

# LEVELS OF PESTICIDE RESIDUES AND METABOLITES IN SOIL AT VIKUGE FARM, KIBAHA DISTRICT, TANZANIA - A CLASSIC CASE OF SOIL CONTAMINATION BY OBSOLETE PESTICIDES

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## ABSTRACT

*The paper reports on the state of soil contamination by obsolete pesticides at Vikuge State Farm, Coast Region, Tanzania, where, in 1986, a 170 m<sup>3</sup> "donation" of partially expired pesticides were stored in an open shed that eventually collapsed. Analyses of soil samples collected in 2000 from the old storage site at the farm for 80 different pesticide residues and metabolites have revealed alarmingly high concentrations of pesticide residues to qualify Vikuge as one of the most contaminated sites in the world. Most of the residues found in the soil at high concentrations were organochlorines, their concentrations being up to 282,000 mg/kg dry weight for total DDT (28.2% by mass). Commercial formulations contain only between 5 and 10 % DDT. The concentrations of  $\Sigma$ HCH were up to 63,360 mg/kg (6.4 % by dry mass). A herbicide, pendimethalin [N-(1-ethylpropyl)-2,6-dinitro-3,4-xylidine], was also found at concentrations up to 40,900 mg/kg dry weight (4% by mass). As expected, higher concentrations of the residues were found in the surface soil samples and the concentrations of the residues were decreased with increasing depth and distance from the point source. Immediate decontamination of this site is highly recommended.*

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## INTRODUCTION

Obsolete pesticides no longer be used and therefore require disposal (Betlem *et al.* 1998, FAO 2001a). Although such pesticides are a common problem globally, they pose a more serious threat not only to the environment, but also to public health in African countries and the rest of the third world countries because these countries do not have the resources necessary for the safe disposal of these hazardous wastes. The amount of obsolete pesticides stocks in Africa is currently estimated to be more than 20,000 tonnes; with only seven countries including Tanzania, having more than 1,000 tonnes (FAO 2001b, Basel Convention 2001). They include large quantities of internationally banned organochlorine pesticides such as DDT, dieldrin, hexachlorocyclohexane (HCH), and highly toxic organophosphorous insecticides such as parathion and dichlorvos (FAO, 1998). The majority of obsolete pesticides stocks in Tanzania are leftovers of pesticide donations (Betlem *et al.* 1998). Whilst most of the

donations were genuine, some might have been opportunities to dump unwanted pesticides into poor and unsuspecting countries (FAO 2001a), as is apparent for the Vikuge case.

In 1986, Greece donated 170 m<sup>3</sup> of partly expired pesticides to the government of Tanzania through the Ministry of Agriculture. Without prior arrangements, the consignment was transported to Vikuge Farm for temporary storage before distribution to farmers (Betlem *et al.* 1998). The consignment was in poor condition and in damaged packages. Besides, most of the labels on containers were written in Greek, strongly indicating that the pesticides were intended for use locally in Greece. The consignment was stored in an open shed with an earthen floor. In 1993, the shed collapsed and the pesticides were exposed to direct sunlight, wind and rain. Though they were eventually collected and re-stored in a new building specially built for the purpose in 1998, the ground surface at the old

storage site was still completely bare at the time of sampling in May - August 2000.

Vikuge Farm, besides being a storage site, is a hay production centre, with hay being grown within a radius of 100 metres from the old storage site. The hay is mostly sold to dairy farms in Dar es Salaam and Coast Regions. Villagers grow food crops for their own use such as maize and rice on the lowland areas that become periodically flooded with flowing water emanating from the high-rise areas including the old storage site. The present study reports the concentrations and distribution of pesticide residues in soil samples collected in March and August 2000, from the point source at Vikuge Farm, Coast Region and its immediate environs.

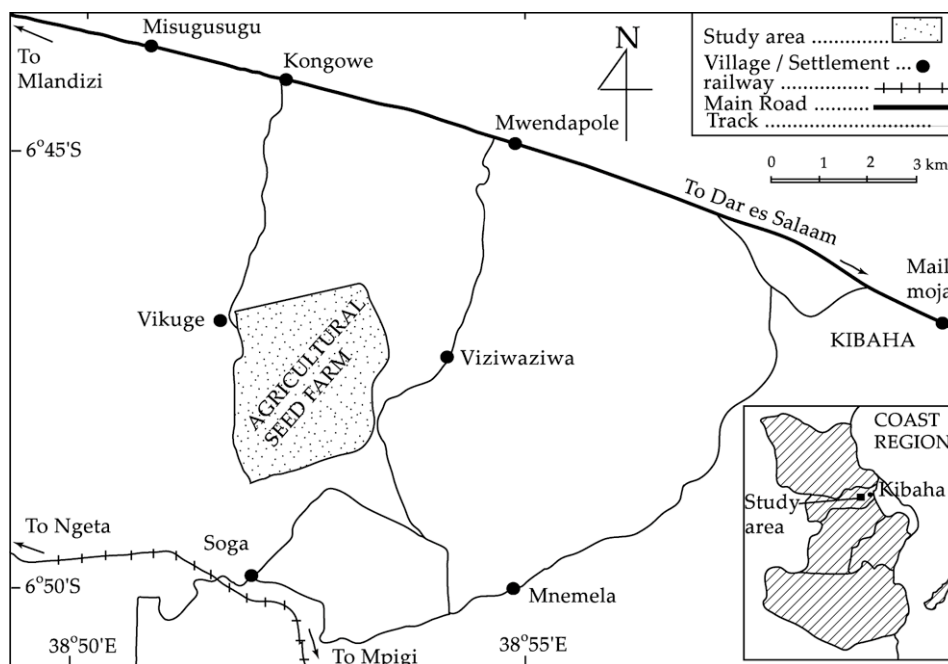
## METHODS

### Materials

All the reagents and solvents used were of analytical grade and included eighty (80) different pesticide standards ordered from Dr. Ehrenstorfer GmbH (Ausburg, Germany). Working standard solutions were made by dilution of the stock standards and mixtures of standards of different concentrations were used in most cases for the screening of the pesticide residues and metabolites. All volumetric glassware used was teflon stoppered. Varian Star 3400 and Hewlett Packard 5890A gas chromatographs equipped with  $^{63}\text{Ni}$  Electron Capture, (EC) and Nitrogen-Phosphorous, (NP) detectors were used for analysis.

### Sampling

Soil samples were collected from Vikuge Farm, Kibaha district, Coast Region, Tanzania (Figure 1).



**Figure 1** Map showing the Vikuge Study Area, Coast region, Tanzania

The soil samples were collected in March and August 2000. Samples were collected at the point source, 20 m and 50 m away from the point source, downhill. At each of these sub-locations, samples were taken at the surface (up to 5 cm deep) and at depths of 20 cm and 50 cm. Samples were taken using a hand hoe and a spade. The samples were wrapped in aluminium foil, put into plastic bags and kept frozen until extraction. A total of 7 sampling points were established: five points were within the point source and other two (20 m and 50 m), downhill, away from the source.

#### Extraction

Extraction of pesticides in soil samples was performed as per Åkerblom (1995). To a stoppered flask containing 20 g sample, 0.2 M ammonium chloride solution (14 ml) was added. The mixture was swirled for two minutes after which the flask and its contents were left to stand for 15 minutes before addition of cyclohexane:acetone (1:1, 100 ml). The flask was then tightly stoppered and vigorously shaken for one minute, and then less vigorously after every ten minutes for one hour. The contents were subsequently subjected to ultrasound for ten minutes. Distilled water was added cautiously until the organic layer rose to the neck of the flask. The organic phase was then quantitatively Pasteur pipetted into an E-flask that contained oven pre-dried anhydrous sodium sulphate (*ca.* 15 g) after which the contents were decanted through a plug of glass wool into an evaporation flask. The remaining sodium sulphate was rinsed with acetone (30 ml) and again decanted through the same glass wool plug. The resulting organic layer was concentrated to appropriate volumes.

#### Clean up

Most of the extracts required high dilutions of up to 10,000,000, which by itself was the major clean up procedure. Acid and alkali treatments were also employed as described by Åkerblom (1995). In the acid treatment, concentrated sulphuric acid (1

ml) saturated with cyclohexane was added to the extract (2 ml) in a test tube. The mixture was then swirled for one minute before centrifugation after which the organic layer was carefully transferred using a Pasteur pipette into another test tube and diluted with cyclohexane:acetone (9:1, 2 ml) ready for analysis.

In alkali treatment, potassium hydroxide (two pellets) was dissolved in a mixture of water (0.1 ml) and 99% ethanol (2 ml) in a test tube. The extract (1 ml) in cyclohexane was added into the mixture and placed in a water bath at 50 °C for 30 minutes, followed by cooling at room temperature. Sodium chloride-phosphoric acid solution (5 ml), (prepared by dissolving 12 g of sodium chloride in a litre of 0.1 M ortho-phosphoric acid), was added and the mixture was shaken and centrifuged. The organic layer was transferred into a round bottomed flask, followed by changing the solvent to cyclohexane:acetone (9:1) for GC analysis.

#### Analysis and quantification

Analysis for the residues and metabolites was done as described by Åkerblom (1995). Varian Star 3400 and Hewlett Packard 5890A gas chromatographs equipped with <sup>63</sup>Ni Electron Capture (EC) and Nitrogen-Phosphorous (NP) detectors were used for the analysis. SE-30 and OV-1701 megabore columns (30 m x 0.32 mm x 0.5 µm) were used in each detector. Nitrogen was used as both a carrier and make up gas in the ECD at a flow rate of 30 ± 1 ml/min. In the NPD, helium was used as a carrier gas at a flow rate of 0.5 - 1 ml/min and nitrogen, at a flow rate of 29 ± 1 ml/min, was used as the make up gas. The temperature programme was 90 °C held for 1 min, 30 °C/min to 180 °C, 4 °C/min to 260 °C held for 12 minutes. The injector and detector temperatures were 250 °C and 300 °C, respectively. Identification of residues was effected by running samples and external reference standards in GC and then comparing the chromatograms. A peak was not considered

relevant unless it appeared in both columns in a given detector. The method average detection limits are given in Table 1.

**Table 1** Average Method Detection Limits (mg/kg dry weight)  $\times 10^{-2}$

$\alpha$ -HCH	3	heptachlor	0.05
$\beta$ -HCH	2	Heptachlor epoxide	0.06
$\gamma$ -HCH	0.1	<i>p,p'</i> -DDE	0.06
$\delta$ -HCH	0.1	<i>p,p'</i> -DDD	0.7
Aldrin	0.08	<i>o,p'</i> -DDT	2
P'methalin	4.5	<i>p,p'</i> -DDT	10
-chlordane	0.05		

Recoveries of residues were in the range 59 – 80 % for HCH and 70 – 99 % for DDT which is within the acceptable range (Åkerblom 1995).

## RESULTS AND DISCUSSION

Organochlorines were the most frequently detected pesticides in the soil samples. These included the HCH isomers  $\alpha$ -,  $\beta$ -,  $\gamma$ -,

$\delta$ -HCH and DDT isomers, *p,p'*-DDT and *o,p'*-DDT, and metabolites, *p,p'*-DDE and *p,p'*-DDD. The total organochlorines concentrations were up to 345,000 ppm (34.6 %, dry mass). Pendimethalin [N-(1-ethylpropyl)-2,6-dinitro-3,4-xylidine], an organic herbicide was also found at concentrations ranging from 39.9 mg/kg to 40,900 mg/kg dry weight.

### Distribution of HCH residues in soil

The  $\alpha$ -HCH and  $\beta$ -HCH isomers were found in surface samples in the range of 230-49,700 mg/kg (i.e., up to 5%) and 340-6,370 mg/kg (i.e., up to 0.6 %) dry weight respectively, representing over 70% of the samples analysed (Table 2). The isomers  $\gamma$ -HCH and  $\delta$ -HCH were detected in the range of 80 - 7,200 mg/kg (i.e., up to 0.7 %) and 90 - 2,360 mg/kg (i.e., up to 0.2 %) dry weight, respectively. The general trend displayed by the concentrations of HCHs in the surface samples was  $\alpha$ -HCH >  $\beta$ -HCH >  $\gamma$ -HCH >  $\delta$ -HCH.

**Table 2** Concentrations of HCH residues in surface soil samples

Sampling Point	Concentration (mg/kg dry weight) $\times 10^3$						$\alpha$ -HCH/ $\gamma$ -HCH ratio
		$\alpha$ -HCH	$\beta$ -HCH	$\gamma$ -HCH	$\delta$ -HCH	$\Sigma$ HCH	
Onsite points	A	49.7 $\pm$ 0.08	4.1 $\pm$ 0.15	7.2 $\pm$ 0.04	2.36 $\pm$ 0.05	63.36	6.9
	B	34.2 $\pm$ 0.08	4.89 $\pm$ 0.15	5.05 $\pm$ 0.04	0.78 $\pm$ 0.05	44.92	6.8
	C	0.23 $\pm$ 0.08	1.77 $\pm$ 0.15	0.08 $\pm$ 0.04	0.19 $\pm$ 0.05	2.27	2.9
	D	2.85 $\pm$ 0.08	0.34 $\pm$ 0.15	0.15 $\pm$ 0.04	0.09 $\pm$ 0.05	3.43	18.6
	E	22.2 $\pm$ 0.08	6.37 $\pm$ 0.15	0.46 $\pm$ 0.04	0.21 $\pm$ 0.05	29.24	48.3
Away Points	20 m	1.13 $\pm$ 0.08	2.43 $\pm$ 0.15	< 0.07	< 0.09	3.56	-
	50 m	< 0.15	< 0.3	< 0.07	< 0.09	-	-

In the 20 cm deep samples,  $\alpha$ -HCH and  $\beta$ -HCH isomers were detected in all the samples with concentrations ranging from 0.16 mg/kg to 3,800 mg/kg (i.e., up to 0.4%) dry weight (Table 3) and Figure 2).

The  $\gamma$ -HCH and  $\delta$ -HCH isomers were not detected in some samples. In general the HCHs concentrations trend was in the order;  $\alpha$ -HCH >  $\beta$ -HCH >  $\delta$ -HCH >  $\gamma$ -HCH.

**Table 3** Concentrations of HCH residues in soil samples at a depth of 20 cm

Sampling Point		Concentration (in mg/kg dry weight)					$\alpha$ -HCH/ $\gamma$ -HCH ratio
		$\alpha$ -HCH	$\beta$ -HCH	$\gamma$ -HCH	$\delta$ -HCH	$\Sigma$ HCH	
<b>Onsite points</b>	A	3800 $\pm$ 0.04	590 $\pm$ 0.1	392 $\pm$ 0.06	296 $\pm$ 0.07	5078	9.7
	B	1.81 $\pm$ 0.04	1.56 $\pm$ 0.1	2.23 $\pm$ 0.06	16 $\pm$ 0.07	21.59	0.8
	C	144 $\pm$ 0.04	0.21 $\pm$ 0.1	< 0.12	< 0.13	144.2	-
	D	45 $\pm$ 0.04	32 $\pm$ 0.1	23 $\pm$ 0.06	144 $\pm$ 0.07	244	2
	E	0.22 $\pm$ 0.04	0.3 $\pm$ 0.15	0.19 $\pm$ 0.06	1.03 $\pm$ 0.07	1.76	1.2
<b>Away points</b>	20 m	0.16 $\pm$ 0.04	0.39 $\pm$ 0.1	< 0.12	< 0.13	0.55	-
	50 m	< 0.08	< 0.2	< 0.12	< 0.13	-	-

HCH residues were also detected in some of the samples at the depth of 50 cm indicating possible risk to ground water contamination (Table 4). The onsite samples had higher

concentrations relative to away samples but much lower than those from the surface and the samples collected from a depth of 20 cm.

**Table 4** Concentrations of HCH residues in 50 cm deep soil samples

Sampling Point		Concentration (in mg/kg dry weight)					$\alpha$ -HCH/ $\gamma$ -HCH ratio
		$\alpha$ -HCH	$\beta$ -HCH	$\gamma$ -HCH	$\delta$ -HCH	$\Sigma$ HCH	
<b>Onsite points</b>	A	< 0.08	< 0.3	< 0.1	< 0.13	-	-
	B	0.26 $\pm$ 0.04	0.65 $\pm$ 0.1	0.2 $\pm$ 0.05	< 0.13	1.19	0.93
	C	0.89 $\pm$ 0.04	0.38 $\pm$ 0.1	< 0.1	0.16 $\pm$ 0.08	1.43	-
	D	0.17 $\pm$ 0.04	0.3 $\pm$ 0.1	0.2 $\pm$ 0.05	1.6 $\pm$ 0.08	2.31	0.71
	E	0.53 $\pm$ 0.04	0.68 $\pm$ 0.1	< 0.1	0.96 $\pm$ 0.08	2.17	-
<b>Away points</b>	20 m	0.2 $\pm$ 0.04	< 0.3	0.1	< 0.13	0.3	2
	50 m	< 0.08	< 0.3	< 0.1	< 0.13	-	-

**Table 5** Concentrations of HCH residues as compared to depth.

Depth	Mean concentrations (mg/kg dry weight) for onsite samples			
	$\alpha$ -HCH	$\beta$ -HCH	$\gamma$ -HCH	$\delta$ -HCH
surface	21856.6 $\pm$ 0.08	3493.2 $\pm$ 0.15	2588.8 $\pm$ 0.05	727.8 $\pm$ 0.05
20 cm	798.2 $\pm$ 0.04	124.8 $\pm$ 0.1	83.5 $\pm$ 0.06	91.4 $\pm$ 0.07
50 cm	0.37 $\pm$ 0.04	0.4 $\pm$ 0.15	0.11 $\pm$ 0.08	0.56 $\pm$ 0.08

A comparison between the mean levels HCH residues at different depths for the onsite samples are given in Table 5

The results from the pesticide residues' determinations in the surface soil revealed very high pesticide levels. The  $\alpha$ -HCH isomer was detected in high amounts, especially in samples from the point source,

resulting to high  $\alpha$ -HCH/ $\gamma$ -HCH ratios. Ratios from 2.9 to 48.3 were obtained (Table 2), with an average ratio of 16.78 for surface soil samples within the old storage site. These ratios are three times more than the ratio of the isomers in the technical HCH commercially available (about 5.3). This is clearly indicative of contamination by a technical HCH product. There are eight

(8) possible isomers of HCH, but it is usually the  $\alpha$ -,  $\beta$ -,  $\gamma$ - and  $\delta$ -isomers that are of importance in the technical product (Tomlin 2000). The  $\gamma$ -isomer (lindane) is the only isomer with insecticidal properties. In Western Europe and North America, the use of such technical products ceased in the 1970s and instead purified lindane has been used (Environment Canada 2000). Technical HCH, however, is still used in some developing countries.

All the HCH isomers are stable and have the potential to be transported over long distances and to bioaccumulate in organisms. In the environment, lindane is potentially transformed into a variety of chemicals most of which are volatile. These include  $\gamma$ -pentachlorocyclohex-1-ene,  $\gamma$ -3,4,5,6-tetrachlorocyclohex-1-ene,  $\alpha$ -HCH,  $\beta$ -HCH and  $\delta$ -HCH (Sang *et al.* 1999). However, the thermodynamically most favourable structure is the  $\alpha$ -isomer, which constitutes up to 70 % of the HCH in the technical product. The  $\beta$ -isomer, constituting only 6 - 7% in technical HCH, is the most persistent in the environment. Thus  $\beta$ -HCH, may accumulate relative to other isomers in an aged technical product.  $\delta$ -HCH is rarely found in the environment, except when there is a fresh release of the technical product.

The presence of high  $\alpha$ -HCH residues with respect to  $\gamma$ -HCH in soil samples can be attributed to two major factors; the different degradation rates and variable physico-chemical properties of the isomers. HCH isomers have different degradation rates under environmental conditions. The difference in degradation rates of HCH isomers could have contributed to the variable accumulation of the isomers in this area. The isomers also vary in their physico-chemical properties.  $\alpha$ -HCH has a Henry's Law Constant of 0.524 Pa m<sup>3</sup>/mol while that for lindane is 0.257 Pa m<sup>3</sup>/mol at 20

°C (Tomlin 2000). This indicates relatively high water solubility of lindane and its tendency to partition faster from a gas phase into the water phase. Therefore during global distillation of HCH isomers, lindane is readily removed from the troposphere by rain, leaving proportionally higher levels of  $\alpha$ -HCH (Sang *et al.* 1999). Besides the significant influence of temperature, humidity and solar radiation on the rapid dissipation of HCH isomers in a tropical coastal environment like the Vikuge environment, there are still high levels of the residues detected in soil. Though  $\alpha$ -HCH is expected to be the fastest isomer to dissipate from the soil due to its high vapour pressure and hence high volatilisation rate, it has been detected in soil samples at very high levels. This again is an indication of the large amount of the technical HCH spilled in the area. Tables 2 - 5 show that the levels of HCH isomers were decreasing with increasing distance from the surface. This observation is consistent with the hypothesis that HCH isomers will stay on the upper layers of the soil; and there is little movement of the isomers to lower soil layers (Sang *et al.* 1999).

#### Distribution of DDT residues in soil

The pesticide residue analysis results showed the presence of *p,p'*-DDT and *p,p'*-DDD in more than 86 % of the samples, with concentrations from 5,200 to 172,000 mg/kg dry weight (i.e., up to 17.2 %) for *p,p'*-DDT and from 4,700 to 69,600 mg/kg dry weight (i.e., up to 7 %) for *p,p'*-DDD (Table 6). The *p,p'*-DDE and *o,p'*-DDT concentrations ranges were 140 - 4,050 mg/kg and 2,000 - 36,100 mg/kg dry weight, respectively. A concentration trend in the order of *p,p'*-DDT > *p,p'*-DDD > *o,p'*-DDT > *p,p'*-DDE was observed in surface samples. These figures for *p,p'*-DDT are higher than the concentrations of in commercial formulations, which are usually between 5 and 10 %.

**Table 6** Concentrations of DDT residues in surface soil samples

Sampling Point		Concentration (in mg/kg dry weight) x 10 <sup>3</sup>					DDE/DDT
		<i>p,p'</i> -DDE	<i>p,p'</i> -DDD	<i>o,p'</i> -DDT	<i>p,p'</i> -DDT	ΣDDT	
<b>Onsite points</b>	A	4.05	69.6	36.1	172	281.75	0.02
	B	0.31	21.5	7.45	30	59.26	0.01
	C	0.7	12.24	6.6	13.8	33.34	0.03
	D	0.14	4.7	2	5.2	12.04	0.02
	E	0.53	41.6	13.46	65.25	120.84	0.01
<b>Away points</b>	20 m	0.27	12.1	3.76	16.82	32.95	0.01
	50 m	< 0.1	0.94	< 1.03	< 1.6	0.94	-

The concentrations of ΣDDT and of individual DDT residues decreased with increasing distance from the site. In surface samples, the DDT residue concentrations were higher than the HCH residue concentrations.

DDT residues and metabolites were detected in all the 20 cm-deep samples (Table 7). The

concentrations ranged between 0.11 mg/kg (*p,p'*-DDE) and 14,800 mg/kg dry weight (*p,p'*-DDT). Concentrations of the DDTs in 20 cm-deep samples were of the trend: *p,p'*-DDT > *o,p'*-DDT > *p,p'*-DDD > *p,p'*-DDE. The concentrations of the DDTs in these samples were generally higher than those of HCHs, but lower than those of DDTs in the surface samples.

**Table 7** Concentrations of DDT residues in 20 cm-deep soil samples.

Sampling Point		Concentration (in mg/kg dry weight)					DDE/DDT ratio
		<i>p,p'</i> -DDE	<i>p,p'</i> -DDD	<i>o,p'</i> -DDT	<i>p,p'</i> -DDT	ΣDDT	
<b>Onsite points</b>	A	40 ±0.05	773 ±0.05	2444 ±0.1	14800 ±0.5	18057	0.002
	B	< 0.1	0.27 ±0.05	0.33 ±0.1	2.8 ±0.5	3.4	-
	C	14 ±0.05	459 ±0.05	150 ±0.1	820 ±0.5	1443	0.01
	D	22 ±0.05	304 ±0.05	455 ±0.1	1900 ±0.5	2681	0.01
	E	0.14 ±0.05	0.64 ±0.05	4.71 ±0.1	7.96 ±0.5	13.45	0.01
<b>Away points</b>	20 m	0.11 ±0.05	0.41 ±0.05	0.98 ±0.1	5.2 ±0.5	6.7	0.02
	50 m	1.24 ±0.05	1.67 ±0.05	7.01 ±0.1	32.41 ±0.5	42.33	0.03

DDT and its metabolites were also detected in 50 cm-deep soil samples with concentrations ranging from 0.21 mg/kg (*p,p'*-DDE) to 33 mg/kg dry weight (*o,p'*-DDT) (Table 8). This showed nearly the same order in the concentration trend: *p,p'*-DDT > *o,p'*-DDT > *p,p'*-DDD > *p,p'*-DDE as observed in the surface and 20 cm-deep

samples. DDT residues, (*o,p'*-DDT and *p,p'*-DDT), showed higher concentrations compared to the metabolites, (*p,p'*-DDE and *p,p'*-DDD). The concentrations of pesticide residues in the 50-cm deep samples were lower than those of both the surface and 20-cm deep samples.

**Table 8** Concentrations of DDT residues in 50-cm deep soil samples

Sampling Point		Concentration (in mg/kg dry weight)				$\Sigma$ DDT	DDE/DDT ratio
		<i>p,p'</i> -DDE	<i>p,p'</i> -DDD	<i>o,p'</i> -DDT	<i>p,p'</i> -DDT		
<b>Onsite points</b>	A	< 0.14	< 0.14	< 0.82	< 2	-	-
	B	0.3 $\pm$ 0.07	0.43 $\pm$ 0.07	< 0.82	2.62 $\pm$ 1.0	3.76	0.1
	C	0.16 $\pm$ 0.07	1.39 $\pm$ 0.07	1.59 $\pm$ 0.41	9.39 $\pm$ 1.0	12.53	0.01
	D	2.25 $\pm$ 0.07	18 $\pm$ 0.07	33 $\pm$ 0.41	< 2	53.25	0.07
	E	0.21 $\pm$ 0.07	3.6 $\pm$ 0.07	5.97 $\pm$ 0.04	27 $\pm$ 1.0	36.78	0.01
<b>Away points</b>	20 m	< 0.14	0.31 $\pm$ 0.07	< 0.82	< 2	0.31	-
	50 m	< 0.14	0.29 $\pm$ 0.07	< 0.82	< 2	0.29	-

**Table 9** Concentrations of DDT residues with respect to depth.

Depth	Mean concentrations (in mg/kg dry weight) for A, B, C, D and E			
	<i>p,p'</i> -DDE	<i>p,p'</i> -DDD	<i>o,p'</i> -DDT	<i>p,p'</i> -DDT
<b>surface</b>	1145.8 $\pm$ 0.05	29928 $\pm$ 0.07	13122 $\pm$ 0.5	57250 $\pm$ 0.5
<b>20 cm</b>	15.3 $\pm$ 0.05	307.4 $\pm$ 0.05	610.8 $\pm$ 0.1	3506.2 $\pm$ 0.5
<b>50 cm</b>	0.58 $\pm$ 0.07	4.7 $\pm$ 0.07	8.2 $\pm$ 0.04	7.8 $\pm$ 1.0

Table 9 gives the concentrations of different DDT residues at different depths.

The high  $\Sigma$ DDT (that is *p,p'*-DDE + *p,p'*-DDD + *o,p'*-DDT + *p,p'*-DDT) in each of the onsite soil samples (Tables 6-8) suggests that a large amount of DDT leaked onto the soil at the area. The percentage of *p,p'*-DDT was higher than those of the other DDT isomer and metabolites, supporting the hypothesis that a large quantity of technical grade DDT was stored at the old storage area (the point source). The DDE/DDT ratios of less than one in the onsite samples (Table 6) suggest that there has been little or no degradation of DDT to its metabolites such as DDD and DDE in surface soil. A ratio larger than 3 is normally expected for aged mixtures in the environment (Tomlin 2000).

Higher DDD concentrations as compared to those of DDE in surface samples (6) suggests a possibility of the consignment containing DDD as a pesticide of its own (Tomlin 2000). DDD, has been observed to be persistent in soil, sediment and water for as long as 190 years (WWF 1999). It is also

possible that some of the DDD residues have been formed as a result of degradation of DDT during injection in the GC. This is supported by experimental evidence for the DDT conversion to its metabolites, DDD and DDE, depending on the matrix co-extractives present in the analyte, some of which appear to catalyse the process (Miglioranza *et al* 1999).

While there is literature support (Lalah *et al* 1994, Wandiga 1996, Lalah & Wandiga 1998) for significantly more rapid pesticide dissipation from tropical than under temperate conditions largely as a result of enhanced volatility and microbial degradation, soils are often dry which significantly delays, or even stops any transformation (Brooks *et al* 1999). Vikuge has a sandy loam type of soil (84.5 % sand, 11.3 % clay and 2.7 % silt) with very low organic matter content (1.5 %). For mobile and/or persistent pesticides, this has serious implications for ground water contamination, particularly for high water table areas like the Tanzanian coastal areas. On the other hand, the acidic (pH 3.9) nature of the soil at Vikuge significantly



hampers the DDT dehydrochlorination reaction in the soil, hence the high DDT levels and low DDE levels in the study area.

#### Other pesticide residues

Other organochlorines detected in soil samples were the cyclodienes:  $\gamma$ -chlordane, heptachlor and aldrin. Whereas  $\gamma$ -chlordane was detected in more than 70% of the samples, heptachlor and aldrin were detected in less than 15% of the samples only.  $\gamma$ -Chlordane was detected in most of the onsite samples, with concentration ranging from 49 mg/kg dry weight to 822 mg/kg dry weight. Heptachlor and aldrin were detected at concentrations of 36 mg/kg and 107 mg/kg dry mass, respectively. On the other hand, the pre-emergence organic herbicide, pendimethalin was detected in one onsite surface soil sample at a concentration of 40,900 mg/kg dry weight. Pendimethalin is reported to be fairly immobile and persistent in soil, with its leaching potential being very low (WHO 1993). This may explain its being found in a single surface soil sample. The quarternary ammonium herbicides: paraquat and diquat, were also analysed for but found to have concentrations below the method detection limit (1.1 mg/kg dry weight) in the surface soil samples.

Soils exposed to hazardous chemicals like these pesticides can be severely damaged by alteration of their physical and chemical properties and thus reducing the ability to support plants (Manahan 2001) as well as other living organisms. This is evidently clear in the study area where there has been no plant growth and the soil has remained sterile for more than fifteen years now.

#### CONCLUSION

There was a presence of high levels of pesticide residues and metabolites in the top-soil, up to 2.8 times the strongest commercial formulation of DDT, and at different depths at the old storage site at Vikuge farm, Kibaha district. This advocates

for more serious consequences of even more dispersion of the pesticide residues and pollution of ground water in the area. The pesticides were stored at Vikuge in 1986, whereas the samples analysed were taken in 2000. The prevalence of such high levels of pesticide residues raises questions like "*What was the situation fifteen years ago, after the first rains? How much of the water-soluble pesticides contaminated drinking water and what were the consequences*". Whatever the case, the old storage site at Vikuge is probably the most contaminated site in the world and immediate decontamination measures need to be undertaken, with the hope that a similar situation shall never again arise in Tanzania, Africa and the world.

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