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ScienceDirect
Chemosphere 68 (2007) 832–837
CHEMOSPHERE
www.elsevier.com/locate/chemosphere

# Organochlorine pesticides and metabolites in young leaves of *Mangifera indica* from sites near a point source in Coast region, Tanzania

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Received 17 November 2006; received in revised form 7 February 2007; accepted 13 February 2007
Available online 28 March 2007

**Abstract**

Young leaves of *Mangifera indica* (mango tree) from nine sites were used as bioindicators of local atmospheric contamination by organochlorine pesticides and metabolites from a point source, an old storage site at Vikuge farm in Tanzania. Sample extracts were analysed by GC-ECD and GC–MS. The concentrations ranged 2.7–649 ng $g^{-1}$ *p,p′*-DDT, below detection limit (bdl)–290 ng $g^{-1}$*o,p′*-DDT, 0.4–13 ng $g^{-1}$*p,p′*-DDE, bdl to 4 ng $g^{-1}$ *o,p′*-DDE, 1–231 ng $g^{-1}$ *p,p′*-DDD and 0.5–55 ng $g^{-1}$ *o,p′*-DDD. The concentrations of other compounds were up to 3.9 ng $g^{-1}$ pentachloroanisole, 1.3 ng $g^{-1}$ α-HCH, 12 ng $g^{-1}$ β-HCH and 2 ng $g^{-1}$ γ-HCH, on fresh weight basis. The compounds *p,p′*-DDT, *p,p′*-DDE, *p,p′*DDD and *o,p′*-DDD were found in 100% of the samples, while pentachloroanisole, *o,p′*-DDT and *o,p′*-DDE were detected in 78%, 56% and 67% of the samples, respectively. The low DDE/DDT ratios (0.01–0.20) in all samples indicate recent input of significantly non-degraded DDT from the point source. The low α-/γ-HCH ratios (<0.3–0.7) in most samples indicate recent input of lindane (99% γ-HCH). The slightly high α-/γ-HCH ratios in some samples might be due to photochemical or bacterial transformation of γ-HCH to α-HCH, or could reflect input of technical HCH. The very strong positive correlations in the concentrations of *p,p′*-DDT, *p,p′*-DDE, p,p′-DDD, *o,p′*-DDT, *o,p′*-DDE and *o,p′*-DDD ($r = 0.91$–$0.98$, $n = 18$, $p < 0.01$) indicate that they have a common source. The results suggest that young mango leaves are suitable bioindicators of recent inputs of organochlorine contaminants from a point source.


*Keywords:* Organochlorine pesticides; Metabolites; Mango leaves; Tanzania

## 1. Introduction

The epicuticular wax of plant leaves, which consists mainly of long-chain polyesters, has been shown to accumulate lipophilic compounds such as organochlorine pesticides (Reischl et al., 1989; Calamari et al., 1991). At the air/plant interface, semi-volatile organic compounds may either partition into the waxy cuticle of the leaves (Riederer, 1990) or transfer from air through the stomata followed by translocation through the phloem (Barber et al., 2002). Pollutants in soil can also influence the levels in leaves of plants by means of their uptake and translocation via root systems (Lichtenstein, 1959; Cooke and Stringer, 1982). With vegetation covering more than 80% of the terrestrial portion of the earth, the analysis of vegetation samples is of great interest since contaminant levels in vegetation can be used as indicators of environmental pollution (Ockenden et al., 1998).

Mango leaves (fallen leaves at the end of their natural cycle i.e., 1–2 years) have been employed for evaluating regional distribution of lipophilic air pollutants in different African states (Bacci et al., 1988; Calamari et al., 1991; Tremolada et al., 1993). Studies on local sources, however, are limited. The concentrations of pesticide residues in mango leaves may vary depending on a number of factors including plant age, age of the sample, stage of development of the waxy cuticle in leaves, location of the leaves, density and height of the trees, physico-chemical properties

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0045-6535/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.chemosphere.2007.02.026

of the compounds (e.g., vapour pressure, water solubilities and thus the Henry's law constants) and environmental conditions (e.g., temperature, humidity, moisture content, pH, wind velocity and direction) (Paterson et al., 1994). Thus, caution must be exercised when using mango leaves as bioindicators.

In this study the suitability of young leaves of mango trees as biological indicators of the spatial distribution of pesticide residues from a point source was investigated.

## 2. Study site

In 2001, high levels of pesticide residues including DDTs and HCHs were detected in soil at an old storage site at Vikuge farm (6°47′S, 38°52′E) in Coast region, Tanzania. The levels of total DDT and total HCH were up to 282 000 mg $kg^{-1}$ dry weight (dw) and 63 400 mg $kg^{-1}$ dw, respectively (Elfvendahl et al., 2004). This pollution is attributed to collapsing of a shed in 1990, which was used for temporary storage of about 170 metric tons of pesticides donated by Greece to the Tanzanian government in 1986. The pesticides remained exposed to sunlight, wind and rain for about six years before a new store was built and the pesticides were repacked and restored in 1996. The soil at the old storage site was found to be heavily contaminated in 2001 and this prompted us to design a study with the aim of establishing the spatial distribution of pesticide residues from this point source.

## 3. Materials and methods

### 3.1. Sampling

Young leaves of mango trees (*Mangifera indica*), 1–3 months old, brown or light green in colour, were collected from nine sampling locations at increasing distances from the source along the wind direction, which blew in the S–N direction in the area and occasionally in the SE–NW direction. The samples were collected from the sites in September 2002. The first sampling point was located very close to the point source (0.2 km). Other sampling points were located at 1 km, 2 km, 3 km, 4 km, 6 km, 7 km, and 20 km, north of the source (Fig. 1). At each sampling point, four samples (20–30 leaves each) were obtained from one tree (approximately 2.5–4.5 m above the ground). The samples were wrapped in aluminium foil, placed in polyethylene bags, immediately transported to the laboratory and stored at about 5 °C for two weeks, after which they were deep frozen until extraction.

### 3.2. Chemicals

All pesticide standards were obtained from Dr. Ehrenstorfer, Augsburg, Germany, and most of them were of over 99% certified purity. Concentrations of standard solutions were corrected for the certified purity of standards if below 99%. Individual stock solutions of standard pesticides were prepared by dissolving 10–50 mg of each compound in cyclohexane and were stored in glass-stoppered flasks at −18 °C. Mixed compounds, calibration and measuring standards in cyclohexane were prepared from the stock solutions. Chromatography grade dichloromethane, *n*-hexane, acetone, cyclohexane, and ethyl acetate were purchased from Ultrafine Ltd., London. Glassware, teflon-stoppered where applicable, was washed with detergent, rinsed with distilled water followed by acetone, and then dried in an oven at 110 °C overnight prior to use.

### 3.3. Extraction and clean up

The samples were partially air-dried at 30 °C for 6 h before extraction, then minced by stainless scissors and homogenized with a commercial blender. A sub sample (10 g in each case) was put in a 250 ml stoppered flask and 50 ml mixture of *n*-hexane: dichloromethane (1:1 v/v) was added, the flask was then stoppered tightly, shaken for 5 min, and left to stand for 24 h. The solvent was decanted and a fresh solvent mixture (50 ml) added; the flask was stoppered and shaken for 5 min then let to stand for 15 min after which the solvent was decanted again. The pooled extracts were mixed vigorously and extracted in a separating funnel with 15 ml of 0.9% NaCl solution. The extract was filtered through a plug of glass wool into a flask containing anhydrous sodium sulphate (20 g) and the organic extract was reduced with a rotary evaporator operated at 30 °C, solvent reconstituted in 1 ml cyclohexane/ethylacetate (1:1 v/v) for Gel Permeation Chromatography (GPC).

The GPC clean up was performed using 50 cm × 1 cm i.d. chromatographic tube, with two adaptors, six-way valve with 1 ml sample injector loop and teflon tubing (Pharmacia no SR 10/50, Uppsala, Sweden), and eluted with 36 ml cyclohexane/ethylacetate (1:1 v/v). The GPC was calibrated using a standard solution containing 1 μg $ml^{-1}$of *p*,*p*′-DDD and *p*,*p*′-DDE (Åkerblom, 1995). Pesticides were eluted in the range 17–35 ml. During the clean up, the first fraction (0–16 ml) was discarded. The second fraction (17–36 ml) was collected and concentrated using a rotary evaporator for analysis. The column was cleaned with 20 ml cyclohexane/ethylacetate (1:1 v/v) before injection of the next sample. The solvent was evaporated using a rotary evaporator and reconstituted in cyclohexane to 2 ml for gas chromatographic (GC) analyses.

### 3.4. Gas chromatographic analyses

The gas chromatographic analyses were performed using a Varian Star 3400 gas chromatograph, equipped with SE-30 and OV-1701 columns (30 m long, 0.32 mm i.d., 0.25 μm film thickness), with $^{63}Ni$ electron capture detector at the Department of Chemistry, University of Dar es Salaam. Hydrogen was used as both a carrier and make-up gas at a flow rate of 30 ± 1 ml/min. The temperature was