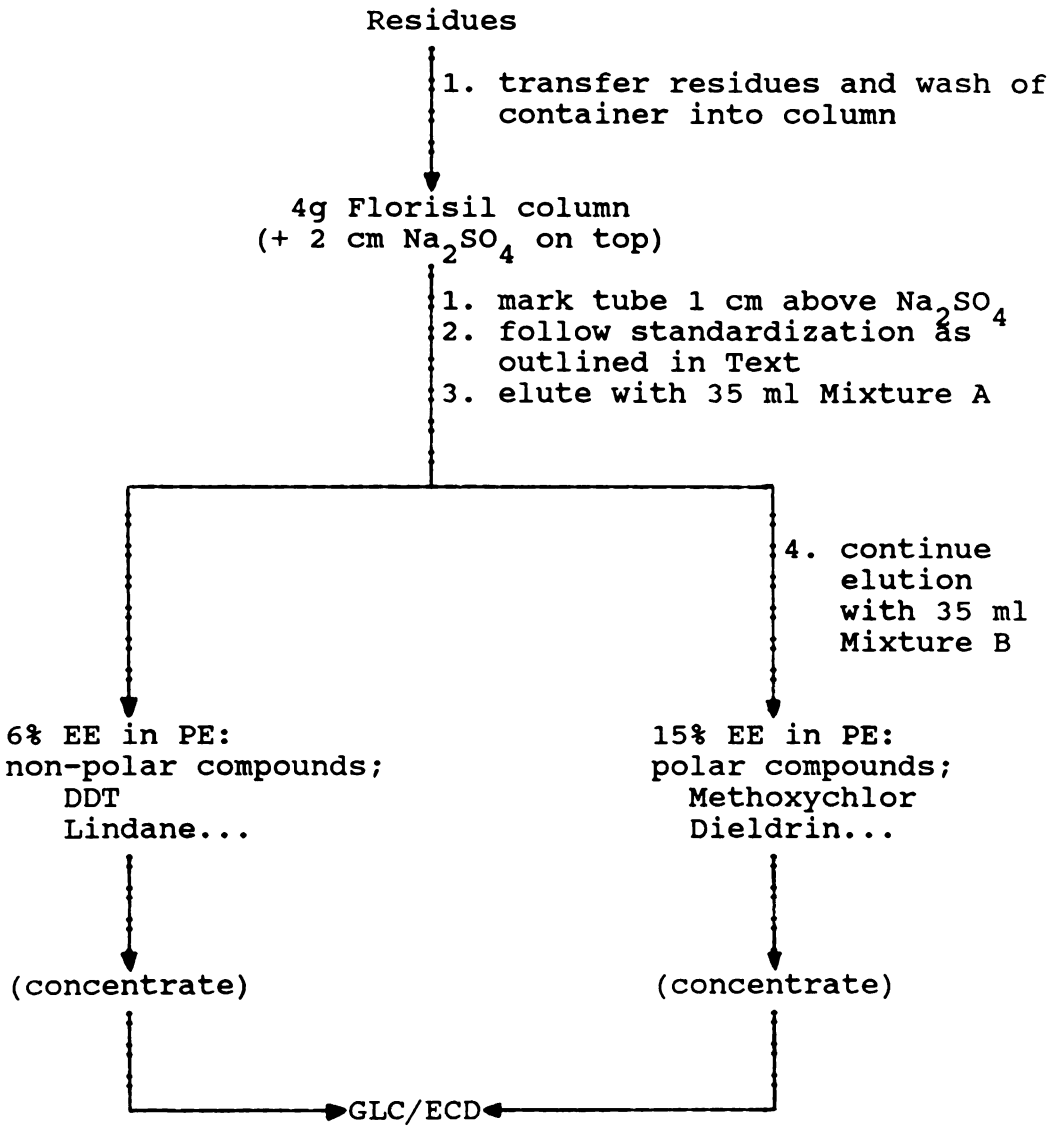


Figure 2 - Clean-up scheme for organochlorine pesticides



Standard mixtures were injected at the beginning of each run, after every three samples, and at the end of the run. Figures 3 & 4 illustrate reconstructed chromatograms of a standard mixture and a sample.

Quantitations were based upon peak heights (or areas) and the concentration levels for each compound were determined on the basis of wet weight of fish according to the following universal equation :

$$R = \frac{a\ b\ e}{c\ d} \qquad \text{(eq. \#1)}$$

where a = nanograms of pesticide represented by the standard peak

b = height (or area) of sample

c = height (or area) of standard peak

d = grams of original sample

R = residue concentration in parts per million or billion (ppm or ppb)

e = Dilution Factor derived from eq. #2 below:

$$e = \frac{\text{ml of extracting solvent x volume of final extract*}}{\text{aliquot taken of original extract (ml) x ul injected}}$$

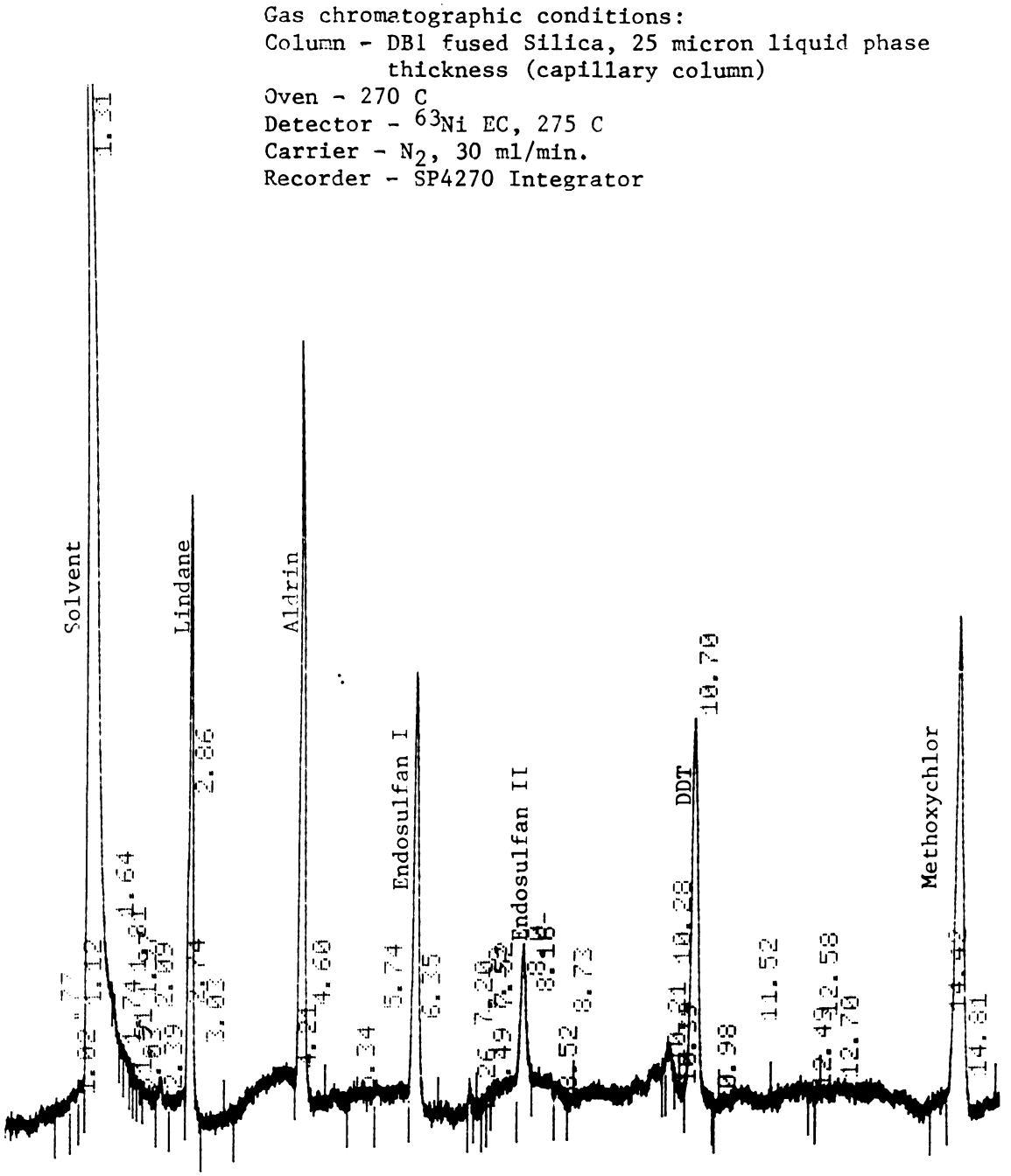
* This value is in ul for ppb and in ml for ppm

2. Organophosphorus (OP) pesticides

a. Extraction

After adding 10g of Na_2SO_4 and 100 ml (or 2 x 50 ml) of acetonitrile, the fish sample (10g) was blended in Sorvall Omni-Mixer, for 1-2 minutes, and filtered on filter papers 17G3 (or Whatman glass microfilter-GF/C). The extract

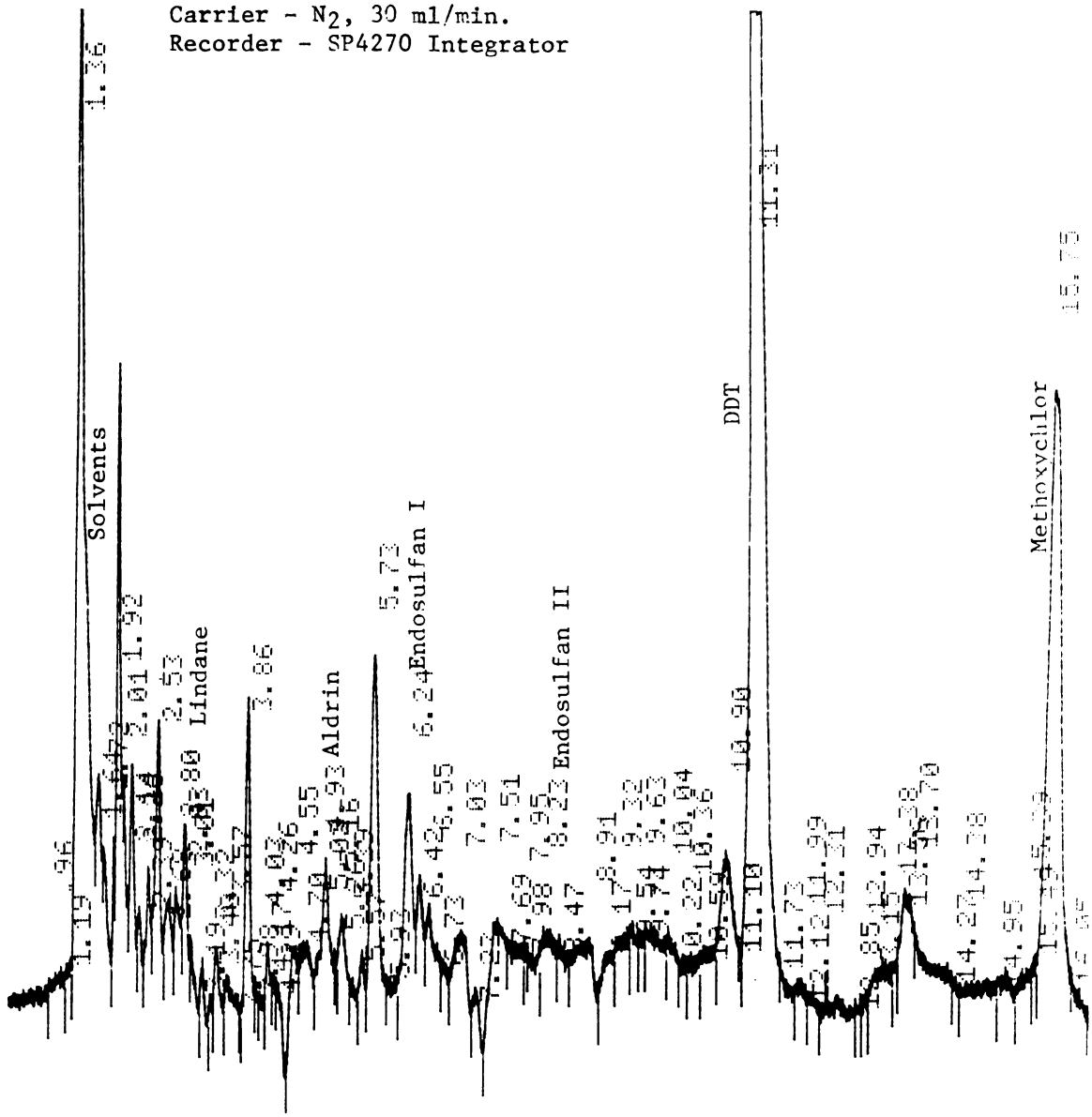
Figure 3 - Reconstructed chromatogram of a standard mixture of chlorinated pesticides studied



Note : Numbers represent retention times (minutes) for standard chemicals

Figure 4 - Reconstructed chromatogram of a sample of fish analyzed for residues of chlorinated pesticides

Gas chromatographic conditions:
Column - DB1 fused Silica, 25 micron liquid phase thickness (capillary column)
Oven - 270 C
Detector - ^{63}Ni EC, 275 C
Carrier - N_2, 30 ml/min.
Recorder - SP4270 Integrator



Note : Numbers represent retention times (minutes) for components in injected sample

was concentrated below 50 ^{o}C on a rotary film evaporator for clean-up.

b. Clean-up procedure

The concentrate (residues) was dissolved in hexane (25 ml) and transfered into a 100 ml separatory funnel, and extracted twice with each 25 ml of acetonitrile. The acetonitrile extracts were combined, and concentrated as in above and dissolved again in appropriate volume of acetone for GLC determination.

These extraction and clean-up procedures strictly followed those developed by Jun Kanazawa (1975) and were used as described with no modifications. The experimental section is given in Figure 5.

c. Quantitation

As in the case of the organochlorine (OC) pesticides a standard curve was also obtained for every OP compound. In a similar manner to the OCs, samples and standard solutions were injected into the GLC as well. Figures 6 & 7 show reconstructed chromatograms of a standard mixture and a sample.

OP residues were determined on a Beckman GC-65 gas-liquid chromatograph equipped with a flame photometric detector in the phosphorus mode. Analyses were performed at the following operating conditions :

- Column : Pyrex, 6 ft. (1.83 m) x 1/18 in. (1.59 mm) i.d. packed with 4% SE 30 + 6% OV 210 on 80/100 Chromosorb W-HP

Figure 5 - Analytical scheme for organophosphate pesticides

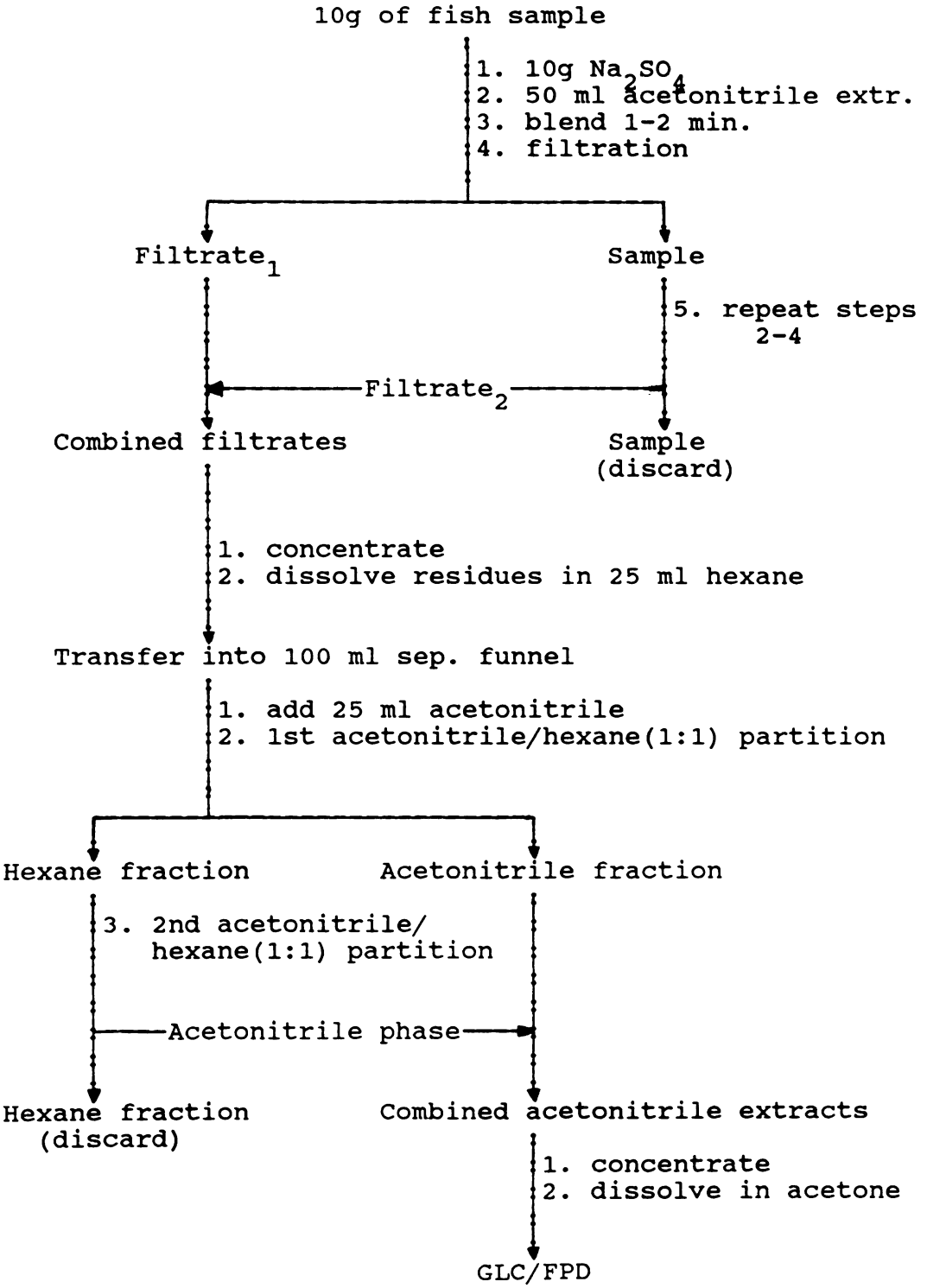
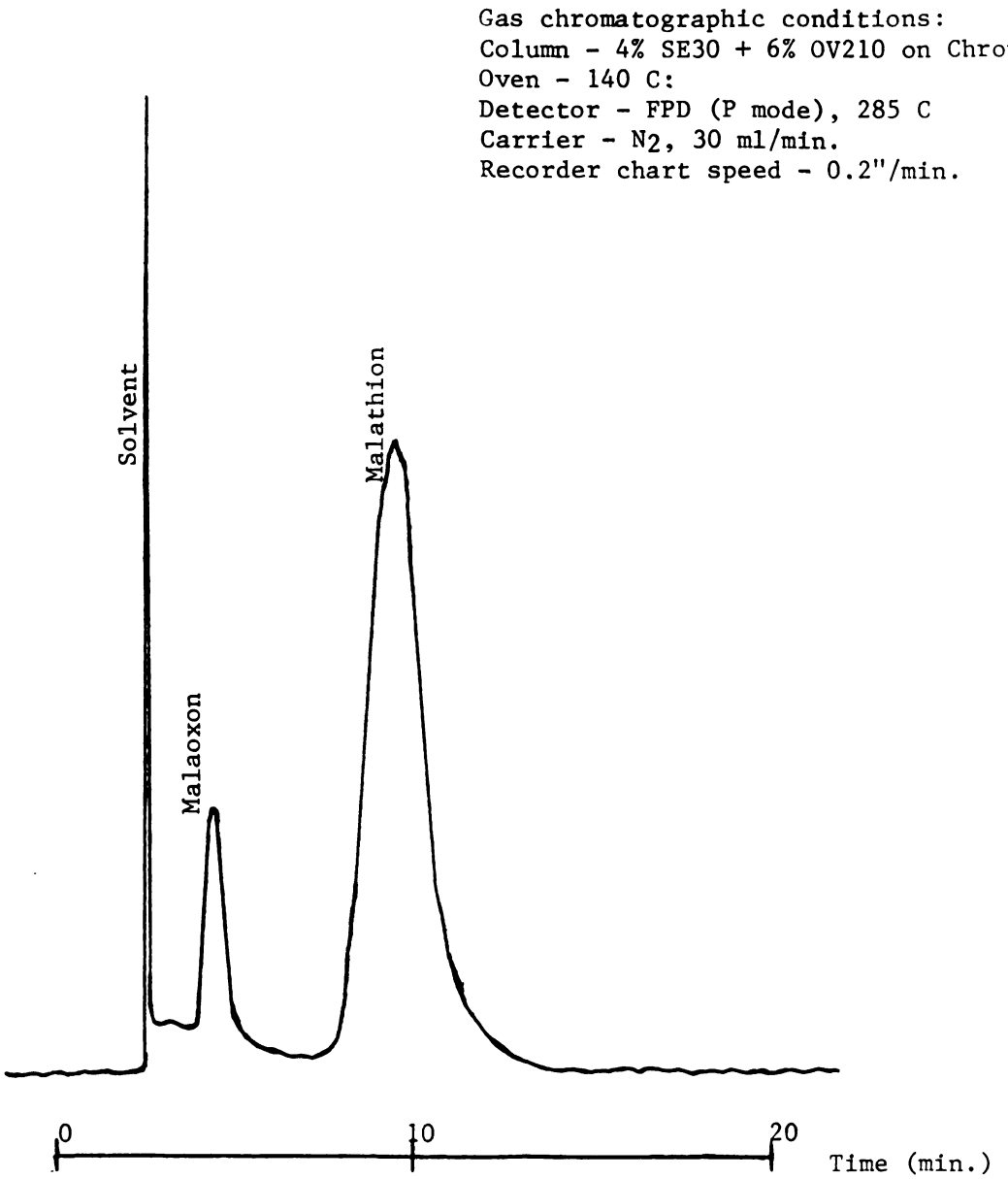
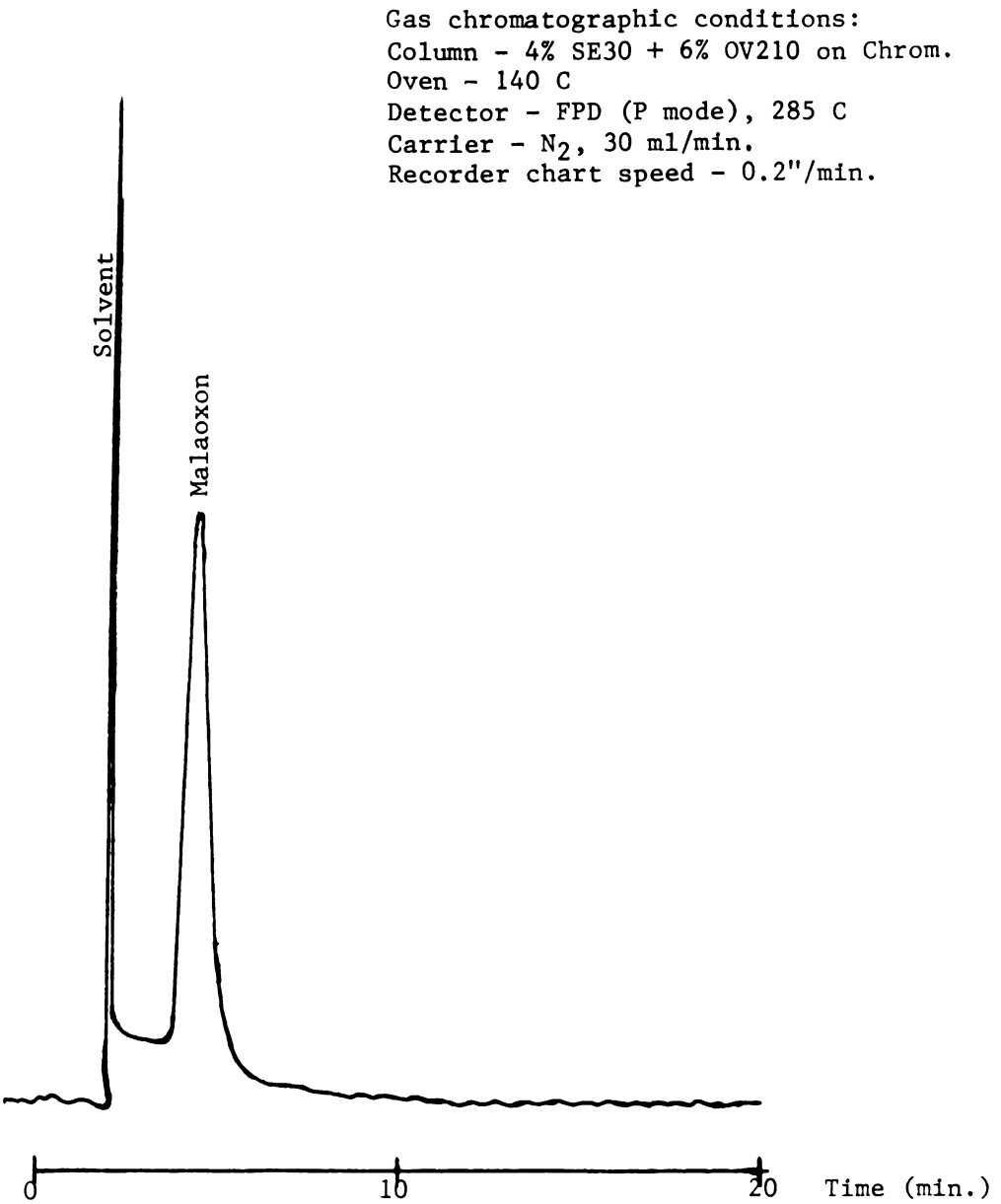


Figure 6 - Reconstructed chromatogram of a standard mixture of organophosphorus pesticides studied



Note : Monocrotophos is not chromatographed because it has about the same retention time as Malathion

Figure 7 - Reconstructed chromatogram of a sample of fish analyzed for residues of organophosphorus pesticides



- Detector temperature : 285 ^{o}C
- Column (oven) temperature : 140 ^{o}C
- Injection port temperature : 280 ^{o}C
- Nitrogen flow rate : 30 ml/min.
- Air flow rate : 115 ml/min.
- Helium flow rate : 120 ml/min.
- Recorder chart speed : 0.2 in./min. (0.5 cm/min.)

Quantitations and concentration levels of each compound were performed under the same conditions as outlined for the OC pesticides. Therefore, the residue equation (eq. #1) would be applicable to the OPs accordingly, that is,

$$R = \frac{a\ b\ e}{c\ d} \qquad \text{(eq. \#1)}$$

where only "e" spells different, the other parameters remaining the same. In this particular case the Dilution Factor (e) is given by equation #3 as follows :

$$e = \frac{\text{volume of final extract (ul or ml)}}{\text{ul injected}} \qquad \text{(eq. \#3)}$$

Since the final extract (concentrate) contained the entire original sample (no aliquot was taken), the values for the "ml of extracting solvent" and the "aliquot taken of original extract" in eq. #2 would cancel out to give "e" as in eq. #3 above.

3. Fortification/Recovery

To evaluate performence of the foregoing analytical procedures, known amounts of different concentration levels of pesticides to be determined (2, 5, and 20 times the limits of detection) were added to samples prior to extraction. This process is referred to as fortification.

Recoveries (or per cent recovery) were determined at fortification levels ranging from 0.01 to 3.0 ppm for the OC pesticides and from 1.0 to 15.0 ppm for OP chemicals before the blending operations, and the fortified samples were then carried through the above procedures . Per cent recovery was derived from equation #4 below :

$$\% \text{ recovery} = \frac{\text{amount of pesticide obtained}}{\text{amount of pesticide added}} \times 100 \quad \text{(eq. \#4)}$$

Table 3 gives % recovery for every compound of interest. Per cent recovery ranging from 79% to 99.8% are indication of good and dependable analytical procedures regardless of modifications undertaken in our study.

Table 3 - Recovery of selected organochlorine and organophosphorus pesticides studied

Compound	Average percent recovery (%)
Lindane	99.8
Aldrin	89.8
Endosulfan I	88.5
Endosulfan II	85.7
p,p'-DDT	90.0
Methoxychlor	79.3
Malathion	91.2
Malaoxon	95.6
Monocrotophos	85.2

III. RESULTS AND DISCUSSION

A. Results

Residue levels in fish are expressed as mg/kg wet weight. All of the six organochlorine (OC) pesticides listed in Table 2 were found in all samples of fish studied (Table 4). On no occasion was there any indication of polychlorinated biphenyl (PCB) contamination. Residue concentrations varied from trace to a maximum average of 0.593 mg/kg. DDT and Lindane ranked high in the majority of the samples, the main one being DDT in all species at average concentration levels ranging from 0.143 to 0.593 mg/kg wet weight whereas Lindane ranged from 0.443 down to 0.036 mg/kg wet weight. Aldrin, Endosulfan I & II, and Methoxychlor had a highly scattered distribution in all species with an overall average concentration levels of 0.004 up to 0.114 mg/kg wet weight. Among species the highest residue levels of DDT (0.593 mg/kg) were detected in samples of a specimen of Oreochromis niloticus (Nile Tilapia), those of Lindane (0.443 mg/kg) and Methoxychlor (0.114 mg/kg) in samples of Heterotis niloticus (Stone Head), and those of Aldrin (0.076 mg/kg) and Endosulfan I (0.133 mg/kg) in samples of Auchenoglanis occidentalis (Yellow Catfish) whereas those of Endosulfan II (0.088 mg/kg) were found in samples of Mormygrops delicious. All in all, residues of DDT followed by Lindane were constantly higher in samples of every single fish species in comparison with concentration levels of Methoxychlor, Aldrin, and the two isomers of Endosulfan,

Table 4 - Average and range of concentration (mg/kg wet weight) of organochlorine pesticides found in samples of fish collected from Main Lake (IITA) in Ibadan

Species	% Fat (Aver. & Range)	Lindane	Aldrin	Endosulfan I	Endosulfan II	p,p'-DDT	Methoxychlor
Oreochromis niloticus	17.0 (9.42-26.78)	0.103 (.095-.303)	0.025 (ND-.068)	0.005 (ND-.085)	0.006 (ND-.020)	0.593 (.256-.890)	0.063 (ND-.095)
Tilapia guineensis	5.5 (2.90-10.65)	0.045 (ND-.076)	0.031 (ND-.042)	0.010 (ND-.022)	0.009 (ND-.015)	0.143 (.099-.318)	0.042 (ND-.059)
Tilapia zillii	8.5 (1.90-10.65)	0.075 (ND-.135)	0.030 (ND-.058)	0.011 (ND-.025)	0.049 (ND-.074)	0.236 (.125-.580)	0.059 (ND-.078)
Sarotherodon galilaeus	15.1 (12.0-21.36)	0.236 (.157-.428)	0.016 (ND-.027)	0.028 (ND-.041)	0.005 (ND-.012)	0.323 (.110-.575)	0.045 (ND-.070)
Lates niloticus	12.7 (5.65-19.84)	0.036 (ND-.098)	0.055 (ND-.072)	0.010 (ND-.017)	0.073 (ND-.111)	0.268 (.089-.410)	0.040 (ND-.065)
Chromidotilapia guntheri	9.4 (3.00-12.50)	0.159 (.059-.392)	0.008 (ND-.014)	0.018 (ND-.027)	0.026 (ND-.030)	0.238 (.104-.627)	0.078 (ND-.085)
Hepsetus odoe	18.9 (9.29-25.60)	0.153 (.150-.326)	0.065 (ND-.087)	0.032 (ND-.046)	0.036 (ND-.078)	0.562 (.347-.915)	0.080 (ND-.093)
Channa obscura	14.8 (5.80-20.18)	0.064 (ND-.093)	0.007 (ND-.023)	0.004 (ND-.054)	0.059 (ND-.187)	0.449 (.245-.872)	0.069 (ND-.093)
Mormygrops delicious	16.3 (13.34-23.8)	0.127 (.025-.184)	0.032 (ND-.050)	0.048 (ND-.066)	0.088 (ND-.132)	0.520 (.198-.668)	0.042 (ND-.067)

Table 4 - (continued)

Species	% Fat (Aver. & Range)	Lindane	Aldrin	Endosulfan I	Endosulfan II	p,p'-DDT	Methoxychlor
Clarias lazera	14.3 (12.74-19.1)	0.175 (.020-.325)	0.015 (ND-.030)	0.056 (ND-.071)	0.078 (ND-.142)	0.334 (.279-.591)	0.046 (ND-.069)
Auchenoglanis occidentalis	15.1 (6.96-17.32)	0.093 (.063-.129)	0.076 (ND-.095)	0.133 (.112-.327)	0.084 (ND-.168)	0.384 (.129-.450)	0.055 (ND-.086)
Heterotis niloticus	20.6 (15.62-23.0)	0.443 (.371-.902)	0.030 (ND-.058)	0.085 (ND-.104)	0.081 (ND-.179)	0.546 (.328-.981)	0.114 (.103-.187)

Notes : ND - Non-detectable concentration level
Sample size : 5 - 8

which were relatively lower in the majority of fish specimens.

Although each sample was screened for three organophosphate (OP) pesticide residues, Malaoxon (Malathion oxygen analog) was the only residue detected in some samples of fish at concentration levels ranging from trace to a maximum average of 0.220 mg/kg wet weight (Table 5). Lates niloticus (Niger Perch) followed by Clarias lazera (African Mudfish) carried the highest residues; 0.220 and 0.189 mg/kg, respectively. The tabulated results of the study indicate the essential absence of any other OP pesticides, including Malathion and Monocrotophos.

B. Discussion

There must always be some ambiguity in the comparison of residue data from different species in the absence of controlled experiments on their ability to accumulate pesticides. In addition, since apparently no other trace studies in fish of Main Lake have been conducted and no detailed information on pesticide use patterns at this location is available, it is difficult to assess whether the scattered distribution of concentration levels reported here is common in this environment or whether it is particularly due to species differences. In an effort to explain the significance of the degree of contamination of the organisms sampled, substancial information available in the literature was primarily considered.

Table 5 - Average and range of concentration (mg/kg wet weight) of organophosphorus pesticides found in samples of fish collected from Main Lake (IITA) in Ibadan

Species	Malathion	Malaoxon	Monocrotophos
Oreochromis niloticus	ND	0.026 (ND-.034)	ND
Tilapia guineensis	ND	0.013 (ND-.016)	ND
Tilapia zillii	ND	0.005 (ND-.011)	ND
Sarotherodon galilaeus	ND	0.006 (ND-.009)	ND
Lates niloticus	ND	0.220 (T-.305)	ND
Chromidotilapia guntheri	ND	T (ND-T)	ND
Hepsetus odoe	ND	T (ND-T)	ND
Channa obscura	ND	0.003 (ND-.018)	ND
Mormygrops delicious	ND	0.103 (T-.114)	ND
Clarias lazera	ND	0.189 (T-.215)	ND
Auchenoglanis occidentalis	ND	0.087 (T-.105)	ND
Heterotis niloticus	ND	0.120 (T-.196)	ND

Notes : ND - Non-detectable concentration level
T - Trace level
Sample size : 5 - 8

None of the twelve fish species analyzed contained individual and average residue levels in excess of the 5 ppm (mg/kg) tolerance level of DDT established by the Food and Drug Administration (FDA), US Department of Health, Education, and Welfare or Health and Welfare in Canada. The relatively low concentrations of all the chlorinated pesticides studied at individual and maximum average residue levels less than 1.0 ppm or mg/kg wet weight in all fish specimens probably are biologically insignificant. However, DDT burdens ranging from 1.0 to 4.0 ppm if any could cause physiological stress and lessen reproductive capacity in fish populations (Butler et al., 1972). Many samples of freshwater fish were reported to contain higher pesticide concentration of chlorinated pesticide residues (mainly DDT and Dieldrin) than those of commercial fish, most of which are of marine origine (Hays,1975). Fish are able to take up all organochlorine pesticides (DDT being the best example in this case) rapidly and directly from water; the absorption occurs mainly through the gills and does not depend on food. Although fish can absorb DDT from that source also, two factors involved in direct uptake from water are absorption and lipid partitioning. Both factors are in the behavior of DDT and other chlorinated pesticides. DDT for instance is not only absorbed on the surface of the gills, living algae, and particles of dead organisms but also on surfaces generally, including those of silts (McKim et al.,1974), which probably

reflects relatively high concentrations of this compound in this study. It was reported elsewhere that fish were able to accumulate materilal from the suspended materials (Zitko,1974), however the mechanism by which uptake occurs is not understood. Neely et al. (1974) and Kanazawa (1982) reported that for many non-ionic organic compounds, including several pesticides the bioconcentration factor (BCF) increased as the molecular weights increased. According to the same authors, the BCF from water by fish increases as the solubility in water decreases, or as the 1-octanol-water partition coefficient increases. Our data also support this contention, at least for DDT residue levels. Furthermore, the constency higher concentration levels for DDT and Lindane in the majority of fish species probably were due to differences in age, in species, and more likely to the high fat content and the carnivorous behavior of some of these specimens, which in turn lead to biomagnification in top-order consumers. Because DDT is metabolized to DDD and DDE (Menzie,1978) proportionately high concentrations of DDT in fish suggest possible build-up and/or continuing inputs of this material to the aquatic ecosystem (Aguillar,1984). Our data support these observations. However, as Table 4 illustrates, our data sometimes refute the hypothesis that differences in organochlorine pesticide residues between species at a given site (Main Lake) are related to their differing lipid levels. These results support one conclusion reported by Schmitt et al. (1981): lipid content alone does not

adequately explain differences in residue levels between species at a given location.

The BHC isomers are relatively shorted-lived compared with some organochlorine (OC) pesticides. The gamma isomer, Lindane, is one of the OC pesticides that has been widely used at the IITA. It has a BCF of 50 - 900, depending on species and environmental conditions, and thus does not normally accumulate (Kanazawa,1978; Sugiriura et al.,1979). Its occurence, at more than trace, therefore indicates build-up and/or continuing inputs in the aquatic habitat.

Aldrin and the two isomers of Endosulfan , which have relatively high BCF's and long half-lives in fish samples (Clark et al.,1983), were found at very low concentration levels in the majority of fish species, but their presence has no apparent correlation with their chemical properties. Another consideration in determining fish body burdens is the fact that the rate and frequency of use of these chemicals in the Ibadan area (IITA) might be relatively low compared with those of DDT and Lindane, which could explain residue differences in fish. Aldrin which is metabolized to Dieldrin (0.3 ppm tolerance guideline set by USFDA) probably does not represent at this point in time any threat to fish, wildlife, and the consumer. A similar argumentation can be made on the behalf of the two isomers of Endosulfan.

On the basis of the information gathered (Appendix), Methoxychlor has not been used at the IITA. Its presence in all samples studied therefore suggests an

outside source of contamination. This may be attributed to atmospheric transport into the lake or to the migratory behavior of the majority of the specimens sampled, which probably explains the subsequent uptake of this material. Because Methoxychlor is shorted-lived and bioaccumulates to a lesser degree than DDT and many other OC pesticides (Kapoor et al.,1973) the residue levels found in fish probably reflect the continuing outside inputs of this compound in the aquatic environment. The current concentration levels probably are biologically insignificant and therefore should not be of concern to the consumer.

The almost non-detectable levels of organophosphate (OP) pesticide residues in this study, Malaoxon (a Malathion metabolite) being sometimes the exception in some samples, are consistent with observations made in many other parts of the world (Spehar et al.,1980; Reish et al.,1981; Chovelon et al.,1984). This reflects the relatively slow uptake and high metabolism/excretion rate of these substances by aquatic organisms (McLeese et al.,1979) which in turn produce relatively low concentration factors. For example, the 7 - 14 day concentration factor of Diazinon varies from 18 - 206, depending on species (Kanazawa,1978). Jun kanazawa (1975) reported that Malathion among other OP compounds taken up by fish was metabolized rapidily, which is also consistent with our observation. Although Malathion was not directly detected, residues of Malaoxon found in samples indicate that uptake followed by metabolism/excre-

tion of this material by fish had occured before the sampling time. Another important consideration in determining fish body burdens is the fact that the rate and frequency of OP pesticide usage at the IITA might be relatively low compared with those of the OC pesticides. In addition, the sultry tropical climate in Nigeria might have drastically impacted on the effective life of pesticides, including the OPs which degrade rather easily by hydrolysis. By large, the OP pesticides are more toxic and less persistent than the OCs and residue levels reported here probably are insignificant to biological systems.

IV. CONCLUSIONS

The results of this trace study in fish of Main Lake (IITA) show basically that residues of organochlorine (OC) pesticides (and the OPs to some extent) are present, though at low concentrations, in the majority of common fish species. Although it is generally the case that marine fish are contaminated with OC compounds (Portmann,1975), there is little evidence that levels currently found in most parts of the world are of any significance to the fish. It is, therefore, unlikely that the reported low residue levels from Main Lake will have even a sublethal effect on healthy animals. Animals forced to mobolize their lipid reserves during periods of starvation may be an exception. The significance of the latter circumstance is difficult to evaluate and will certainly vary with species, season, and such body burdens as diseases and parasites (Olafson,1978). These residues have apparently originated from the areas of intense pesticide application in the Ibadan region (IITA). The natural processes of weathering are likely to result in the transfer of pesticide residues to the main body of the lake, especially during wet seasons, where they can accumulate and persist. Since OC pesticides have high ecological magnification values and low biodegradation indices in a laboratory model ecosystem, compounds like DDT accumulate in the tissues of levels 200 to 84,000 times those found in the actual water (McKim, 1974). The water treatment if any actually has no effect on the concentration

of DDT in the water (Sunshine, Z. Editor,1969). In other words, OC pesticides (unlike the OPs) in water will be taken up very rapidly by living organisms (Sodergren,1968) or are either completely adsorbed by particulate matter (Keith and Hunt,1966). Main Lake is the site of deposition (limited outflow) of xenobiotics and suspended matter. Under these circumstances, and in view of the continuous use of OC pesticides in agriculture in this region, it is expected that an appreciable build-up of residues with time will take place in this lake. Increased contamination with residues is certain to adversly affect the fish populations (Holden,1965; Kanazawa,1975; Sheila et al.,1982) and hence endanger the plans for the development of a fisheries industry in this vital area.

Effective management of toxic substances in the environment requires a committment to long-term monitoring. Consequently, in order to keep the situation (environmental pollution) under control, it is essential that a system or fate models for the continuous monitoring of pesticide residues and even of toxic trace metals in the environmental components, for the entire region and/or the whole country, be established in that comparisons of residue data for instance in a single fish species over a wide geographic range will permit valid judgements of the regional differences in pollution levels.

APPENDIX

APPENDIX

Table 6 - List of pesticides in use and/or in stock at the International Institute of Tropical Agriculture (IITA)

INSECTICIDES		
Trade Name	Common Name	Active Ingredient
Actellic 25	Pirimiphosmethyl	25 EC
Actellic Dust	Pirimiphosmethyl	2% D
Agrothion	Fenitrothion	20 EC
Aldrex T	Aldrin + Thian	
Aldrin Dust	Aldrin	25 D
Ambush ULV	Permethrin	5 ULV
Baygon 20	Propoxur	
Baygon Aerosol	Propoxur	
Cymbush Super	Cypermethrin	ED
Decis/Dimethoate	Decis + Dimetheoate	ULV
Decis EC	Decis + Enosulfan	EC
Decis ULV	Decis + Demitheoate	ULV
Detia	Alum Phosphide	57%
Didimac	DDT	25 EC
Difolatan	Captafol	80 WP
Dimecron	Phosphamidon	50 SWC
Durban 4	Chlorpyrifos	40 EC
Furdan 56	Carbofuran	56

Table 6 - (continued)

Trade Name	Common Name	Active Ingredient
Furdan 106		106
Furdan 35 S+		35 EC
Gammalin 20	Lindane	20
Gammalin Dust	Lindane	5 D
Lindane Dust	Lindane	5 D
Kelthane	Chlorophenyl Trio-chloroethanol	42%
Malathion	Malathion	50 EC
Navan	Dichloroous	100 SC
Nogeos	DDVP	50 EC
Nuvacron EC	Monocrotophos	40 EC
Nuvacron ULV	Monocrotophos	ULV
Orthene 75	Acephate	75 WP
Phostoxin Tabs	Aluminum Phosphate	56%
Pirimor ULV	Pirimicarb	5
Roach Pruff	Boric Acid	
Roqar/ Perfekthion	Dimetheoate	40 EC
Sevin 85	Carbaryl	85 WP
Sherpa Plus EC	Cypermethrine	EC
Sherpa Plus ULV		ULV
Thiodan 25 ULV	Endosulfan	25 ULV
Thionex	Endosulfan	EC
Ultracide	Methidathion - ?	40 EC
Vetox 5	Carbaryl	5 DL

Table 6 - (continued)

Trade Name	Common Name	Active Ingredient
Vetox 85	Cabaryl	85 DL
Vetox 85	"	

HERBICIDES

Aatrex	Atrazine	40 EC
Amiben	Chloramben	240 EC
Atranex	Atrazine	80 EC
Avirosan	Piperophos + Dimethane	500 EC
Blazer	Acifluorfen	20 EC
Cobex	Dinitramine	20 EC
Cotoran	Fluometuron	500 EC
Cotoran Multi	Fluometuron + Metolachlor	75 WP
Dachtal	DCPA	75 WP
Dual	Metolachlor	500 EC
Enide	Difenamid	50 WP
Galex	Metolachlor + Metobromuron	500 FW
Gesaprin	Atrazine	500 FW
Gesatop	Simazine	500 FW
Hyvar X	Bromacil	80 WP
Hyvar X	"	80 WP
Hyvar XL	"	20 EC
Karmex	Diuron	80 WP

Table 6 - (continued)

Trade Name	Common Name	Active Ingredient
Lasso	Alachlor	480 EC
Paraquat	Gramoxone	
Patoran	Metobromuron	50 WP
Patoran	"	670
Preforan	Fluorodifen	30 EC
Primagram	Atrazine + Metolachlor	500 FW
Primextra	Atrazine + Metolachlor	500 FW
Prowl	Pedimenthalin	420 EC
Rinsane	Fluorodifen + Proponil	300 EC
Round Up	Glyphosate	36 WSP
Ronstar	Oxadiazon	25 EC
Sencor	Metribuzin	70 WP
Stam F-34	Proponil	360 EC
Stomp	Pedimenthalin	330 EC
Tamariz	Proponil + Bethocarb	200 EC
Treflan	Trifluvalin	480 EC
Weed Killer 66	2,4-D Amine	60EC
Weedone LV-4	2,4-D	60 EC
Wet ALD	Surfactant	

Table 6 - (continued)

Trade Name	Common Name	Active Ingredient
FUNGICIDES		
Benlate	Benomyl	50 WP
Demosan	Cholroneb	65 WP
Difolatan	Captafol	80 WP
Fernasan	Thiram/Lindane	25 D
Maneb	Dithane	46 WP
SOIL STERLIENTS		
Basmid Granular	Dazomet	
Telone II	Dichloropropene	92%
Vapan	Metam-Sodium	
FERTILIZERS		
Ammonium Sulphate		21% N
Calcium Ammonium Nitrate		26% N
Compound NPK 15-15-15		15-15-15
Compound NPK 26-12-0		26-12-0
Hydrate Lime		98% $Ca(OH)_2$
Iron Chelate		138 FE

Table 6 - (continued)

Trade Name	Common Name	Active Ingredient
Magnesium Sulfate		98% Ng SO_4
Muriate of Potash		60% K_2O
Single Super Phosphate		18% P_2O_5
Triple Super Phosphate		44% P_2O_5
Urea		46% N
Zinc Durham Sulfate Mono-hydrate		36% ZN
Boron Foliar Spray		
Zinc Foliar Spray		

Notes : EC = Emulsible Concentrates
D = Dusts
ULV = Ultra-Low-Volume (Concentrates)
ED = Emulsible Dusts
WP = Wettable Powders
SWC = Sprayable Water Concentrates
SC = Sprayable Concentrates
DL = Dust
FW = Flowable
WSP = Water Soluble Powders

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