

PROFILE OF ORGANOCHLORINE PESTICIDE DEGRADATION IN SOIL OF WURNO IRRIGATION FARM AREAS IN SOKOTO STATE, NIGERIA.

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ABSTRACT

The degradation patterns of organochlorine pesticides (OCPs) in soil of Wurno irrigation farm areas were investigated. Thirteen organochlorine pesticides were analyzed in soils from the irrigation land, dry land and fallow land using GC-MS after extraction of the residues with a mixture of acetone/hexane (1:1). Results obtained revealed that the total organochlorine pesticide residues were higher in agricultural soils than in uncultivated fallow land soils. Among all the pesticides, $\sum DDX$ (DDD, DDE and DDT) had the highest concentration for all the soil samples, ranging from 3.95 $\mu\text{g/g}$ to 10.74 $\mu\text{g/g}$ with a mean value of 7.35 $\mu\text{g/g}$ and followed by $\sum HCH$, ranging from 0.79 $\mu\text{g/g}$ to 3.25 $\mu\text{g/g}$ with a mean value of 2.02 $\mu\text{g/g}$. Dieldrin, endrin, and endosulfan were also found in the soils with less than 4.0 $\mu\text{g/g}$. Ratios of $p,p^1-(DDD+DDE)/DDT$ in soils under three land usages were: irrigation land > dry land > fallow land, indicating that land usage influenced the degradation of DDT in soils. Ratios of $p,p^1-(DDD+DDE)/DDT > 1$, showing aged residues of DDTs in soils of the Wurno irrigation farm area. The results also revealed recent applications of the banned organochlorine pesticides as indicated by the ratio of $p,p^1-DDD/DDT$ less than unity. Although agricultural practices can influence the degradation of pesticides residues in soils, the mean concentration levels of residues observed is high and will need more remediation processes.

Keywords: Pesticide residues, organochlorine, degradation, fallow land, irrigation land.

INTRODUCTION

Organochlorine pesticides (OCPs) are among the agrochemicals that have been used extensively for long periods. They have been used widely in agriculture, as well as, in mosquito, termite and tsetse fly control programs (Guo *et al.*, 2015). OC pesticides are characterized by low polarity, low aqueous solubility and high lipid solubility (lipophilicity) and as a result they have a potential for bioaccumulation in the food chain posing a great threat to human health and the environment globally (Afful *et al.*, 2010). Residues and metabolites of many OC pesticides are very stable, with long half lives in the environment (El-Mekkawi *et al.*, 2009).

Intensive agricultural practices often include the use of pesticides to enhance crop yields. However the improvement in yield is sometimes concomitant with the occurrence and persistence of pesticide residues in soil and other environmental matrices (Wares and Whitacre, 2012).

Pesticides may reach the soil through direct application to the soil surface, incorporation in the top few inches of soil, or during application to crops (McEwen and Stephenson, 2012). The fate of pesticide in soil environment is influence by the physico-chemical properties of the pesticide, the properties of the soil system (pressure of clay materials, organic matter, pH, climate, biology, and other factors (Singh, 2011). The increased and indiscriminate use of pesticides has caused pollution of soils worldwide. Organochlorine pesticide residues, particularly the oxidized form of heptachlor, remain in soils compartment long after their use has been discontinued (Kim and Smith, 2011). Residues of toxaphene, Dichlorodiphenyltrichloroethane (DDT), trifluralin, and hexachlorocyclohexane (lindane) have been detected in soils from cotton fields in South Carolina (Kannan *et al.*, 2013). The DDTs were the main contaminants detected in soil from Banjul and Dakar in West Africa (Maniratiza *et al.*, 2013).

The use of pesticides in Nigeria has continued to increase, particularly in large-scale commercial farming enterprises due to increases in acreage and need to intensify agricultural production. Present figures show the doubling in importation of pesticides from approximately 50,000 tonnes in 2010, with very significant increases in application in rice, maize, wheat and fruits and vegetables farming (PCPC, 2010). In particular, the tremendous growth in cereals production with subsequent increase in their yield has been attributed to the use of herbicides. However, with this increase in pesticide usage in agriculture, better management and control of pesticides application will be required in future because of the residue limit specification as well as the need to safeguard against the potential adverse effects on the local environment and human (Schulz, 2012; Lalah *et al.*, 2011). In addition to keeping accurate records of pesticide usage in the farms, it is necessary to monitor the distribution, fate, and effects of pesticide residues within the ecosystem. Monitoring of pesticide residues in agricultural soil, streams, and rivers within catchments and modeling of their fate and toxicity have become useful global approaches of assessing pesticide efficacy

and ecological impact on a given area (Muller *et al.*, 2011; Batch *et al.*, 2010; Liess *et al.*, 2009; Krenger, 2008).

There are a large number of pesticides currently in use, with a wide range of physico-chemical properties and belonging to a wide variety of chemical classes. Clearly, the physico-chemical properties of a given pesticide will govern its behaviour in the soil and its biological activity.

Molecular size, ionisability, water solubility, lipophilicity, polarisability and volatility are all key properties, but generally one or two properties have a dominating influence (Weber, 2012; Bailey and White, 2010; Stevenson, 2006; White, 2006). Pesticides can be classified in many different ways: according to the target pest, the chemical structure of the compound used, or the degree or type of health hazard involved.

Adsorption is probably the most important mode of interaction between soil and pesticides and controls the concentration of the latter in the soil liquid phase. Adsorption processes may vary from complete reversibility to total irreversibility. The extent of adsorption depends on the properties of soil and the compound, which include size, shape, configuration, molecular structure, chemical functions, solubility, polarity, polarizability and charge distribution of interacting species, and the acid-base nature of the pesticide molecule (Senesi, 2012; Pignatello and Xing, 2012; Bailey and White, 2010).

Adsorption may be purely physical, as with van der Waals forces, or chemical in nature, as with electrostatic interactions. Chemical reactions between unaltered pesticides or their metabolites often lead to the formation of stable chemical linkages, resulting in an increase in the persistence of the residue in soil, while causing it to lose its chemical identity (Bollag, 2012; Dec and Bollag, 2012; Berry and Boyd, 2011; Calderbank, 2011). From a toxicological perspective, binding of xenobiotics to humus leads to: (1) a decrease of material available to interact with biota; (2) a reduction in the toxicity of the compound; and (3) immobilising the compound, thereby reducing its leaching and transport properties (Bollag, 2012; Dec and Bollag, 2012).

Presently the pesticides used are mostly synthetic organic compounds. The soil may act as an important sink for persistent organic pollutants including many pesticides used presently or in the past. They are relatively insoluble in water and are retained strongly by the soil. Soil acts as filter buffer and degradation of pollutants with respect to storage of pollutants with the help of soil organic carbon (Bourauel and Bassmann, 2005). Soil acts as a pathway of pesticide transport to contaminate ground/surface water, plants, food and effects on human via runoff, leaching, transfer of mineral nutrients and pesticides from soil into the plants and animals that constitute the human food chain (Abraham, 2012). Persistent pesticides slowly break down in the soil and lead to contamination which is closely correlated to human activities like industrial discharge, agricultural applications and deforestation which lead to soil erosion (Bhattacharya *et al.*, 2013).

It is generally acceptable that climatic conditions in the tropics facilitate the breakdown of bioactive compounds, thus eliminating most of the side effects of pesticides. Pesticide monitoring in the environment is therefore necessary for risk assessment and environmental management in Nigeria due to its different climatic conditions when compared with those of temperate countries. Depending on their chemical stability, these substances may undergo decomposition processes; therefore, not only active ingredients but their metabolites may also occur as contaminants. Thus, it becomes very imperative to understanding the levels and the distribution characteristics of OCPs in soils from different land usage systems in the Wurno irrigation farm areas.

MATERIALS AND METHODS

Description of the Study Site.

The study area was in Wurno Irrigation farm located in Wurno Local Government Area of Sokoto state. The total farm areas cover over 1200 hectre. The area is densely populated, rich in agriculture and a major producer of rice, millet, maize, onions and vegetables, etc. for the state and neighbouring country. Cattle, sheep, goat, and poultry are also kept. The area is popularly known for the extensive dry season farming which is facilitated by the establishment of a dam. Within the farm area is also dry land used only for rain season farming unlike the irrigation farmland where farming activities is done in both seasons (dry and rainy). The sampling sites for residue determination were specifically located in the farm irrigation area, where pesticides are extensively used to control weeds and other pests, in the dry land that is seasonally cultivated and also in the residential area where pesticides may never have been used directly for agricultural activities. These serve as control (Fig. 1).

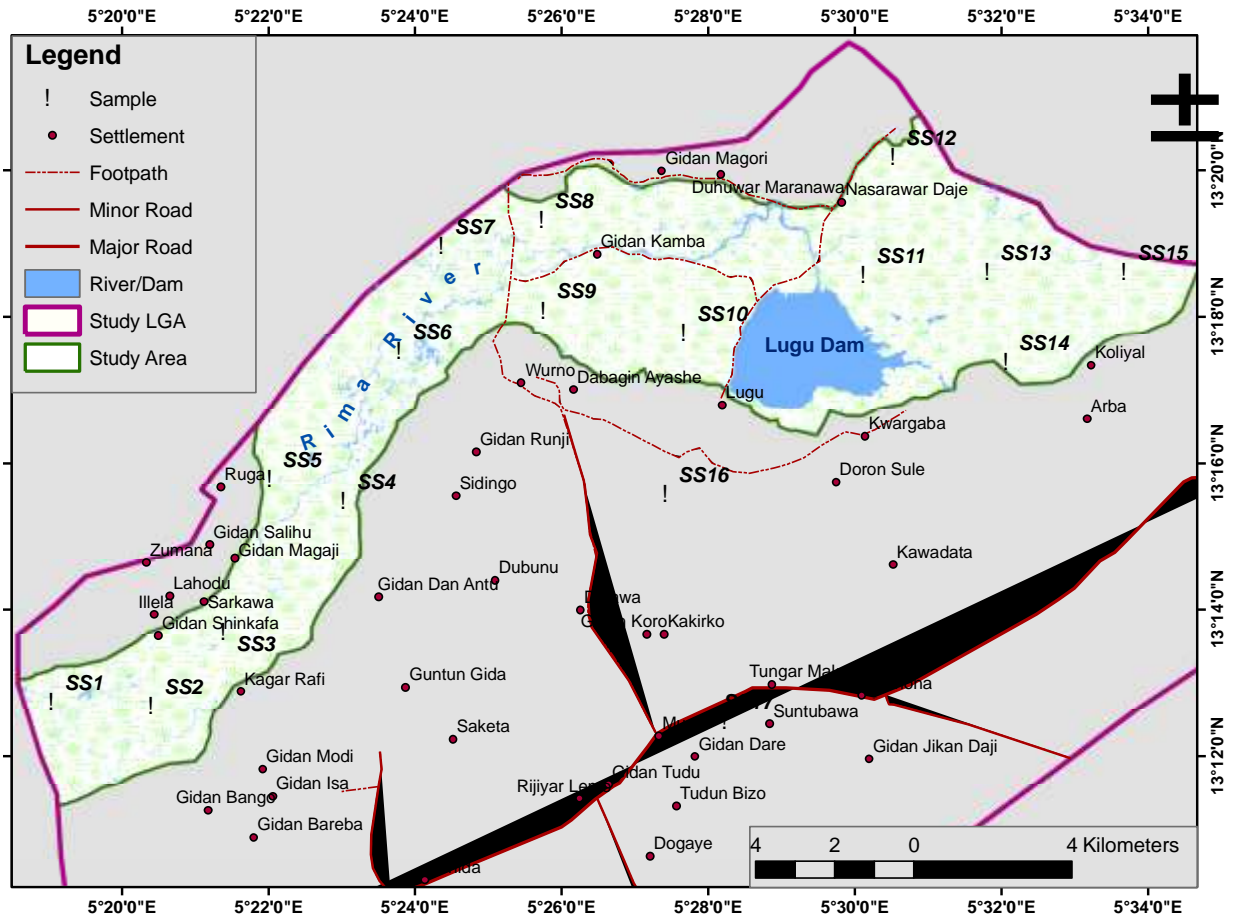


Fig. 1: Map of the study area and the sampled sites.

Sampling Method

A 500-gram composite soil sample was collected from the surface (0-15cm deep) and subsurface (16-30cm deep) with a stainless steel soil auger, and stored in a Ziploc bag. The location and description of each sampling site was recorded in details shown in Table 1. A diagram of composite sampling is shown in Figure 2. After sampling, the soil samples are air-dried at 20⁰C, sieved (< 2mm sieve).to eliminate organic fragment and aggregates, and transferred into clean glass-amber container and stored at ambient temperature prior to analysis

Soil pH and Total Organic Carbon Analysis

Soil pH and total organic carbon (TOC) analysis were conducted by conventional standard procedures (Lu, 2010): soil pH was determined at a soil to water ratio of 1:2.5 by a potentiometric glass electrode; TOC was measured by digestion of soil samples with K₂Cr₂O₇ and subsequently titration with H₂SO₄.

Table 1 Soil sampling code, soil pH and Total Organic Carbon (TOC) concentrations in the soil from each sampled area

Sample code	Land Usage	GPS Coordinate	Soil Dept. (cm)	pH (H ₂ O) Value	TOC (g/Kg)	
X	Y					
SS1	Irrigated Land	531831	1321230	0 – 15	6.78	17.35
				16 – 30	7.14	11.01
SS2	Irrigated Land	534103	1321140	0 – 15	6.12	21.31
				16 – 30	5.43	13.20
SS3	Irrigated Land	535744	1322820	0 – 15	5.90	19.98
				16 – 30	5.61	18.73
SS4	Irrigated Land	538478	1325810	0 – 15	5.99	23.11
				16 – 30	6.11	15.41
SS5	Irrigated Land	536795	1326320	0 – 15	6.74	18.93
				16 – 30	5.82	19.22
SS6	Irrigated Land	539740	1329220	0 – 15	5.21	27.32
				16 – 30	5.11	16.94
SS7	Dry Land	540708	1331620	0 – 15	4.22	29.81
				16 – 30	6.77	20.98
SS8	Dry Land	542980	1332210	0 – 15	5.32	23.12
				16 – 30	5.02	21.24
SS9	Dry Land	543022	1330140	0 – 15	6.65	19.90
				16 – 30	6.21	21.33
SS10	Dry Land	546219	1329640	0 – 15	5.09	20.50
				16 – 30	6.23	14.69
SS11	Dry Land	550300	1330940	0 – 15	6.39	22.17
				16 – 30	6.12	20.21
SS12	Dry Land	550973	1333640	0 – 15	6.72	23.81
				16 – 30	5.98	17.54
SS13	Fallow Land	553118	1331030	0 – 15	6.22	17.97
				16 – 30	6.33	21.43
SS14	Fallow Land	553539	1328970	0 – 15	6.77	20.10
				16 – 30	6.31	15.39
SS15	Fallow Land	556231	1331030	0 – 15	6.02	27.80
				16 – 30	6.33	20.11
SS16	Fallow Land	545789	1325980	0 – 15	5.93	21.29
				16 – 30	6.60	19.97
SS17	Fallow Land	547144	1320800	0 – 15	6.31	21.77
				16 – 30	6.78	18.88

Note. X = Latitude, Y = Longitude; SS = Soil Sample.

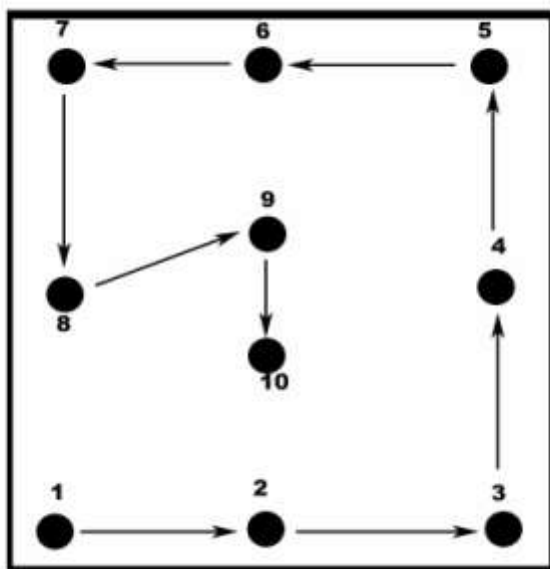


Figure 2 Diagram of composite sampling.

Treatment of Samples

Soil samples were collected in the study areas. Each soil sample was a composite of 10 subsamples collected at each site using random sampling within a grid (Fig 2). A grid was established by identifying the approximate center of a field and dividing the field into 3 rows, 20 paces apart, with 3 core samples taken per row for a total of 10 cores (Mullins *et al.*, 2011). Soil was collected from the surface (0-15 cm layer) and subsurface (16-30 cm layer) using a 19” stainless steel soil auger. The subsamples were placed into a 16-liter bucket, thoroughly mixed, and sifted through a No.5 (4 mm/0.1575”) brass soil sieve (W.S. Tyler™) at the collection site. After each sample was collected, the auger, bucket, sieve and mixing tool were rinsed before next use. Five of the seventeen samples collected at each site was obtained from an uncultivated field and used as a control. Soil samples were then air dried and sieved through a No.20 (850 $\mu\text{m}/0.0335$ ”) brass soil sieve (W.S. Tyler™) and refrigerated at about 4°C prior to laboratory analysis.

The method reported by Tahir *et al.*, (2009) was followed for the extraction of pesticide residues in soil. 50g of soil sample were taken in a conical flask and then 150ml of a mixture of acetone, hexane (1:1) was added. This was shaken for 1hr with the help of mechanical shaker at a rate of 300 osc/min. The mixture was filtered through a glass wool plug with whatman filter paper No 542 into a separatory funnel. The extract was washed with distilled water (2x100ml).

The lower aqueous layer was discarded and a few grams of anhydrous sodium sulphate were added. 20ml of the aliquot was transferred to round bottom flask and evaporated to dryness at 40°C in a rotary evaporator. The contents of the flask were reconstituted in 6ml ethylacetate

and cyclohexane (1:1) mixture. The sample was again dried and reconstituted in 1ml ethylacetate and then passed through high flow super cells. 2ml of the sample was applied on Gel Permeation Chromatography (GPC) for further cleanup. After passing through GPC column, the samples were again dried under vacuum and reconstituted in 1ml ethyl acetate for analysis on GC.

Pesticide Standards

All pesticide standards were purchased from Bristol Scientific Co. Nig, a subsidiary of Sigma Aldrich Germany. Stock solutions were prepared using pesticide grade solvents. Spiking solutions for measuring method efficacy (percent recovery) were prepared from stock solutions. Calibration standards in at least three concentrations were also prepared from stock solutions and diluted in hexane. All stock, spiking and calibration standards were transferred to Qorpak™ glass jars after preparation and stored at 4°C. Calibration curves of working standards were used to evaluate the linearity of the gas chromatograph response each day of analysis and pesticide residues were quantified based on these external standards.

Gas Chromatographic Analysis

Soil extracts were analyzed using an Agilent 6890 gas chromatograph equipped with a ⁶³Ni micro-electron capture detector (μECD), capillary column, and Hewlett Packard Chemstation software (GC 2071, Rev.A.06.01). The primary capillary column for separation of pesticides was RTX-5 (Restek, 30 m x 250 μm x 0.25 μm) and confirmation runs were completed using RTX-35 (Restek, 30 m x 250 μm x 0.25 μm). Helium was used as the carrier gas at a constant column flow rate of 1.1 mL/min and the detector makeup gas was nitrogen at a flow rate of 60 mL/min. Samples were injected in the splitless mode with the purge flow to split vent set at 35 mL/min at 1 min and pressure at 15 psi and total flow at 39 mL/min. The injector temperature was either 250°C (RTX-5 injections) or 225°C (RTX-35 injections) and the detector temperature was 350°C. Two different temperature programs were used for the RTX-5 and RTX-35 columns to achieve the separation of pesticides of interest. The temperature program on the RTX-5 capillary column was as follows: 90°C for 0.00 min, 30°C/min to 190°C held for 20 min, 20°C/min to 275°C held for 10 min. For confirmation runs, the temperature program on the RTX-35 column was as follows: 100°C for 2.0 min, 15°C/min to 160°C, 5°C/min to 270°C held for 5 min.

Quantification Limit

The quantification limit (QL), for pesticides reported in this study, was based upon the lowest concentration that could be consistently and/or reliably recovered (> 70%) in our laboratory from fortified samples (Mullins *et al.*, 2011). If this percent recovery could not be achieved, the most consistent pesticide recovery was used to establish the quantification limit. All the data were analysed using a software package SPSS 12.0 for the purpose of statistics and the significance level was $p < 0.05$.

RESULTS AND DISCUSSION

Table 2: Mean Concentration of Organochlorine Pesticides in the soil Samples from Wurno Irrigation Field.

OCP	Mean Concentration ($\mu\text{g/g}$)					
	Irrigated Land		Dry Land		Fallow Land	
	0-15cm	16-30cm	0-15cm	16-30cm	0-15cm	16-30cm
α -HCH	1.53 \pm 0.11	1.22 \pm 0.99	1.21 \pm 0.10	1.23 \pm 0.09	0.99 \pm 0.03	0.93 \pm 0.05
β -HCH	3.15 \pm 0.87	2.55 \pm 0.99	2.79 \pm 0.66	1.90 \pm 0.12	1.00 \pm 0.09	0.79 \pm 0.09
γ -HCH	3.25 \pm 1.20	2.98 \pm 1.02	2.80 \pm 0.76	2.11 \pm 1.07	2.07 \pm 0.01	1.78 \pm 0.43
δ -HCH	1.51 \pm 0.71	1.09 \pm 0.06	1.02 \pm 0.22	1.09 \pm 0.06	0.87 \pm 0.01	ND
Σ HCH	9.44 \pm 2.89	7.84 \pm 3.06	7.82 \pm 1.74	6.33 \pm 1.34	4.93 \pm 0.14	3.50 \pm 0.57
O,p/-DDE	6.67 \pm 1.42	7.05 \pm 1.43	5.98 \pm 0.99	5.41 \pm 0.74	4.96 \pm 1.07	3.95 \pm 1.06
P,p/-DDE	9.31 \pm 2.17	9.98 \pm 1.22	7.91 \pm 2.13	7.98 \pm 1.23	6.25 \pm 1.50	3.96 \pm 1.21
P,p/-DDD	9.27 \pm 1.66	8.85 \pm 1.09	9.14 \pm 1.09	6.37 \pm 1.18	6.41 \pm 1.08	5.67 \pm 1.05
O,p-DDT	10.41 \pm 2.24	8.87 \pm 1.21	10.11 \pm 1.27	9.74 \pm 2.76	6.76 \pm 1.81	4.96 \pm 2.02
P,p/-DDT	10.74 \pm 1.29	9.83 \pm 2.71	9.72 \pm 2.19	9.99 \pm 1.37	4.94 \pm 2.16	6.77 \pm 1.70
Σ DDX	46.40 \pm 8.78	44.58 \pm 7.66	42.86 \pm 7.67	39.49 \pm 7.28	29.32 \pm 7.62	25.31 \pm 7.04
α -Endosulfan	2.97 \pm 0.98	2.19 \pm 0.60	1.79 \pm 0.31	1.08 \pm 0.03	1.02 \pm 0.07	0.96 \pm 0.08
β -Endosulfan	1.77 \pm 0.06	1.05 \pm 0.70	1.28 \pm 0.93	0.74 \pm 0.02	0.79 \pm 0.03	ND
Σ Endosulfan	4.74 \pm 1.04	3.24 \pm 1.30	3.07 \pm 1.24	1.82 \pm 0.05	1.81 \pm 0.10	0.96 \pm 0.08
Dieldrin	3.17 \pm 1.01	2.28 \pm 0.98	2.38 \pm 0.65	1.99 \pm 0.06	1.75 \pm 0.09	0.96 \pm 0.08
Endrin	1.68 \pm 0.88	0.95 \pm 0.06	1.08 \pm 0.05	0.86 \pm 0.07	0.72 \pm 0.03	ND
Σ Drins	4.85 \pm 1.89	3.23 \pm 1.04	3.46 \pm 0.70	2.85 \pm 0.13	2.47 \pm 0.12	1.30 \pm 0.13
Σ OCP	65.43 \pm 14.60	58.89 \pm 13.06	57.21 \pm 11.35	50.49 \pm 8.80	38.53 \pm 7.98	30.73 \pm 7.77

Mean of Triplicate \pm SD; ND=Not Detected; Σ HCH; α -HCH+ β -HCH+ γ -HCH+ δ HCH; Σ DDX;o,p-DDE+pp¹-DDE+pp¹-DDD+op - DDT+p,p¹-DDT; Σ Endosulfan: α -endosulfan+ β -endosulfan; Σ Drins: Dieldrin+Endrin; Σ OCP: Σ HCH+ Σ DDX+ Σ endo+ Σ Drins.

Discussion

The total organochlorine pesticide (\sum OCP, as a sum of all single organochlorine pesticide) concentrations in surface and subsurface soil samples of investigated sampling stations are shown in Table 2. \sum OCP concentrations in most soil samples were in the range 30–65 μ g/g. The highest \sum OCP concentration (65.43 μ g/g) was in the surface soil at irrigated land. Low \sum OCP concentrations were found (30.73 μ g/g) in fallow land soils. The total contaminant levels throughout the soil profile showed different distribution patterns among samples. The results showed that although organic matter was known to be the most important OCPs' sorbent in soil surface horizons, additional factors such as particle-size characteristics and organic matter composition and physicochemical characteristics of OCPs were involved in pesticide retention (Manz *et al.*, 2011; Gong *et al.*, 2014).

The mean concentrations of organochlorine pesticides in soils under three land usages are presented in Table 2. Most of the OCPs were detected in soils from all land usages except δ -HCH, β -endosulfan and endrin in subsurface soils from the fallow land. Among all the pesticide concentrations, \sum DDX (DDD, DDE and DDT) had the highest concentration, followed by \sum HCH. Relative to \sum DDX and \sum HCH, lower concentrations of drins (dieldrin+endrin) and \sum endosulfan were found in soils, being less than 4 μ g/g. The concentrations of pesticides in soil samples from different land usages were in the decreasing order of \sum DDX > \sum HCH > \sum drins > \sum endosulfan.

For OCP residues in soils under the three land usage systems, mean values were in the order of irrigation land > dry land > fallow land. The lower pesticide concentrations detected in soils from fallow land might mainly result from the drift of pesticides application and volatilization from agricultural soil, followed by atmospheric deposition on fallow land soils (Harner *et al.*, 2013).

The concentrations of OCPs in these soils were compared with the minimum allowable values specified by the WHO standards (WHO, 2014). Although all the OCP concentrations in soils were much lower than the environmental quality standard for agricultural soils, the OCP concentrations, especially DDT, in soils were much higher than the values for unpolluted soils in the soil protection guideline as stipulated by the WHO suggesting that further soil remediation is essential for improving soil quality to reach the international standard for producing and exporting agricultural products in this region.

The fate of organic compounds in soils depends on chemical-specific parameters, environmental factors and on soil parameters such as temperature, soil type, pH, water content and organic matter (Manz *et al.*, 2011; Wenzel *et al.*, 2012; Miglioranza *et al.*, 2013). pH-value can affect the concentrations of OCP in soil by influencing the microbiological activity in the soil (Wenzel *et al.*, 2012). Increase of organic matter content in soil can increase the amount of

microbial biomass and thus can induce the degradation of organochlorine pesticides (Wu *et al.*, 2015; Zhang *et al.*, 2016).

On the other hand, a larger amount of organic chemicals can be adsorbed on the organic matter of soils with a higher amount of humus (Zhang *et al.*, 2016). As the doses of the applied pesticides in the various sites were probably varying in the past, the ratios of metabolites and parent compounds of the pesticides in soils were calculated to receive a “dose in dependent degradation pattern”; this value was compared with soil pH and TOC. Multiple analysis of linear regression between pH, TOC and ratios of metabolite/parent compound including the factor of land usages were calculated. The results showed that no influence of pH on OCP residue in soils was observed. Moreover, no correlations between concentrations of TOC and ratios of both β -HCH/ γ -HCH and p,p' -(DDD+DDE)/DDT were found, indicating that the residue levels of HCH and DDT were a reflection of OCPs application history and dissipation rates rather than air-soil equilibrium in the Wurno irrigation farm areas, which was similar to OCP residues in soils in Alabama (Harner *et al.*, 2013) and in Beijing (Zhu *et al.*, 2015).

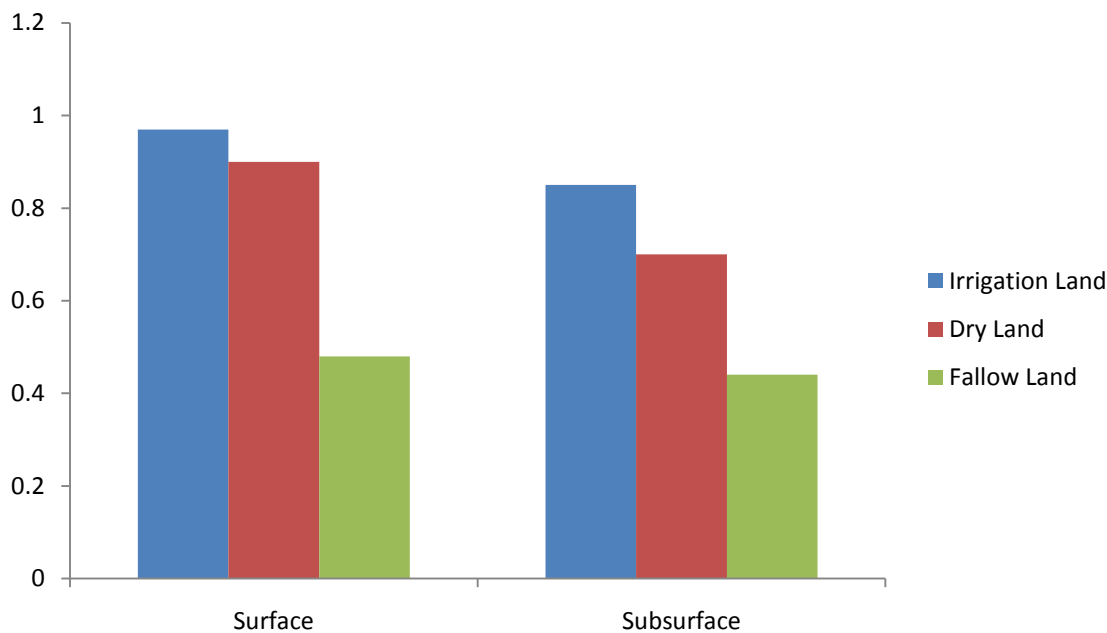


Fig. 2: Ratio of β -HCH/ γ -HCH

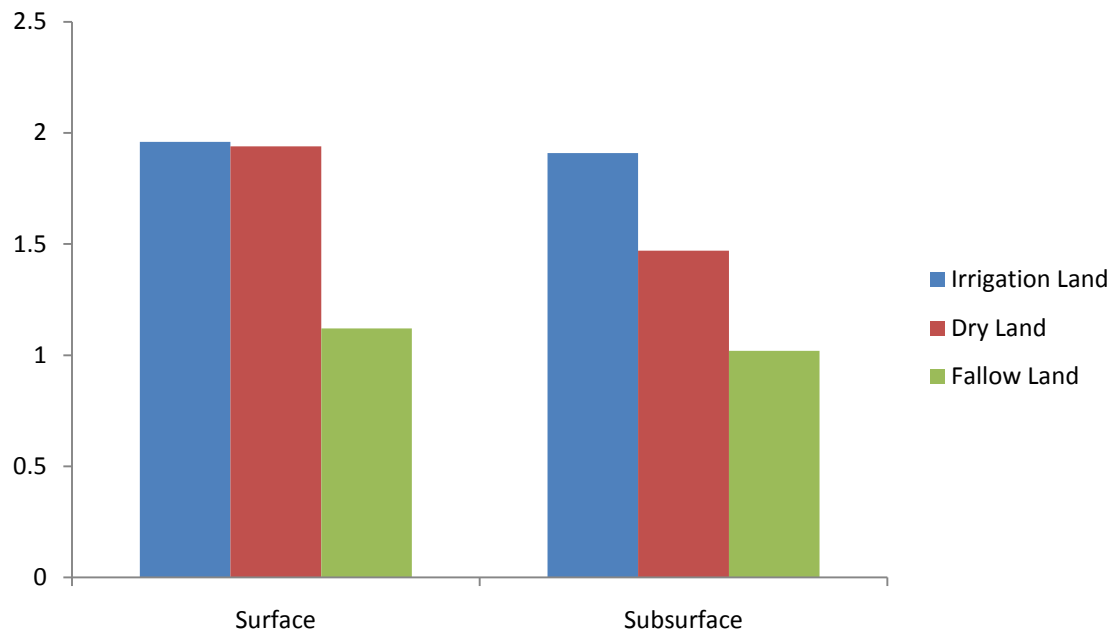


Fig. 3: Ratio of DDE+DDD/DDT

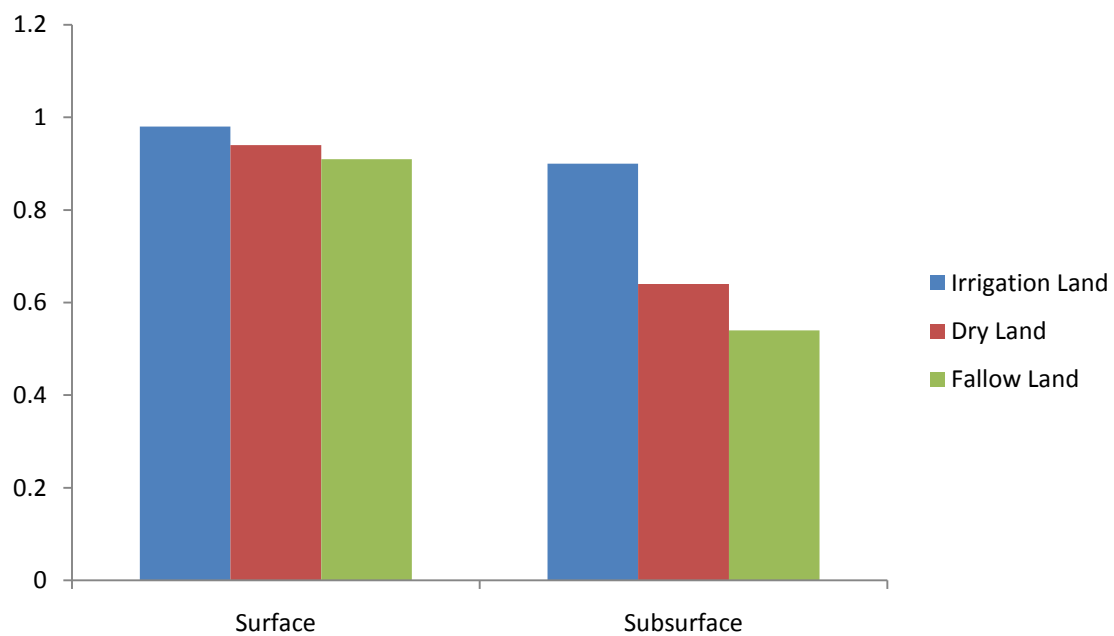


Fig. 4: Ratio of DDD/DDT

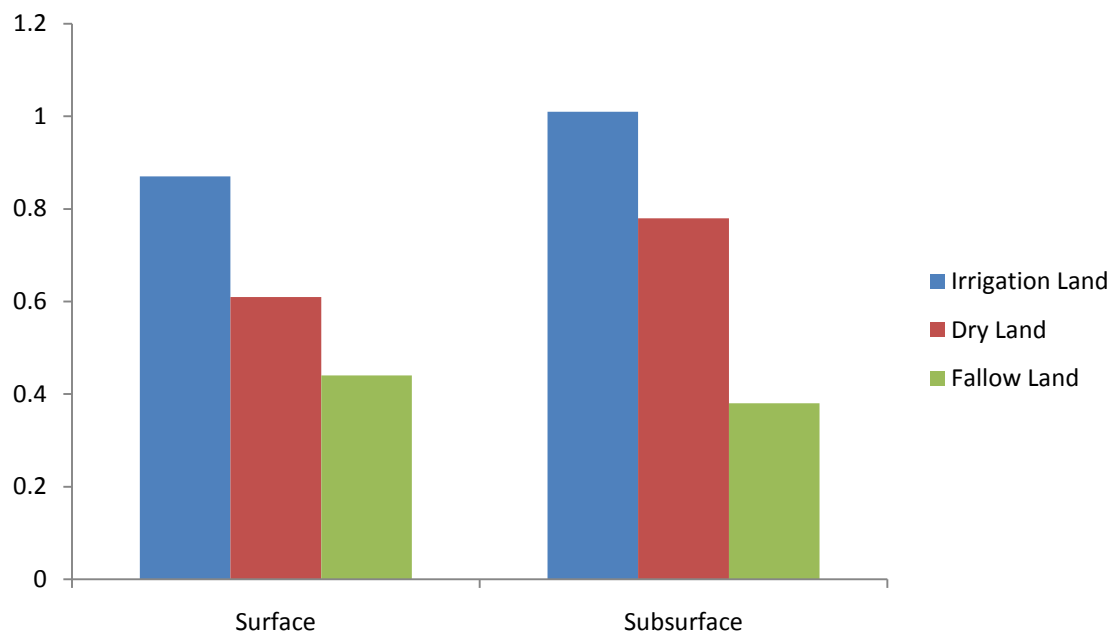


Fig. 5: Ratio of DDE/DDT

Technical HCH contains 60%–70% α -HCH, 5%–12% β -HCH, 10%–12% γ -HCH, 6%–10% δ -HCH and 3%–4% ϵ -HCH, while lindane contained almost pure γ -HCH (Willett *et al.*, 2010). γ -HCH is the most stable and persistent HCH-isomer with respect to microbial degradation (Wu *et al.*, 2015; Willett *et al.*, 2010; Manz *et al.*, 2011; Concha-Graña *et al.*, 2016). The ratio of β -HCH/ γ -HCH might increase during their degradation process. We tried using the ratio of β -HCH/ γ -HCH to reflect the degradation of HCH in soils. As shown in Fig.2, the ratios were mostly lower than the technical ratios, indicating both technical HCH and lindane were used in this region (Qiu *et al.*, 2014). However, no significant difference was observed between the ratios of β -HCH/ γ -HCH in soils under three land usages, which showed two possibilities. One is that the land usage has no significant influence on the degradation of HCH in soils. Another is that the land usage might affect the degradation of HCH in soils, but the ratio of β -HCH/ γ -HCH is not enough to directly show the influence of land-use on the HCH degradation in soils.

Degradation of HCH in the environment is complicated. Although it is clear that their degradation products are different under aerobic and anaerobic conditions, degradation pathways of HCH isomers in the environment are still unclear since identification of their degradation products is a challenge. - Pentachlorocyclohexene and - tetrachlorocyclohexene have been identified as degradation products of HCH, however, other suspected degradation products, such as cyclopentiltrichloroethene and 4,6,6,6-tetrachloro-1-hexenewere also detected in soil (Concha-Graña *et al.*, 2016). Thus, further study needs to be conducted to identify degradation

products of HCH in soils for a better evaluation of land usage on the degradation of HCH in soils.

DDT is reductively dechlorinated to DDD and dehydrochlorinated to DDE and the metabolites are more stable and persistent than the parent compound (Quensen *et al.*, 2012; Yao *et al.*, 2016). Ratios of metabolite/parent compound were calculated to understand the degradation pathway of DDT in soils. Ratios of p,p^1 -(DDD+DDE)/DDT $>p,p^1$ -DDE/DDT $>p,p^1$ -DDD/DDT (Figs.3,4 and 5) show that the main degradation pathway was from DDT to DDE.

Generally, a value of (DDD+DDE)/DDT ratio greater than 1.0 indicates aged (microbiologically degraded) DDT while a value much less than 1.0 indicates new pesticide application (Harner *et al.*, 2013; Tavares *et al.*, 2014; Miglioranza *et al.*, 2013; Zhang *et al.*, 2016). The average value of p,p^1 -(DDD+DDE)/DDT ratios were greater than 1.0 (Fig.3), indicating aged DDT in the soils. However, the ratios with a value lower than 1.0 were found in soil samples from the irrigation land (value is 0.97) and fallow land (value is 0.44). According to the average value of p,p^1 -(DDD+DDE)/DDT ratio, the contamination of the irrigation land area could be caused by a new input of DDT. Small ratio of p,p^1 -(DDD+DDE)/DDT in the fallow land soils could thus be explained by a new DDT deposition caused by its unwished application in irrigation land in the neighborhood. This new input of DDT in this area is most likely the pesticide dicofol which contains DDT related compounds 300 g/kg (Qiu *et al.*, 2014). Dicofol is still in restrictive use as a compensation pesticide of DDT to control mites after the usage of DDT was banned in several countries since 1983 (Qiu *et al.*, 2014, 2015; Zhu *et al.*, 2015).

Ratios of p,p^1 -(DDD+DDE)/DDT in soils under three land usages were: irrigation land $>$ dry land $>$ fallow land (Fig.3). Degradation of DDT was the slowest in the fallow land soils, indicating that remediation of the fallow land soils might be retarded. This could be explained by the fact that the fallow land soils were not subject to mechanical mixing (e.g., plowing and disking) which would otherwise enhance microbial action (Harner *et al.*, 2013). Ratios of p,p^1 -DDD/DDT in irrigation soils were higher than those in dry land soils, indicating that degradation of DDT could be accelerated under reductive conditions as it was observed in various studies by different authors (Boul *et al.*, 2014; Yao *et al.*, 2016). In irrigation soils, agricultural practices generate alternations of aerobic and anaerobic periods (Cary and Trolard, 2016), which could promote dechlorination of DDT to DDE and DDD (Quensen *et al.*, 2012; Yao *et al.*, 2016).

CONCLUSION

The usage of many organochlorine pesticides including HCH and DDT in most advanced countries have been banned for over 20 years, they are still used illegally in most developing countries although this sanction has resulted in a tremendous decrease in the use of OCP for agricultural purposes, the high residues of HCH and DDT in soils observed in this study will still need further remediation measures. Ratios of metabolites to parent compounds showed mostly

aged residue of DDT in soils in this region. Depending on land usage and agricultural management the degradation of contaminants increased in soils which showed intensive soil cultivation and intensive fluctuation of soil humidity like in the irrigation land; in contrast, in “undisturbed” soil systems like fallow land the decontamination process in general was slower. It can be concluded that intensive soil cultivation without applying agro-chemicals is a suitable method for a long-lasting soil decontamination of persistent organic chemicals like DDT and HCH.

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