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Levels, compositions and distributions of organochlorine pesticide residues in soil 5–14 years after clean-up of former storage sites in Tanzania

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HIGHLIGHTS

- The level of contamination has been indicated to be high.
- No significant degradation of the parent compounds.
- Remediation measures are required to reduce the levels of the contaminants.

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ABSTRACT

The levels, compositions and distributions of organochlorine pesticides and metabolites were determined in soil samples collected 5–14 years after clean-up was carried out at seven contaminated sites in Tanzania. Samples were collected from various depths (5–10 cm, 30 cm, and 50 cm for most sites and up to 300 cm for one site. Determination of the analytes was performed using a high resolution GC–MS and isotope dilution technology. DDT, DDD, DDE, HCH isomers, aldrin, dieldrin, endrin, endosulfans, chlordanes and heptachlor were the major compounds detected. The concentrations of total DDT and total HCH were up to 250 000 and 164 000 mg kg^{-1}, respectively, while the highest concentrations for other compounds ranged from 29 to 3300 mg kg^{-1}. The results indicated that there were no significant degradations/transformations of the pesticides for most of the sites. The highest concentrations of the compounds were mostly found in surface soil samples and there were variations in distribution among the sampling depths. The results indicate risks and concerns for public health and the environment.

1. Introduction

Organochlorine pesticides such as dichlorodiphenyltrichloroethane (DDT), dieldrin and hexachlorocyclohexanes (HCHs) have been withdrawn or banned in many countries for public health and environmental reasons. However, many countries in the migratory locust zone often still have large quantities of these compounds remaining from old strategic stocks for locust control and other uses. Several of these stocks were acquired in the 1970s and 1980s. These stocked pesticides have become obsolete; they can no longer be used for their intended purpose or any other purpose and therefore require disposal. In many cases, obsolete pesticides are stored under conditions that do not meet basic standards for safe and responsible storage of such hazardous materials, such as storage in poorly ventilated stores, stores that do not have concrete floor, stored in the open, in torn or deteriorated bags, in corroded and leaking drums or drums that have ballooned as a result of heat especially in tropical countries (FAO, 1996).

Improper storage of pesticides often leads to pesticides being spilled in the surroundings of the storage site, where they seep into the soil or are dispersed by wind. In some cases pesticide spillage has been going on for many years. Such spillage has caused serious soil or groundwater contamination. When soil and groundwater are contaminated, crops, livestock and drinking water may become affected and, when they are consumed by human beings, health risks may occur (FAO, 2000).

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The effects of organochlorine pesticides on health and the environment range from acute toxicity to chronic toxicity. Clearly there are heavy costs associated with people becoming ill as a result of exposure. Chronic illness, reproductive problems, endocrine disrupting effects, cancers and physical deformities bear high long-term costs for individuals and communities (Hart and Pimentel, 2002). Environmental contamination by organochlorine pesticides is prohibitively expensive to remedy because they have high persistence in the environment and have adverse effects to human health. In some cases the technical resources do not exist even if money were available. The contamination may be carried beyond the national boundaries resulting into high health and environmental consequences. Organochlorine pesticides are bioaccumulative and are also transported by climatic and environmental processes over long distances. They tend to move from warmer climate regions to colder climates, even as far as the poles where they accumulate in the fat tissues of humans and wildlife at the top of food chains (FAO, 2001).

The major purpose of this study was to investigate the concentrations, compositions and distributions of organochlorine pesticides in soils from seven sites in Tanzania, which were contaminated as the storage sheds collapsed or due to leakage and spillage of pesticides as a consequence of improper storage. Clean-up was carried out at these sites about 5–14 years before this study and this involved mainly collecting the stockpiles and repacking them into new containers for storage in new buildings or for disposal sites. No study had been focused on the contamination status at most of these sites. Contamination at Vikuge had been focused on in an earlier study which collected samples in 2000 and detected very high concentrations of pesticides in soil (Kishimba and Mihale, 2004). Despite such findings, no remediation measures have been taken. Hence the need for further investigation to assess the current status of the compounds at that site.

2. Materials and methods

2.1. Sampling

Soil samples were collected from the following sites: (i) Murbadaw–located at the Hanang wheat complex in Manyara region, contamination due to leakage and spillage during storage, clean-up was conducted in 2004/2005 by repacking in drums and bags and disposal by burying about 100 m away from the former storage site. (ii) Katundu–located in Geita town, contamination as the stores collapsed, clean-up was carried out in 1995 by collecting the pesticides and disposal by open burning at a different site. (iii) Mwanakombo store–located within the Mahonda sugar plantations in Zanzibar, contamination due to spillage and leakage, clean-up was carried out in 1995/96 whereby the pesticides were collected and transported for disposal. (iv) Mbarali rice farm–located in Mbarali district in Mbeya region, the storage shed collapsed, clean-up by repacking and storage in a new building was carried out in 2004. (v) Mbozi NAFCO maize farm–located in Mbozi district in Mbeya region, contamination due to leakage of pesticides from containers which were kept outside, the containers were removed in 2000.
(vi) Vingunguti storage site–located in Dar es Salaam, contamination due to leakage from drums, clean-up was carried out in 2003 by repacking in new drums, and (vii) Vikuge pasture farm, located in Kibaha district-Coast region, the shed collapsed, clean-up involving repacking the pesticides and storage in a new building was carried out in 1996. The locations of the sampling sites are shown in Fig. 1.

Soil samples were collected from the sites in January–April 2009. Samples were collected at points within the former storage areas and at short distances away from those points (10 m for Murbadaw, Mbarali and Mbozi NAFCO, 20 m for Zanzibar, 5–30 m for Vingunguti and Vikuge and 50 m for Geita). The sampling distances were varied roughly based on different sizes of the contaminated areas, location of neighbouring buildings or other structures around the sites and slopes. The samples were collected by taking the surface soil (5–10 cm deep) and 30 cm deep for most sites whose soils appeared to be high in clay content, while for two sites (Vingunguti and Vikuge) which had sandy soils, samples were collected at 10–30 cm and at deeper depths from 50 cm to 3 m deep.

The tools used for sampling of soil included clean spades, hoes, small spades, clean aluminium foil, clean buckets, measuring tapes, folding rulers, insulating boxes, solvents for cleaning, bottles for waste solvents, kitchen roll papers, polyethylene bags, waste plastic bags and stainless steel spoons. Using a hoe and spade, a test pit was prepared a little deeper than the desired depth, then using a clean spade a slice about 5 cm thick was made along the vertical wall of the pit at the desired depth and the soil was thrown away (Åkerblom, 1995). Another clean spade or spoon was used to take the sample. Samples at deeper points and presumably less contaminated points were collected first before the surface or presumably contaminated depths or points. A sample was obtained by collecting at least five subsamples from different points at the same depth within the pit. The stones, sticks, plant roots and other unwanted materials were removed by using a clean spoon. The sample was ground and mixed very thoroughly on aluminium foil. The sample was immediately wrapped in an aluminium foil and placed in a polyethylene bag then put in an insulated box. The samples were transported to the laboratory and stored in a freezer at −28 °C until extraction.

2.2. Extraction, clean up and gas chromatographic analysis

Extraction, clean-up and analysis of the soil samples were conducted at the Molecular EXposomics unit, German Research Centre for Environmental Health. The procedures by Schramm et al. (2008) were adopted with modifications. A cellulose filter was inserted into the inner bottom of the extraction cell, then sea sand dried at 550 °C (ca. 1 g) was added. The sample (0.5–5 g) mixed with hydromatrix for drying and dispersing was added into the cell and a filter placed on top. Prior to extraction, the sample was spiked with ^{13}C-labelled and deuterated internal standards (10 μL of a mixture containing 333–1000 pg μL^{-1} of organochlorine compounds in nonane). All the internal standards for the compounds determined were ^{13}C–labelled except for 4,4′-DDD, which was a deuterated standard. Highly contaminated samples were not spiked with internal standards prior to extraction, but the diluted extracts were spiked during clean-up so that the concentrations and detection of internal standards were not affected due to large dilutions of extracts. The samples were quantitatively extracted by pressurized fluid extraction using an Accelerated Solvent Extractor (ASE 200 Dionex) at a temperature of 120 °C and pressure of 120 bar and with *n*-hexane:acetone (75:25) as the extraction solvent mixture. Two static cycles of 10 min were applied for a complete extraction. Another sub-sample of each original sample was dried in oven for 24 h at 105 °C and then weighed for dry mass determination. The extracts were passed over anhydrous sodium sulfate to remove water. The extracts were concentrated using vacuum rotary evaporation and the solvent was changed to *n*-hexane:dichloromethane (1:1) and concentrated to 0.5–1 mL. Extracts of highly contaminated samples were diluted to 5 or 10 mL, then 50 or 100 μL of diluted extracts were measured and diluted further to 0.5 or 1 mL or used directly for clean-up.

To remove interferences, the concentrated and diluted extracts were cleaned-up using silica gel and alumina in a glass column (30 cm long with an internal diameter of 2.5 cm) containing 10 g sil-