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Levels of Dichlorodiphenyltrichloroethane and its Metabolites in the Blood of Agrochemicals Retailers

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Abstract: Problem statement: In tropical countries like Nigeria, the storage, sales and handling of pesticide by agrochemical retailers in indoor stores located in open markets and residential areas were fraught with problem of undesirable side effect. Serum levels of 1, 1, 1-trichloro-2, 2-di (4-chlorophenyl) ethane (DDT) and its metabolite were measured among agrochemicals retailers in Taraba, Nigeria. **Approach:** Blood samples from 50 retailers were taken and analyzed by gas chromatography with an electron capture detector. The retailers were group into five exposure duration based on their years of involvement in trade viz; 1-5 years, 6-10 years, 11-15 years, 16-20 years, ≥ 21 years. **Results:** Test detected 34 (50) retailers had residues of DDE, DDD, DDT and Aldrin in their blood. 68% of the retailers had DDE at mean concentration of 0.047 mg L^{-1}, ranged from n.d-0.0721 mg L^{-1}. 62% DDD (mean = 0.0101 mg L^{-1}, range = n.d-0.034 mg L^{-1}), 58% DDT (mean = 0.0120 mg L^{-1}, ranged = n.d-0.1120 mg L^{-1}) and 52% Aldrin (mean = 0.0045 mg L^{-1}, ranged = 0.0100-0.0265 mg L^{-1}), The total content DDT(sum of DDE, DDD and DDT) in the whole blood samples was 0.062 mg L^{-1} and ranged from 0.0008-0.185 mg L^{-1}. Dieldrin was not detected in any of the samples analyzed. **Conclusion:** Despite the banned, the observed trend for all the DDTs and metabolites shows that retailers are occupationally exposed due to the sales and handling of agrochemicals in retailers' stores. The need for stiff monitoring and enforcement by regulatory bodies is of paramount important.

Key words: DDT, pesticide retailers, occupational exposure

INTRODUCTION

Persistent organochlorine pesticide such has Dichlorodiphenyltrichloroethane (DDT) and its metabolites have provided great benefits to human since their introduction in public health to control mosquito-borne malaria and in agriculture. DDT is highly hydrophobic, colorless and with a weak chemical odor. It has a good solubility in most organic solvents which is readily absorbed through the gastrointestinal tract with increase absorption in fat. Their intensive use throughout decades and their high persistence, accumulation in food chains and in the human body especially in lipid-rich tissues has raised the interest in knowing the extent of their spread leading to investigation of the magnitude of their residues in all compound of the human environment. In tropical countries like Nigeria, after the flagging off, of Nigerian green revolution in 1977-78; the consumption of pesticide in Nigeria increased several thousand fold, according to Hotton *et al*. (2010) pesticide importation raised steadily from about 13 million dollars in 2001 to 28 million dollars in 2003 with insecticide accounting for about 32% of the imports.As agricultural production system move more and more from subsistence to market oriented large scale farming, a concomitant increase in pesticide usage seem inevitable. The spread and proliferation of the sales of pesticide in traditional local markets and small-scale retailing in indoor rented stores located in open markets, streets and residential areas are continue to dominate the Northeastern Nigeria retail section (Hotton *et al*., 2010). The Stockholm convention, which took effect in 2004, outlawed several persistent organic pollutants and restricted DDT use to vector control. The convention has been ratified by more than 160 countries including Nigeria and is endorsed by most environmental groups. Most studies of DDTs human health effects have been conducted in developed countries where DDT is not used and exposure is relatively low. Eskenazi *et al*. (2009)

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concluded that there is a growing body of evidence that exposure to DDT and DDE (dichlorodiphenyldichloroethylene) may be associated with breast cancer, diabetes, decreased semen quality, spontaneous abortion and impaired neurodevelopment in children. Exposure to DDT in relation to Indoor Residual Spraying (IRS) is of particular concern (Gatto *et al*., 2009), Commercial DDT is a mixture of several closely-related compounds. The major component (77%) is the p, p' isomers and 15% o, p' isomer. Potential mechanisms of action on humans are genotoxicity and endocrine disruption. A number of studies from the US, Canada and Sweden have found that the prevalence of the disease in a population increase with Serum DDT or DDE levels (Turyk *et al*., 2009; Philibert *et al*., 2009; Goldner *et al*., 2010). Several recent studies demonstrate a link between in utero exposure to DDT or DDE and development neurotoxicity in humans, a University of California, Berkeley study suggests that children exposed while in the womb have a greater chance of development problem and other studies document decreases in semen quality among men with high exposures (Jurewicz *et al*., 2010). According to a study published in Neurology (Hayden *et al*., 2010) repeated exposure such as occur with occupational is associated with an increase in the risk for incident dementia and Alzheimer disease, children with high levels of metabolite were likely to meet the diagnostic Attention Deficit/Hyperactivity Disorder (Shim *et al*., 2009; Harnly *et al*., 2005; 2009).

The storage, sales and handling of pesticide in an indoor environment in Nigeria is fraught with problem of undesirable side effect (Hotton *et al*., 2010). To this end, there were several uninvestigated cases of threat to public health as a result of occupational exposure associated with the retailing of pesticide in Nigeria. Hence, it becomes imperative to ascertain the extent of pesticides load among the retailers and the knowledge of biological levels of these contaminants in human blood is necessary for the risk assessment of adverse health effects and identification of vulnerable groups (Hotton *et al*., 2011).

The aim of the present study was to assess the levels of DDT and its metabolites in the blood of agrochemical retailers.

MATERIALS AND METHODS

Recruitment: The study was conducted in the North and Southern Senatorial districts of Taraba, Nigeria. Potential subjects were initially identified using a site-based sampling approach. This approach first identified locations where pesticide retail outlets were predominantly found in the two districts which comprise, Jalingo, Mutum Biyu, Garba Chede, Wukari-Ibi, Donga, Maraba-Donga, Takum, Bali and Lau. To be eligible for the study the retailer most have a minimum of one year in the same trade.50 retailers were recruited one on one through word of mouth from 50 different retail outlets mapped out for the study across the two districts. The researches returned to the sites at the appropriate time and were introduced to the subjects by the support and partnership of the leadership of Agrochemical Dealers Association of Nigerian, Taraba State chapter. Retailers were eligible to participate in the study if they had not worked in agriculture or involved in any fumigation exercise during previous 12 months.

Sampling methodology: Venous blood (10 mL) of 50 agrochemical retailers selected for the study were collected with the technical assistance from the department of Hematology Federal medical centre Jalingo, Taraba State Nigeria. Prior to obtaining blood at close of work all donor washed their hands and arms with soap and water to remove any contamination. After drying with tissue paper, the skin was swabbed with an alcohol-based tissue swab before sampling. Blood samples were collected in residue free heparins 20 mL glass vials containing 200 USP units of heparin in 0.2 mL solution with the help of sterilized syringe. Blood samples were label appropriately and transported in dry ice to the laboratory and stored at -20°C until analyzed.

Sample extraction and clean up: The samples were analyzed for Organochlorine using U.SEPA. Method 8081A by Gas Chromatography. Extraction was based on the method followed by Agarwal. Blood (5 mL) was diluted with 25 mL distilled water and 2 mL of saturated brine solution added and transferred to a 125 mL capacity separatory funnel and extracted with hexane: acetone (1:1) (20 mL) thrice by shaking the separatory funnel vigorously for 2-3 min releasing the pressure intermittently. The layers were allowed to separate; the three combined extracts were passed through anhydrous sodium sulfate and concentrated to about 1-2 mL using rotary vacuum evaporators. Clean up was done by U.S EPA. Method 3620B-Florisil cleans up by column chromatography. Florisil was activated overnight at 130°C and cooled in desiccators before use.

Laboratory assays of DDT isomers and metabolites: Weight of florisil taken was predetermined by calibration using lauric acid. 1g florisil was packed in

the 20 cm length and 12 mm ID glass chromatographic column, anhydrous sodium sulfate was added to the top of the florisil column (0.5 cm) and the column was pre-eluted with hexane and discarded .The extract were transferred to the column and eluted with hexane (10 mL), 6% diethyl ether in hexane (10 mL). Eluent was collected and evaporated to dryness. Final samples were prepared in 2 mL hexane (HPLC grade). Quantification of residue level was done by shimadzu -17A series Gas chromatograph equipped with ^{63}Ni selective electron capture detector .Quantitative analysis of DDT residue in each sample was done by comparing the peak heights with those obtained from a chromatogram of a mixed DDT standard of known concentration. The LOD were <0.05 pg perchloroethylene. The average recoveries of fortified samples were exceeding 95%. An aliquot of reagent grade water was treated exactly as a sample including exposure to all glass ware, equipments, solvents and reagent used with the sample matrix. No analyte peak was detected in laboratory reagents blank. Blood samples were analyzed based on the categorization of the agrochemical retailers on their years of exposure duration.

Data analysis: All samples were successfully analyzed for pesticides. Description statistics (mean, percentages and Spss) was used to analyze the data.

RESULTS

All the blood samples analyzed, the presence of dieldrin was not detected in any of the samples from the exposed retailers and however, it was excluded from the table. The grouping of agrochemical retailers whose blood samples were taken for DDT and its metabolite residues analysis is presented in Table 1. The grouping shows the distribution of the retailers that had residues in their blood on the basis of their years of involvement in the sales of agrochemicals. Out of the 50 retailers assessed 75% of the retailers were within the 6-10 years and 50% ≥ 21 years categories respectively, while 71.4, 77.8 and 60% were in the 16-20 years, 11-15 years and 1-5 years respectively. All the retailers in the grouping had residues of DDT isomers in their blood except for some few retailers. There were more male retailers with residues 23 (46) in the study than the female 10 (20). Table 2 shows the general mean concentration of DDT isomers detects in the blood samples of Agrochemicals retailers. Among the DDT isomers analyzed in whole blood samples, the mean levels of DDE, DDD.DDT, t DDT and Aldrin were 0.0470, 0.0101, 0.0120 and 0.0045 mg L^{-1} respectively which Values ranges from (n.d-0.034, n.d-0.1120 and 0.0100-0.0265 mg L^{-1}) respectively. The total content DDT (sum of DDE, DDD and DDT) in the whole blood samples was 0.062 mg/L and ranged from 0.0008-0.185 mg L^{-1}. Table 3 gives the overall variation of the mean concentration of DDT and its metabolite detects (mg/L) among the grouping of agrochemicals retailers. The mean concentration of DDE, DDD, DDT, t-DDT and Aldrin residue for the grouping 1-5 years and 6-10 years were (0.0027, 0.0243, 0.0123, 0.0680 and 0.0726 mg L^{-1}) and (0.0530, 0.0214, 0.0155, 0.0660, 0.0019 and 0.0679 mg L^{-1}) respectively. While the grouping 11-15 years, 16-20 years and ≥ 21 years had mean concentration of (0.0242, 0.0109, 0.0058, 0.0520, 0.0037 and 0.0557 mg L^{-1}), (0.1077, 0.0102, 0.0118, 0.1360, 0.0012 and 0.1304 mg L^{-1}) and (0.0096, 0.071, 0.0185, 0.0043, 0.0230, 0.0074 and 0.0304 mg L^{-1}) respectively.

Table 1: Characteristics of subjects by categories of years of exposure by agrochemical retailers with residues of DDT metabolite in their blood

Duration of Exposure (Years)	No of Retailers Assessed	No. with Residue n (%)	No of Male with residue n (%)	No of female with residue
1-5	10 (20)	6 (60)	2 (33.3)	4 (66.7)
6-10	12 (24)	9 (75)	5 (55.6)	4 (44.4)
11-15	9 (18)	7 (77.8)	7 (100)	-------
16-20	7 (14)	5 (71.4)	4 (80)	1 (20)
≥21	12 (24)	6 (50)	5 (83.3)	1 (16.7)

Table 2: General mean concentration and distribution of DDT metabolite detects in blood samples of agrochemical retailers in Taraba, Nigeria

No of Detect (%)	DDE	DDD	DDT	t-DDT	Aldrin
	34(68)	31(62)	29(58)	34(68)	26(52)
Min	0.0000	0.0000	0.0000	0.0008	0.0100
Max	0.0721	0.0340	0.1120	0.0185	0.0265
Mean	0.0470	0.0101	0.0120	0.0620	0.0045

Abbreviations: DDE (Dichlorodiphenyldichloroethylene), DDD (Dichlorodiphenyldichloroethane ethane), t-DDT= ∑(DDE, DDD and DDT), Min (Minimum), Max(Maximum)

Table 3: Mean variation of DDT metabolites detects (mg/L) among retailers of pesticide in Taraba Nigeria

Duration of Exposure (Years)	DDE	DDD	DDT	t-DDT	Aldrin	Total load
1-5	0.0276	0.0243	0.0123	0.0680	0.004	0.0626
6-10	0.0530	0.0214	0.0155	0.0660	0.0019	0.0679
11-15	0.0242	0.0109	0.0058	0.0520	0.0037	0.0857
16-20	0.1077	0.0102	0.0181	0.1360	0.0012	0 .1372
>21	0.0096	0.0071	0.0043	0.0230	0.0074	0.0304

Abbreviations: DDE (Dichlorodiphenyldichloroethylene), DDD (Dichlorodiphenyldichloroethane ethane) DDT (dichlorodiphenyltrichloroethane), t- DDT= ∑(DDE, DDD and DDT)

DISCUSSION

DDT is classified as moderately toxic by US National Toxicology Programmed (NTP) and moderately hazardous by the World Health Organization based on the rat oral LD50 of 113 mg kg^{-1}. DDT metabolite in the present study was detected in 58% of the total number of blood samples analyzed and appeared more frequent within the grouping 16-20 years exposure duration among the retailers at mean concentration of 0.0181 mg L^{-1} and ranged from n.d-0.1120 mg L^{-1} with the male sex having more proportion than the female. From the study it can be deduced that body burden increases with increase in years of exposure as shown in Fig. 1 with a slight different in the greater than 20 years categories which may be due to the metabolic processes over time. The high rate of DDT detected within the grouping may be attributed to the handling and exposure at the time the banned was not in place and also their persistence nature due to slow decomposition rate, long half life and high stability in the environment. Studies have shown that, exposure to DDT at amount that would be needed in malaria control might cause preterm birth and early weaning associated with endocrine disrupting properties. Our findings shows in Table 3 and Fig. 1 that there was significant drop from 0.1372 mg L^{-1} recorded for the 16-20 years categories to 0.0679 mg L^{-1} in the 6-10 years categories when DDT was outlaw in 2004.Interestingly the total body load years after the banned maintained almost the mean same value of 0.0625 mg L^{-1} within the 1-5 years exposed group, pointing to some iota of their existence in circulation or attributed to dietary intake among other factors. Despite the fact that the mean concentrations of the DDT residues among the retailers were relatively low, but not withstanding other studies have found that even low levels of DDT in umbilical cord , serum at birth are associated with decreased attention at infancy and decreased cognitive skill at 4 years of age (Philibert *et al*., 2009). However, a human epidemiological study suggest that exposure is a risk factor for premature birth and low birth weight and may harm mother ability to breast feed, there are some evidence that the daughter of highly exposed women may have more difficulty getting DDE metabolite was detected in 68% of the blood samples analyzed at mean concentration of 0.0470 mg L^{-1} in the ranged n.d-0.462 mg L^{-1} as shown in Table 2. DDE is classified by International Agency for Research on cancer as possible human carcinogen and also in the EPA class B2 probable carcinogens. We observed that the metabolite of DDE were the most predominant residue in the blood of the retailers.

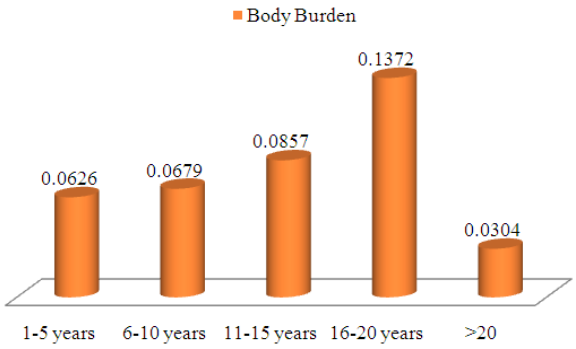

Fig. 1: Showing total load against years of exposure

The high proportion and detect of DDE perhaps may be due to it more persistent nature than the DDT since DDT is known to undergo metabolic conversion and dehydrochlorination to give DDE. The presence of metabolites of DDT i.e., DDE and DDD encountered in this study might be to such metabolic processed. The values obtained in this study were comparatively lower than the earlier reports from Peninsular-Malaysia (1.4 ng g^{-1}), 20.85 ug L^{-1} in Ahmadabad urban area on exposed population and that of Limpopo province in South Africa (Dyk *et al*., 2010). Exposures to DDE were link between in utero exposure and developmental neurotoxicity. Human studies demonstrated that children exposure while in the womb have a greater chance of developmental problem. Similarly, researchers have linked first trimester DDE exposure to retarded psychomotor development. Hence, the exposure of a pregnant retailer may invariably expose the baby in the womb to certain health hazard that may be harmful. The Joint Meeting on Pesticide Residues (JMPR) in 1984 gave an overall NOAEL for human as 0.25 mg kg^{-1} body weight per day and the estimate of provisional tolerable daily intake for human as 0.01 mg kg^{-1} body weight. The risk of bioaccumulation of these pesticides in the near future even though banned the values shows that these pesticide are still in used .Exposure by the retailers maybe via inhalation because of the volatility of the pesticide vapor and via dermal contact or during the unethical dispensing of the pesticide from bigger containers to smaller one. Inhalation exposure explains most of the difference in concentration between the highly exposed and the general population in the tropics (Ritter *et al*., 2011). DDD was detected in 62%of the blood samples analyzed at mean concentration of 0.0101 mg L^{-1}. This low values may be linked to the diminishing use of DDT, thus a lower level of DDD was determined in the human body, which we considered an indicator of recent DDT exposure since DDD is determine in human

body only for a short period immediately after DDT application or exposure. The serum level detected in the sample is therefore either the results of their own metabolite of DDT over the exposure period or from ingestion of DDE present in their food or from exposure to DDT present in the surrounding environment (Sereda *et al*., 2009) Dieldrin a chlorinated hydrocarbon and extremely persistent organic pollutant, it metabolite was not detected in any of the samples analyzed. Both dieldrin and aldrin have been classified in Group 3; however the chemicals cannot be classified as to their carcinogenicity in human being but they are toxic and hazardous to humans. Aldrin was used to control soil pest namely termites and grasshoppers on corn and potatoes crop; we detected very low levels of aldrin in 52% of the samples analyzed. Our data shows that the low values of 0.004 2mg L^{-1} obtained were lower than values previously reported in Punja/India which were 0.0062 mg L^{-1}. Over exposure symptoms may include headache, dizziness, nausea, vomiting weakness in legs and stimulation of the central nervous system with jerks and convulsions sometimes leading to death. Generally, the observed trend for t- DDT i.e., the summation of DDE, DDD and DDT were relatively lower than reports from exposed population in Ahmadabad, Punjab and in Limpopo province in South Africa (Dyk *et al*, 2010). Exposure by the retailers may be via inhalation because of the volatility of the pesticide vapour within the indoor retail stores which are poorly ventilated, facilitated by the high temperature of the region and also via dermal contact as a result of frequent handling of the pesticide containers with hands. In conclusion, the evaluations of the overall data strongly support the view that the body burdens resulting from the present level of exposure may be a pointer to occupational exposure or attributes to dietary intake, however, the risk of bioaccumulation stand a point of concern. The need therefore for stiff monitoring and enforcement by regulatory bodies is of paramount important.

CONCLUSION

Despite the restriction, the observed trend for all the DDTs and metabolites shows that retailers are occupationally exposed due to the sales and handling of agrochemicals in retailers' stores. The need for stiff monitoring and enforcement by regulatory bodies is of paramount important.

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