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Assessment of organochlorine pesticide residues in raw food samples from open markets in two African cities

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HIGHLIGHTS

- Assessment of organochlorine pesticide residues in raw food samples from open markets in two African cities was performed.
- Quick, Easy, Cheap, Effective, Rugged and Safe (QuEChERS) method has been developed as sample preparation technique.
- Health risk estimates were calculated.

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ABSTRACT

This study investigates the level of organochlorine pesticides in the raw food from open markets in Kinshasa, Democratic Republic of Congo (DRC), and Johannesburg, South Africa. It assesses the potential health risks associated with the organochlorine pesticide residues. The Quick, Easy, Cheap, Effective, Rugged, and Safe (QuEChERS) method has been developed for sample preparation. A total of 120 food samples (beans, cabbage, beef, and fish) were obtained from the open markets. The mean concentrations of organochlorine pesticides in raw foods collected from the Johannesburg market were significantly higher ($p < 0.05$) than those from the Kinshasa market. DDE recorded the highest mean concentration (253.58 ± 4.78 μg kg^{-1}) in beef from Johannesburg, and α-BHC recorded the lowest mean concentration (38.54 ± 7.46 μg kg^{-1}) in beans from Kinshasa. The investigation of health risk estimates revealed that the number of organochlorine pesticides exceeded the reference dose in the collected food samples.

1. Introduction

The pollution of the environment and food by organochlorine pesticides is still a major issue of considerable concern in many parts of the world despite the worldwide ban of their use. This has led to many researchers investigation their occurrence, distribution and concentrations in meat, fish, fruit, vegetables and water (Lehotay et al., 2005).

Organochlorine pesticides have constantly proved their importance in agriculture. However, a number of studies have demonstrated that they have negative effects on human's health (Adeyemi et al., 2008; Nakata et al., 2002; Sverdrup et al., 2002). The organochlorine pesticides are more accumulated in the fat. They tend to stay until the fat is broken down for energy. The chlorinated organic pesticides can pass through the mother placenta to the unborn child (Nakata et al., 2002). They lead to many harmful effects such as abnormal development of the immune system, birth defects and fetal death (Ayejuyo et al., 2008). This is why organochlorine pesticides are considered as one of the main environmental and human health problems in the world (Darko and Acquaah, 2007; Doong et al., 2002).

Moreover, dichloro-diphenyl-trichloro-ethane (DDT) is an organochlorine pesticide very persistent in the environment. Its half-life is estimated for 15 years. Their metabolite products in the soil are dichloro-diphenyl-dichloro-ethane (DDD) and dichloro-diphenyl-dichloro-ethylene (DDE). They are also extremely persistent and have comparable physical and chemical properties with DDT (Guan et al., 2009). WHO and FAO have reported high levels of DDT compounds in vegetables, fish and meat eaten by many people in Africa (FAO/WHO, 2010). DDT can cause immunosuppression, reproductive effects, shortened duration of lactation, neurological and behavioral effects. DDE can modulate immune responses in exposed children (Martinez et al., 1997; Lehotay et al., 2005).

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Due to problems related with organochlorine pesticides, many nations and international organizations such as UNEP, WHO and EU have recognized these pollutants as a major risk for health and particularly for children's health (European Commission, 2009; FAO/WHO, 2010). Monitoring of pollutants levels in food helps to prevent a potential catastrophic situation that might occur from ignorant consumption of polluted food (FAO/WHO, 2010).

South Africa has a number of provinces with a diverse environment. However, the majority of the country has summer rainfall, and the south western coastal region is predominantly a winter rainfall area. These variations in climate allows for a large variety of crop. Each individual crop is susceptible to a unique host of pests that in-turn require a unique mixture of pesticides to ensure the best resulting turnover. Currently, more than 500 pesticides have been registered in South Africa (PAN, 2010) though use of organochlorine pesticides has been banned except in malaria risk areas where controlled use is allowed (Ayejuyo et al., 2008). Fatoki and Awofolu (2002) reported that South Africa is one the four largest importers of pesticides in Sub-Saharan Africa. These pesticides are used in almost every facet of our everyday lives; ensuring the quantity and quality of food. Although it is evident that there is a vast amount of pesticides present in the South African environment, there are very limited data on the occurrence, distribution and fate in food samples.

In the Democratic Republic of Congo (DRC) as in most developing countries, pesticides have been used for many decades in agricultural practices, for instance in the cultivation of vegetables. Successive wars in the country since 1994 have disorganized the Regulatory Agencies so that, the ministries responsible for Health, Environment, Nature Conservation and Agriculture are not able to control the use of pesticides in the whole country. No monitoring is done in the sense of assessing the daily intake of pesticides in different foods. DRC is a signatory to many protocols, international regulations and acts dealing with environment and pesticides, but has not yet initiated policies for controlling and assessing pesticides in the environment and in human and animal food and feed (FAO/WHO, 2010).

The present study was conducted to determine the level of seventeen organochlorine pesticides in beans, beef, fish (tilapia) and cabbage purchased in Johannesburg (South Africa) and Kinshasa (Democratic Republic of Congo) open markets and to assess the health risk associated with people who eats such food. In South Africa, the study of organochlorine pesticides has so far focused on the environmental compartments, especially aquatic systems (Fatoki and Awofolu, 2002). On the other hand, very few studies have been performed on these compounds in various environmental compartments in the Democratic Republic of Congo.

2. Materials and methods

2.1. Materials and reagents

A mixture of seventeen analytical grade organochlorine pesticides constituted of α − BHC, β −BHC, γ− BHC, δ − BHC, heptachlor, heptachlor epoxide, aldrin,, endrin, endrin aldehyde, dieldrin, endosulfan I, endosulfan II, endosulfan sulphate, 4,4′- DDT, 4,4′ − DDD, 4,4′ − DDE and methoxychlor were purchased from Sigma−Aldrich, South Africa. The purity of the standard was 95%. The stock solutions of 5 mg L^{-1} were prepared in hexane/toluene (50/50) mixture and stored in freezer at 4 °C. The working solutions of different concentrations were prepared daily by dilution of the stock solution with the same solvent mixture. The concentration of 1, 5 and 10 μg L^{-1} were used as working solution for calibration Hexane and toluene used was of analytical grade from Merck (Johannesburg South Africa). Acetonitrile, magnesium sulphate monohydrate, sodium chloride and bondesil primary/secondary amine (PSA) were from Sigma−Aldrich (Johannesburg South Africa). Anhydrous sodium sulphate was from Merck (Johannesburg, South Africa). The analysis was carried out by GC 7890A (Agilent Technologies, DE, USA) equipped with flame ionization detector (FID) and electron capture detector (ECD) and GCxGC/TOFMS, 7890B (LECO Corp., St Joseph, MI, USA) with a 7683 series injector (Agilent Technologies, DE, USA).

2.2. Sampling

120 food samples constituted of beans, cabbage, beef and fish (tilapia) were purchased in Kinshasa (60 samples) and Johannesburg (60 samples) open markets from July till October 2015.

In Kinshasa, the food samples were purchased in the biggest urban open market. In this market, foods are sold on the floor without any hygienic condition and in some areas near the high traffic road. All the food samples were kept in closed polypropylene plastic boxes in refrigerator (- 4 °C) at the University of Kinshasa before being send by courier to South Africa.

In Johannesburg, the food samples were purchased in Johannesburg town market from individual vendors. Concerning the vegetables (cabbage, beans) and beef, the sources were not clarified. The tilapia fish bought were from Mpumalanga province. All the food samples were kept in closed polypropylene plastic boxes in refrigerator (- 4 °C) at the University of the Witwatersrand, Johannesburg.

2.3. QuEChERS extraction method

The QuEChERS extraction method was done using the modified procedure reported by Rawn et al. (2010). Homogenized samples with no pesticides detected on previous occasions were used for recovery studies, and for the preparation of matrix-matched standards for calibration. The homogenised samples were spiked with 1, 5 and 10 μg L^{-1} of a standard mixture of seventeen organochlorines. The spiked samples were allowed to stand for 30 min. Ten grams of homogenized food sample was put in a 50 ml Teflon tube. Then 10 ml of acetonitrile was added and the sample was shaken strongly for 1 min. This was followed by salting-out step with additions 1.5 g sodium chloride and 3 g of anhydrous magnesium sulphate into the tube and the mixture was shaken vigorously for 1 min and then centrifuged. After centrifuge, 6.5 ml of organic supernatant was transferred into the polypropylene centrifuge tube to clean-up with 1.65 g anhydrous magnesium sulphate and 27.5 g primary/secondary amine (PSA). The solution was centrifuged for 5 min and filtered using a 0.45 μm PTFE and injected in the GC −ECD and/or GCxGC/TOFMS for analysis. The GCxGC/TOFMS was used to confirm the identification of compounds in samples.

2.4. GC- ECD conditions

The GC conditions and the detector response were adjusted so as to match the relative retention times and response. The conditions used for the analysis were: capillary column coated with ZB-5 (30 m × 0.25 mm, 0.25 μm film thickness). Nitrogen (99.999%) was used as carrier gas flowing at 1.2 ml min^{-1}. The oven temperature was programmed from 60 °C (1 min) to 180 °C at a rate of 30 °C min^{-1}, 180 °C (3 min) to 300 °C at a rate of 3 °C min^{-1}. The temperature of the injector operating in split less mode (volume injected 1 ml) was held a 300 °C and electron-capture detector temperature was 250 °C. Fig. 1 shows a separation of organochlorine pesticides in beef and cabbage samples.