Chemosphere 164 (2016) 480–487

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

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

Yannick Nuapia, Luke Chimuka, Ewa Cukrowska*

Molecular Sciences Institute, School of Chemistry, University of the Witwatersrand, Private Bag 3, 2050, Johannesburg, South Africa

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.

ARTICLE INFO

Article history:
Received 16 May 2016
Received in revised form
10 August 2016
Accepted 11 August 2016

Handling Editor: J. de Boer

Keywords:
Organochlorine pesticides
Kinshasa
Johannesburg
Health risk

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).

* Corresponding author.
E-mail address: Ewa.Cukrowska@wits.ac.za (E. Cukrowska).

http://dx.doi.org/10.1016/j.chemosphere.2016.08.055
0045-6535/

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.

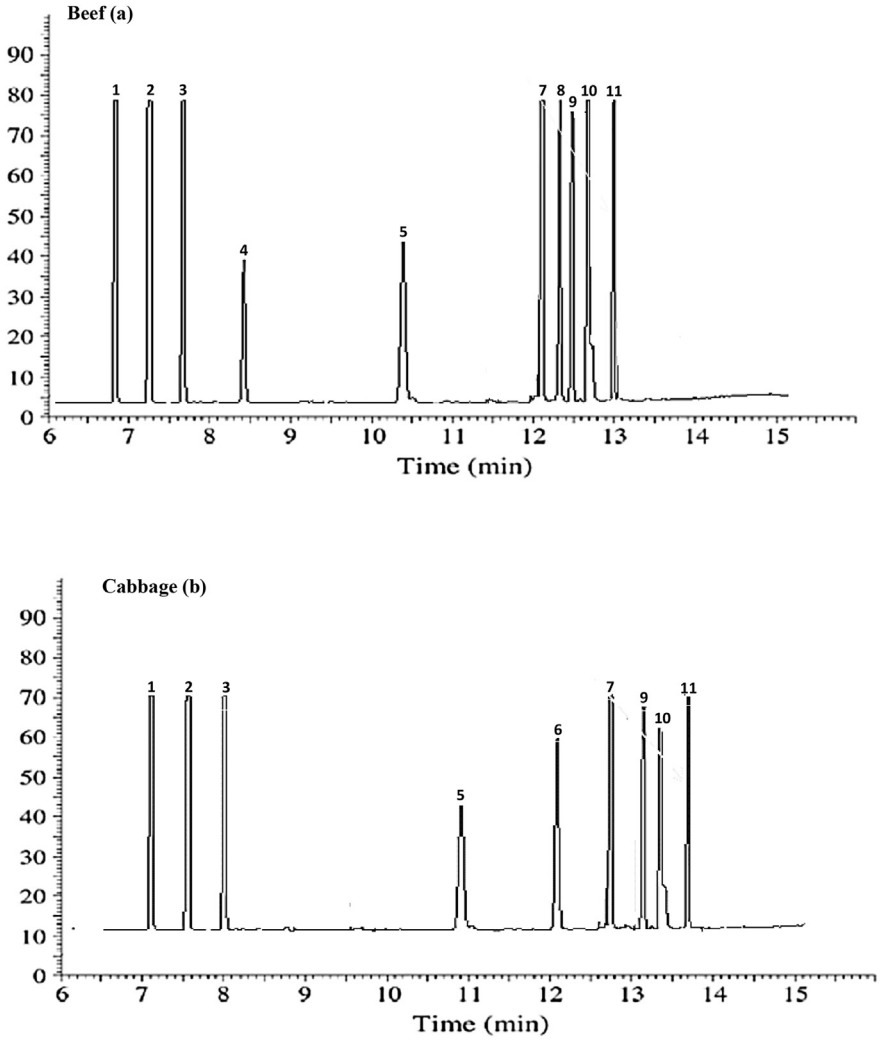

Fig. 1. GC–ECD chromatogram of organochlorine pesticides in beef (a) and cabbage (b) samples. The target compounds: (1) α − BHC, (2) γ − BHC, (3) β -BHC, (4) Heptachlor, (5) Aldrin, (6) Heptachlor epoxide, (7) 4,4′ − DDE, (8) Dieldrin, (9) Endrin, (10) 4,4′ − DDD, (11) 4,4′- DDT.

2.5. GCxGC/TOFMS conditions

The conditions of the mass spectrometer were as follows: transfer line temperature 290 °C; ion source temperature 250 °C and multiplier voltage 1450 V. A programmed temperature vaporization injector operating in solvent-split mode was employed. The volume injected was 9 μl, split flow 50 ml min^{-1} and injection time: 0.50 min, injection flow: 100 ml min^{-1}. The oven temperature program was as follows: initial temperature of 50 °C increased to 150 °C at 10 °C min^{-1} followed by an increase to 300 °C at a rate of 5 °C min^{-1}. He was used as carrier gas flow rate of 1 ml min^{-1}. Ion trap mass detection was operated in full scan mode from 50 to 500 amu.

2.6. Health risk estimation

Health risk estimations were done based on an integration of organochlorine pesticide analysis results and exposure assumptions. The following assumptions were made based on the U.S Environmental Protection Agency's guidelines (USEPA, 1996): hypothetical body weights of 10 kg for children (most vulnerable group), maximum absorption rate of 100% and bioavailability rate of 100%. Food consumption rate for vegetables, meat and fish in South Africa are 235, 77.9 and 20.9 g/person/day, respectively (Vorster et al., 2013). In DRC, the food consumption rate for vegetables, meat and fish are 120, 59.9 and 89.9 g/person/day, respectively. (Yamaguchi, 2015). The estimated lifetime exposure dose (mg/kg/day) for each type of exposure was obtained by multiplying the residual pesticide concentration determined (mg kg^{-1}) in the food of interest by the food consumption rate (kg day^{-1}), and dividing the product by the body weight (kg). The hazard indices to children were estimated as ratios between estimated pesticide exposure doses, and the reference doses which are considered to be safe levels of exposure over the lifetime. If the hazard indices are less than 1, there is not risk associated with the organochlorine pesticides detected in the food samples.

2.7. Statistical analysis and validation of method

Descriptive analysis of data was performed using Minitab 16 Software with level of significance maintained at 95%. The percentage (%) recoveries together with limit of detection (LOD) and limit of quantification (LOQ) were also determined.

3. Results and discussion

3.1. Quality assurance

Beans, cabbage, meat and fish samples were fortified with concentration of 1, 5 and 10 μg L^{-1} of a mixed standard solution. Recovery and standard deviation were calculated in triplicate for all the samples and the data are presented in Table 1. For the analysis of pesticide residues at μg kg^{-1} levels, accuracy and recovery of 70–120% is considered acceptable (Gonzalvez et al., 2008). The method is applicable for the determination of seventeen organochlorine pesticides in food samples. Percent recoveries in spiked samples ranged from 80.2 to 89.9% for cabbage; 80.1–103.1% for beef; 80.2–92.4% for fish. The sensitivity of the method is expressed by limit of detection (LOD), limit of quantification (LOQ) and linearity (R^2) (Table 2). LOD of the method were assessed based on the lowest concentrations of the residues in each of the matrices that could be reproducibly measured at the operating conditions of the GC- ECD. The limit of quantification (LOQ) was ten times of LOD. The precision values for the method was expressed as percentage relative standard deviation (RSD, n = 3) and linearity (R^2). Blank analyses were also carried out in order to check any interfering species in the reagents.

3.2. Levels of organochlorine pesticides in raw food

3.2.1. Kinshasa open market

The following organochlorine pesticides: BHC group and the DDT group were identified in food samples purchased in Kinshasa (Fig. 2).

The means levels of α − BHC in the food samples ranged from 38.54 ± 7.46 in beans to 102.28 ± 10.11 in beef. β-BHC was not detected in all the food samples from Kinshasa open market. The results also showed that the mean concentrations of γ − BHC (lindane) were between 40.83 ± 5.67 μg kg^{-1} in beans and 103.28 ± 8.93 μg kg^{-1} in beef. Lindane is a reasonably stable compound and only under alkaline condition decomposes to yield trichlorobenzene. It is considered as one of the less persistent organochlorine pesticides. The high concentration level (103.28 ± 8.93 μg kg^{-1}) of lindane in beef obtained from the analysis could be connected with the extensive use of technical lindane and used by some farmers for agricultural purposes for crop protection in DRC. The level of lindane detected in the present investigation was lower than the mean concentration level of 200 and 400 μg kg^{-1} reported in Nigeria and India markets respectively (Adeyemi et al., 2008; Bhanti and Taneja, 2005). This further suggested that lindane is extensively used in DRC agricultural sector.

The concentration levels of DDT varied from 63.72 ± 7.82 μg kg^{-1} in fish and 145.12 ± 6.71 μg kg^{-1} in beef. The mean concentrations of DDD ranged to 49.50 ± 3.51 μg kg^{-1} in beans and 97.65 ± 1.67 μg kg^{-1} in beef. Mean concentrations of DDE ranged from 56.57 ± 8.93 μg kg^{-1} in beans and 154.15 ± 4.34 μg kg^{-1} in beef. The high concentration of organochlorine pesticides in meat could be due to the presence of the lipid tissue where these compounds bioconcentrate.

The levels of DDT detected in this work were higher than those found in the similar study done in Ghana (Essumang et al., 2009), (Table 3). This study reported the levels of DDT in food sold from Ghana markets with concentration between 15.67 and 49.42 μg kg^{-1}. Mwevura et al. (2002) reported lower concentration of organochlorine pesticide residues of 4, 4′-DDT (23.02 μg kg^{-1}) and 4, 4′-DDE (15.67 μg kg^{-1}) in food samples from Dar es Salaam markets. The levels of BHC group and DDT group found in the food samples from Kinshasa were above the permissible limit set by FAO/WHO (2012).

3.2.2. Johannesburg open market

The mean levels of organochlorine pesticide residues in the food samples from Johannesburg are summarized in Fig. 2. The mean levels of DDT and its metabolites, α − BHC and γ − BHC were higher than in Kinshasa samples. The mean concentrations of DDT were detected in the range of 109.67 ± 6.92 μg kg^{-1} in beans to 167.89 μg kg^{-1} in beef. The mean level of DDE was detected lower in bean (99.67 ± 7.41 μg kg^{-1}) and higher in beef (253.58 ± 6.23 μg kg^{-1}). In overall, the concentrations of pesticides in the food samples were in the following sequence: beef > fish > cabbage > beans.

The results of the present investigation are comparable with other studies done in the world (Table 3). For example, Darko and Acquaah (2007) found that the levels of organochlorine pesticide residues in meat from Kumasi and Buoho abattoirs were higher than the maximum limits set by FAO/WHO. Adeyemi et al. (2008) found that residue levels of organochlorine pesticide residues in food from Lagos markets were generally above the FAO/WHO maximum residue limits. In a comparable study, Usman et al.

Table 1
Analytical recoveries (%) ±SD of 17 organochlorine pesticides in food samples at 1, 5, and 10 μg kg^{-1} fortification levels (n = 3) in GC–ECD.

Analytical recoveries (%) ± SD at different fortification levels (μg kg^{-1})									
Compounds	Cabbage			Beef			Fish		
	1 μg kg^{-1}	5 μg kg^{-1}	10 μg kg^{-1}	1 μg kg^{-1}	5 μg kg^{-1}	10 μg kg^{-1}	1 μg kg^{-1}	5 μg kg^{-1}	10 μg kg^{-1}
α-BHC	82.7 ± 0.42	83.4 ± 0.43	84.4 ± 0.17	82.8 ± 0.19	82.8 ± 0.17	81.3 ± 0.25	83.8 ± 0.19	83.7 ± 0.15	84.6 ± 0.25
γ-BHC	81.8 ± 0.18	81.1 ± 0.55	80.8 ± 0.13	81.9 ± 0.15	81.6 ± 0.17	82.7 ± 0.21	82.8 ± 0.14	82.7 ± 0.21	80.8 ± 0.10
β-BHC	81.3 ± 0.55	80.6 ± 0.23	81.6 ± 0.28	80.9 ± 0.08	80.8 ± 0.21	81.6 ± 0.15	80.1 ± 0.16	80.1 ± 0.10	81.8 ± 0.23
Heptachlor	85.8 ± 0.17	85.3 ± 0.28	87.8 ± 0.17	85.6 ± 0.31	85.5 ± 0,19	80.4 ± 0.11	86.7 ± 0.23	86.7 ± 0.19	87.6 ± 0.08
δ-BHC	81.9 ± 0.08	81.5 ± 0.27	82.1 ± 0.56	80.7 ± 0.15	80.7 ± 0.27	80.3 ± 0.27	81.9 ± 0.13	81.8 ± 0.32	81.5 ± 0.08
Aldrin	80.9 ± 0.05	80.7 ± 0.18	80.9 ± 0.63	81.8 ± 0.20	81.9 ± 0.23	84.5 ± 0.15	83.5 ± 0.05	83.5 ± 0.34	80.7 ± 0.18
Heptachlor epoxide	87.9 ± 0.08	87.5 ± 0.38	88.7 ± 0.21	87.2 ± 0.20	87.2 ± 0.11	80.7 ± 0.21	86.7 ± 0.29	86.6 ± 0.28	88.6 ± 0.08
Endosulfan	81.3 ± 0.56	80.9 ± 0.06	80.7 ± 0.26	80.8 ± 0.21	80.7 ± 0.25	83.7 ± 0.15	82.2 ± 0.12	82.1 ± 0.06	80.4 ± 0.09
4,4′ DDE	85.8 ± 0.08	85.5 ± 0.09	84.8 ± 0.17	84.4 ± 0.12	84.5 ± 0.20	81.8 ± 0.15	85.2 ± 0.17	85.3 ± 0.09	84.8 ± 0.80
Endrin	81.8 ± 0.13	81.8 ± 0.06	81.2 ± 0.19	82.2 ± 0.17	82.2 ± 0.11	80.8 ± 0.18	80.2 ± 0.17	80.3 ± 0.26	81.1 ± 0.06
Dieldrin	89.9 ± 0.57	89.8 ± 0.29	88.8 ± 0.16	86.3 ± 0.14	86.1 ± 0.09	83.7 ± 0.15	85.8 ± 0.25	85.9 ± 0.16	88.8 ± 0.16
4,4' − DDD′	83.6 ± 0.42	83.8 ± 0.15	82.2 ± 0.18	103.1 ± 0.11	83.2 ± 0.15	81.8 ± 0.23	82.7 ± 0.28	82.5 ± 0.19	82.4 ± 0.09
Endosulfan II	82.7 ± 0.13	82.6 ± 0.15	84.2 ± 0.13	84.7 ± 0.35	84.8 ± 0.09	87.6 ± 0.08	83.8 ± 0.21	83.7 ± 0.15	84.2 ± 0.53
4,4′ DDT	82.5 ± 0.18	82.4 ± 0.06	80.2 ± 0.13	80.1 ± 0.10	80.1 ± 0.12	81.5 ± 0.08	92.4 ± 0.11	82.4 ± 0.15	80.2 ± 0.09
Endrin aldehyde	80.7 ± 0.22	80.6 ± 0.12	81.9 ± 0.22	80.5 ± 0.17	80.7 ± 0.15	80.7 ± 0.18	80.3 ± 0.27	80.4 ± 0.21	81.6 ± 0.09
Endosulfan sulphate	87.8 ± 0.17	87.5 ± 0.11	85.8 ± 0.17	86.6 ± 0.36	86.4 ± 0.11	84.8 ± 0.80	87.8 ± 0.17	87.7 ± 0.29	85.6 ± 0.21
Methoxylchlor	82.7 ± 0.26	82.4 ± 0.09	87.6 ± 0.34	82.3 ± 0.14	82.4 ± 0.25	81.1 ± 0.06	84.9 ± 0.12	84.7 ± 0.20	87.3 ± 0.12

Table 2
Limit of detection (LOD in μg kg^{-1}), limit of Quantification (LOQ in μg kg^{-1}), RSD (%), and linearity (R^2).

Analyte	Beans				Cabbage				Beef				Fish			
	LOD	LOQ	R^2	RSD	LOD	LOQ	R^2	RSD	LOD	LOQ	R^2	RSD	LOD	LOQ	R^2	RSD
α-BHC	1.49	15.01	0.9992	3.5	2.96	29.80	0.9993	2.67	1.29	12.90	0.9997	1.56	1.87	18.70	0.9998	3.86
γ-BHC	1.90	18.90	0.9998	4.9	3.56	35.60	0.9994	3.95	1.98	19.80	0.9992	2.89	5.78	57.80	0.9991	1.23
β-BHC	2.89	29.00	0.9996	2.4	2.97	29.90	0.9991	4.81	7.89	75.90	0.9994	4.12	3.92	39.20	0.9993	4.71
Heptachlor	1.37	14.01	0.9993	1.5	3.04	30.60	0.9992	4.90	2.35	23.50	0.9998	3.91	4.56	45.60	0.9996	3.21
δ-BHC	3.89	38.90	0.9995	3.1	10.89	108.9	0.9997	3.91	5.34	53.40	0.9996	4.18	4.12	41.20	0.9993	2.18
Aldrin	1.90	20.01	0.9998	3.2	1.34	13.40	0.9991	4.21	4.23	42.30	0.9993	3.29	2.39	23.90	0.9995	2.91
Heptachlor epoxide	2.90	28.87	0.9992	4.7	2.99	30.10	0.9993	4.13	3.18	31.80	0.9991	2.23	3.45	34.50	0.9998	3.67
Endosulfan	4.34	43.40	0.9993	4.3	1.08	10.90	0.9991	3.71	3.19	31.90	0.9996	2.71	4.56	45.60	0.9992	3.17
4,4′-DDE	2.81	28.10	0.9995	2.8	1.45	14.50	0.9993	2.82	2.89	28.90	0.9998	1.98	1.81	18.10	0.9992	2.48
Endrin	3.45	34.60	0.9994	4.9	1.90	19.00	0.9998	4.91	3.41	34.10	0.9991	3.81	0.45	4.50	0.9997	3.29
Dieldrin	2.91	29.10	0.9991	3.4	3.83	38.30	0.9992	3.45	1.08	10.80	0.9993	4.76	0.25	2.51	0.9994	4.23
4,4′-DDD	2.05	20.50	0.9991	3.8	3.81	38.10	0.9997	3.21	1.34	13.40	0.9996	4.56	6.73	67.40	0.9995	2.56
Endosulfan II	12.89	128.90	0.9992	3.7	4.53	45.30	0.9994	3.19	10.89	108.90	0.9995	3.92	7.92	79.23	0.9996	3.75
4,4′-DDT	8.02	80.20	0.9994	2.9	3.71	37.10	0.9995	4.22	7.91	79.10	0.9993	3.22	1.90	19.00	0.9993	1.79
Endrin aldehyde	7.82	78.20	0.9995	2.2	2.94	29.40	0.9996	4.83	19.29	193.01	0.9991	3.79	5.93	59.30	0.9995	3.41
Endosulfan sulphate	8.67	86.70	0.9997	1.9	3.29	32.90	0.9992	3.81	4.56	45.60	0.9992	3.22	6.41	64.10	0.9998	2.31
Methoxychlor	9.01	90.10	0.9991	3.1	13.97	140.01	0.9994	2.84	2.19	22.03	0.9994	2.59	3.21	32.10	0.9997	3.64

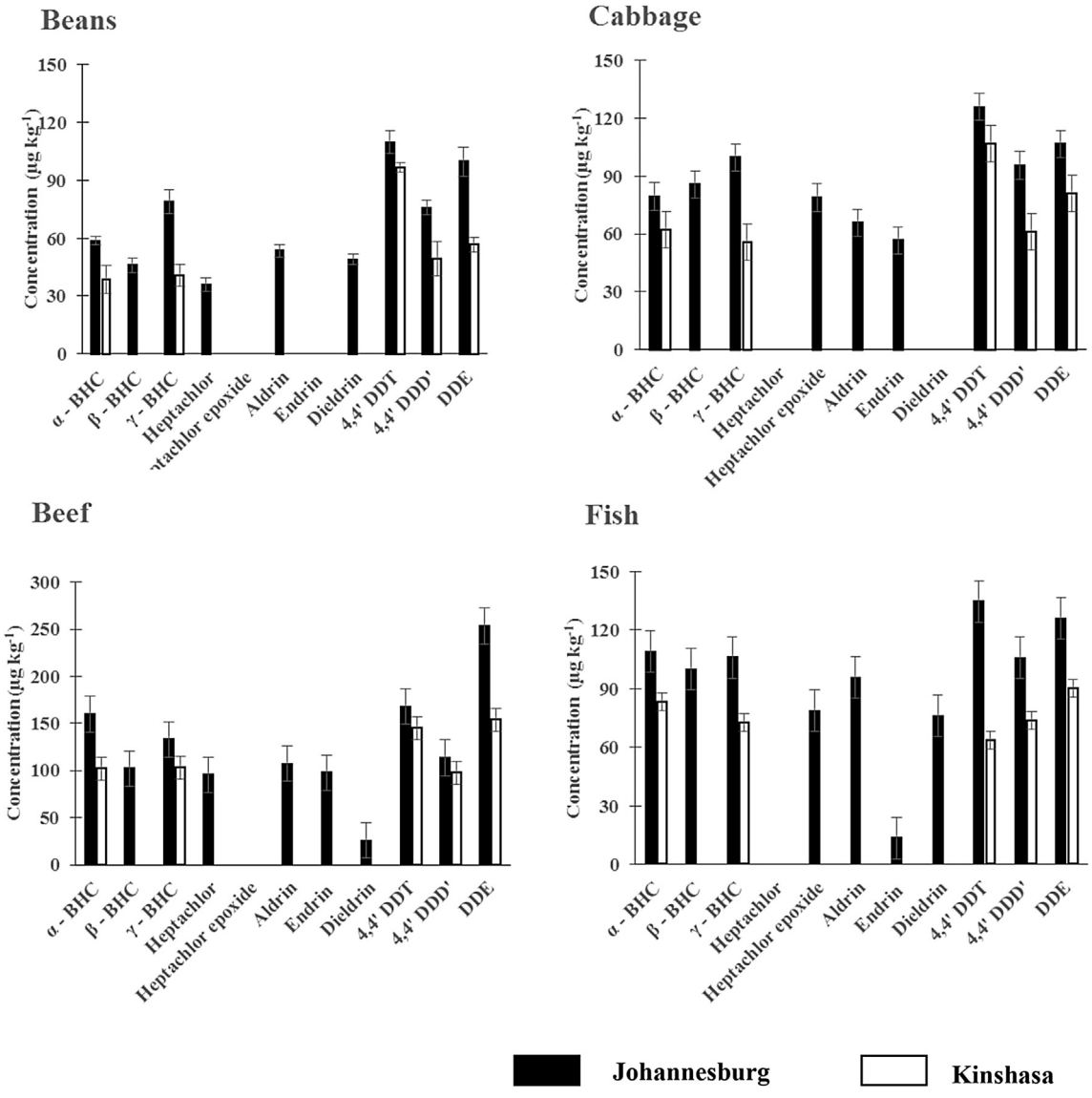

Fig. 2. Comparative levels of organochlorine pesticides in foods purchased in Kinshasa and Johannesburg.

Table 3
Concentration of organochlorine pesticides in food in this study and other countries together with FAO/WHO MRLs (μg kg^{-1}) limits.

	Johannesburg (South Africa) this study				Kinshasa (DRC) this study			
	Beans	Cabbage	Beef	Fish	Beans	Cabbage	Beef	Fish
α-BHC	58.53 ± 2.10	79.51 ± 4.10	159.74 ± 9.50	108.95 ± 7.60	38.54 ± 7.46	62.06 ± 13.16	102.28 ± 10.11	83.19 ± 9.86
β-BHC	45.83 ± 6.50	85.76 ± 3.80	101.97 ± 7.20	99.76 ± 5.70	Nd	Nd	Nd	Nd
γ-BHC	78.95 ± 6.23	99.67 ± 3.20	132.82 ± 8.12	105.78 ± 5.20	40.83 ± 5.67	56.05 ± 4.23	103.28 ± 8.93	72.53 ± 6.83
Heptachlor	35.78 ± 3.40	Nd	95.62 ± 2.70	Nd	Nd	Nd	Nd	Nd
Heptachlor epoxide	Nd	78.93 ± 8.10	Nd	78.56 ± 5.20	Nd	Nd	Nd	Nd
Aldrin	53.45 ± 3.20	65.89 ± 4.20	107.45 ± 5.90	95.45 ± 5.60	Nd	Nd	Nd	Nd
Endrin	Nd	56.78 ± 7.30	97.94 ± 3.80	13.49 ± 1.20	Nd	Nd	Nd	Nd
Dieldrin	48.85 ± 2.70	Nd	25.89 ± 2.30	75.78 ± 3.60	Nd	Nd	Nd	Nd
4,4′-DDT	109.67 ± 6.92	125.87 ± 5.90	167.89 ± 1.50	134.57 ± 5.20	96.70 ± 2.34	106.93 ± 2.91	145.12 ± 6.71	63.72 ± 7.82
4,4′-DDD	75.76 ± 3.74	95.67 ± 2.10	113.64 ± 2.91	105.74 ± 4.20	49.50 ± 3.51	61.05 ± 2.15	97.65 ± 1.67	73.52 ± 5.67
4,4′-DDE	99.67 ± 7.41	106.65 ± 5.60	253.58 ± 4.78	125.78 ± 7.20	56.57 ± 8.93	81.05 ± 7.23	154.15 ± 4.34	90.09 ± 3.82

ND: Not detected.
[a] Darko and Acquaah (2007).
[b] Adeyemi et al. (2008).
[c] Usman et al. (2009).
[d] Amoah et al. (2006).
[e] FAO/WHO (2012).

(2009) reported that all the marketed vegetables samples from Lahore, Pakistan had higher levels of organochlorine pesticides than the maximum residue limit (MRL) set by FAO/WHO. The results of the study showed lower concentration than those found in vegetables from Ghana markets (Amoah et al., 2006) which exceeded the MRLs for consumption. In a similar study by Odhiambo et al. (2009), the organochlorine residues detected in vegetables sold in Lagos exceeded Chinese maximum Residues Limit of 50 μg kg^{-1} for DDT in vegetables.

3.2.3. Comparison of mean levels of organochlorine pesticides in food from open markets in Kinshasa and Johannesburg

Pesticide concentrations in all samples from Johannesburg are significantly higher ($p < 0.05$) than those from Kinshasa (Fig. 2). In both countries, meat samples contained a higher concentration of organochlorine pesticides compared to other food samples. DDT was detected in the range of 96.70 ± 2.34 to 106.93 ± 2.91 μg kg^{-1} in Kinshasa and 75.76 ± 3.74 to 113.64 ± 2.91 μg kg^{-1} in Johannesburg. DDE was detected in the range of 56.57 ± 8.93 to 154.15 ± 4.34 μg kg^{-1} in Kinshasa and 99.67 ± 7.41 to 253.58 ± 6.23 μg kg^{-1} in Johannesburg. The various food sold in Johannesburg were more concentrated with DDT and its metabolites than the food collected in Kinshasa. It was reported in the literature that in South Africa and DRC, pesticides are crucial not only in the agricultural setting but also in the management of disease vectors (Osibanjo et al., 2002). Malaria is the only disease currently treated using DDT in South Africa and it is in a controlled manner (PAN, 2010). The past use of DDT in agriculture and perhaps to a lesser extent in malaria control could explain the presence of DDT and its metabolites (p, p′-DDD and p, p′-DDE) in food samples analyzed from Kinshasa and Johannesburg. In DRC some of the organochlorine pesticides could be used.

The mean level of ɤ-BHC was detected in the range of 40.83 ± 5.67 to 103.28 ± 8.93 μg kg^{-1} in Kinshasa and 78.95 ± 6.23 to 132.82 ± 8.12 μg kg^{-1} in Johannesburg. Lindane was commonly used in the treatment of seed, livestock and as a household biocide although relatively little literature has been published on the use and production of these chemicals in South Africa and DRC. Heptachlor, heptachlor epoxide and aldrin, endrin, dieldrin were detected only in the food samples collected in Johannesburg. The higher level of organochlorine pesticides in food from Johannesburg can be due to the fact that pesticides were extensively used in the past in South Africa compared to their use in Kinshasa. The pesticides residues tend to accumulate in the environment and further transfer in the food chain.

Metabolites of some organochlorine pesticides such as DDT have different concentration ratios in the environment, thereby indicating different contamination sources. Specific ratios of parent/metabolites of organochlorine pesticides compounds have been widely used to identify past and present input application into the environment (Walker et al., 1999).

DDE and DDD are metabolites of DDT formed by degradation under aerobic and anaerobic conditions, respectively. The ratio of concentration of the parent DDT to its metabolites is used as indices for assessing the possible pollution sources (Doong et al., 2002). If the ratio of DDT/DDE is found to be more than 1, then it indicates recent used of DDT compounds while DDE/DDT <1 indicates no fresh application of DDT. In Kinshasa, the ratio of DDT/DDE was more than 1 in beef (1.06) and fish (1.41) indicating that DDT was used in past. The ratio of DDE/DDT was less than one in beans (0.58) and cabbage (0.75), indicating recent input of DDT in the area where the vegetables growing.

In Johannesburg, the ratio of DDE/DDT was >1 in beef (1.51) showing a dominance of past use of DDT in the area where the beef came from. The ratio of DDE/DDT was <1 in beans (0.91), cabbage (0.84) and fish (0.93), that indicating fresh application of DDT in the area where the samples came from.

Similar trends were observed for heptachlor and its metabolite heptachlor epoxide as well as aldrin and its metabolites dieldrin and endrin. Their presence, concentration ratios strongly depend on the foods source, time since pesticide application, and speed of oxidation.

3.3. Tolerance limit

The levels of organochlorine pesticides legally allowed in food are called Maximum Residue Limits (MRLs). The concentration of organochlorine pesticides obtained in various food samples were compared with MRLs set by the various international agencies such as Food and Agricultural Organisation/World Health Organisation (FAO/WHO, 2012). On comparing our results with FAO/WHO (2012) guidelines, all the samples were found to be contaminated and exceeded the limit for BHC group and DDT group. Besides this, the concentration of aldrin, endrin and dieldrin in the food samples were within FAO/WHO (2012) standards (Table 3).

The higher organochlorine pesticide levels in the food samples

Kumasi (Ghana)[a]	Lagos (Nigeria)[b]		Lahore (Pakistan)[c]		ACCRA (Ghana)[d]		FAO/WHO[e] (2012)
Beef	Fish	Beef	Beans	Cabbage	Beans	Cabbage	
152.98 ± 3.00	145.67 ± 3.40	167.89 ± 3.20	42.34 ± 1.2	34.56 ± 1.40	208.45 ± 2.00	309.23 ± 2.10	10
34.51 ± 1.00	–	106.45 ± 2.10	79.00 ± 3.4	80.23 ± 2.00	213.45 ± 1.80	307.56 ± 1.60	10
124.23 ± 1.00	200.00 ± 1.30	145.34 ± 1.20	71.83 ± 2.30	96.45 ± 1.60	234.56 ± 1.3	324.52 ± 1.3	10
–	–	–	12.34 ± 3.20	–	–	–	–
–	–	–	–	–	–	–	–
–	–	–	–	–	–	–	100
–	–	–	–	–	–	–	100
–	–	–	–	–	–	–	100
190 ± 2.30	197.89 ± 1.20	206.34 ± 1.20	71.78 ± 1.90	98.32 ± 1.30	456.89 ± 1.20	506.78 ± 4.50	50
102.01 ± 2.30	98.78 ± 1.9	89.90 ± 2.1	67.81 ± 6.50	71.23 ± 3.40	310.45 ± 2.80	326.78 ± 1.20	50
109.45 ± 2.30	138.41 ± 1.2	120.34 ± 2.30	92.12 ± 2.1	79.03 ± 2.80	356.23 ± 1.90	389.34 ± 2.90	50

could be due to their continued application as pest control. Regular consumption of these foods with even modest contamination can cause health problems in the future. Therefore, the risk associated with the dietary intake of organochlorine pesticides through food consumption was calculated.

3.4. Health risk estimates

From the obtained concentrations of organochlorine pesticides, dietary exposure and health risks were calculated for children. A recent study by Bempah et al. (2011) has reported that children are the most vulnerable population subgroup and susceptible to non-cancer risk caused by organochlorine pesticide compounds. The estimated daily intake and health risk index (HI) were calculated for each chemical contaminant and are summarized in Table 4. In Johannesburg, the non-cancerous risk estimates revealed that total HI ($\sum$HI) values for α-BHC, γ-BHC and DDT were greater than 1 while the value of 1 was found for β-BHC. The total HI values for heptachlor, heptachlor epoxide, aldrin, endrin and dieldrin were all less than one ($\sum$HI < 1). In Kinshasa, the total HI values were more than one for DDT and less than one for α-BHC and γ-BHC. Akoto et al. (2013) demonstrated that total HI values in Ejura region of Ghana were greater than one for heptachlor, aldrin, endrin and dieldrin. However, in the Giza Governorate region of Egypt and Al-Qassim region of Saudi Arabia, total HI values were found to be below one and none of the food samples sold in the markets posed health risks to consumers (Mansour et al., 2009; Osman et al., 2011). Adeyemi et al. (2008) have found the Hazards risk lower than 1 in the vegetables, meat and fish sold in Nigeria open markets. In comparison with other countries, the level of DDT and its metabolities in beans and cabbage were comparable to the level of DDT group compounds found in beans and cabbage sold in Gambia and Senegal (Manirakiza et al., 2003). The level of DDT group found in beef in the presented study were lower than found in beef in Agra, India (Bhanti and Taneja, 2005). In view of the above, it can be presumed that consumption of these foods can cause potential health hazard to α-BHC, γ-BHC and DDT in Johannesburg. In Kinshasa, DDT is the only organochlorine that poses the health risk. To

Table 4
Estimated dose (mg day^{-1} kg^{-1}), reference dose (mg day^{-1} kg^{-1})[a], and health risk index (HI) of food collected in Johannesburg and Kinshasa markets.

	Vegetables			Beef			Fish			∑HI
	Reference dose	Estimated dose	HI	Reference dose	Estimated dose	HI	Reference dose	Estimated dose	HI	
Johannesburg										
α-BHC	0.005	0.0016	0.320	0.005	0.0035	0.700	0.005	0.0011	0.220	1.240
β-BHC	0.005	0.0015	0.300	0.005	0.0022	0.440	0.005	0.0013	0.260	1.000
γ-BHC	0.005	0.0021	0.420	0.005	0.0029	0.580	0.005	0.0019	0.380	1.380
Heptachlor	0.005	0.0004	0.080	0.005	0.0021	0.420	0.005	Nd	Nd	0.500
Heptachlor epoxide	0.005	0.0009	0.180	0.005	Nd	Nd	0.005	0.0008	0.160	0.340
Aldrin	0.005	0.0014	0.280	0.005	0.0023	0.460	0.005	0.0010	0.200	0.940
Endrin	0.005	0.0007	0.140	0.005	0.0021	0.420	0.005	0.0001	0.020	0.580
Dieldrin	0.005	0.0006	0.120	0.005	0.0006	0.120	0.005	0.0008	0.160	0.400
4,4′-DDT	0.0005	0.0003	0.600	0.0005	0.0004	0.800	0.0005	0.0001	0.200	1.600
4,4′-DDD	–	0.0020	–	–	0.0025	–	–	0.0011	–	–
4,4′-DDE	–	0.0240	–	–	0.0550	–	–	0.0130	–	–
Kinshasa										
α-BHC	0.005	0.0013	0.260	0.005	0.0007	0.140	0.005	0.0006	0.120	0.520
γ-BHC	0.005	0.0013	0.260	0.005	0.0009	0.180	0.005	0.0005	0.100	0.540
4,4′-DDT	0.0005	0.0003	0.600	0.0005	0.0001	0.200	0.0005	0.0003	0.600	1.400
4,4′-DDD	–	0.0015	–	–	0.0007	–	–	0.0006	–	–
4,4′–DDE	–	0.0018	–	–	0.0012	–	–	0.0007	–	–

Nd: Not detected.
[a] US EPA (2011).

avoid such hazards, it is suggested that awareness among farmers regarding judicious use of pesticide be strongly recommended.

4. Conclusions

Results of this study show that residues of organochlorine pesticides are present in the food sold in Johannesburg and Kinshasa open markets. Mean concentration of organochlorine pesticide compounds studied in various food samples followed the order; beef > fish > cabbage > beans. Most of the organochlorine pesticide compounds exceeded their prescribed limit set by different international agencies. These residues have originated from agricultural past and present activities. These residues might reach the top of the food chain by bioaccumulation. It is expected that an appreciable build-up of residues with time will occur because of the continuous presence of these pesticides in various environmental compartment. This may pose serious public health problems. To prevent a health disaster, it is essential that a system of monitoring of residues in the key component of food chain is encouraged so as to generate data for policy making on how to address the situation. Both surface and ground water bodies in designated pollution hotspots of these compounds should not be used for agricultural purposes unless evidence of the levels of these compounds is ascertained.

Acknowledgement

The authors would like to thank Dr. Jos Ndelo – di- Phanzu, Professor at University of Kinshasa, Faculty of Pharmacy, for his support and also BEBUC panel for the financial support.

References

Adeyemi, D., Ukpo, G., Anyakora, C., Unyimadu, J.P., 2008. Organochlorine pesticide residues in food samples from Lagos markets, Nigeria. Am. J. Environ. Sci. 4 (6), 649–653.
Akoto, O., Andoh, H., Darko, G., Eshun, K., Osei-Fosu, P., 2013. Health risk assessment of pesticides residues in maize and cowpa from Ejura, Ghana. Chemosphere 92, 67–73.
Amoah, P., Drechsel, P., Abaidoo, R.C., Ntow, W.J., 2006. Pesticides and packaging contamination of vegetables in Ghana"s urban market. Arch. Environ. Contam. Toxicol. 50, 1–6.
Ayejuyo, O.O., Williams, A.B., Igbasan, S.O., 2008. Assessment of organochlorine pesticide residues in irrigation groundwater of Lagos. J. Chem. Soc. Niger. 33, 65–69.
Bempah, C.K., Donkor, A., Yeboah, P.O., Dubey, B., Osei-Fosu, P., 2011. A preliminary assessment of consumer's exposure to organochlorine pesticides marketed in Greater Accra Region of Ghana. Food Control 25, 537–542.
Bhanti, M., Taneja, A., 2005. Monitoring of organochlorine pesticide residues in summer and winter vegetables from Agra, India – a Case Study. Environ. Monit. Assess. 10, 341–346.
Darko, G., Acquaah, S.O., 2007. Levels of organochlorine pesticides residues in meat. Int. J. Environ. Sci. Technol. 4, 521–524.
Doong, R.A., Peng, C.K., Sun, Y.C., Liao, P.L., 2002. Composition and distribution of organochlorine pesticide residues in surface sediments from Wu-Shi River Estuary, Taiwan. Mar. Pollut. Bull. 45, 246–253.
Essumang, D.K., Togoh, G.K., Chokky, L., 2009. Pesticide residues in the water and fish (Tilapia) samples from Lagoons in Ghana. Bull. Chem. Soc. Ethiop. 1, 19–27.
European Commission, 2009. Maximum Residue Levels of Pesticides in or on Food and Feed of Plant and Animal Origin. Commission Amending Regulation (EC) No 396/2005 of the European Parliament and of the Council. Amending Council Directive 91/414/EEC.
FAO/WHO, 2010. Evaluation of Certain Food Additives and Contaminants, vol. 859. WorldHealth Organization, Joint FAO/WHO Expert Committee on Food Additives, Geneva, pp. 29–35. World Health Organization Technical Report Series.
FAO/WHO, 2012. Codex Alimentarius Commission. Pesticide Residues in Food and Feed. Codex Pesticide Residues in Food Online Database.
Fatoki, O.S., Awofolu, O.R., 2002. Levels of organochlorine pesticide residues in marine-, surface-, ground- and drinking waters from the eastern cape province of South Africa. J. Environ. Sci. Health B 39 (1), 101–114.
Gonzalvez, W., Armenta, S., Cervera, M.L., De La Guardia, M., 2008. Elemental composition of seasoning products. Talanta 74, 1085–1095.
Guan, Y., Wang, J., Ni, H., Zeng, E.Y., 2009. Organochlorine pesticides and polychlorinated biphenyls in riverine runoff of the Pearl River Delta, China: assessment of mass loading, input source and environmental fate. Environ. Pollut. 157, 618–624.
Lehotay, S.J., De Kok, A., Hiemstra, M., Van Bodegraven, P., 2005. Validation of a fast and easy method for the determination of residues from 229 pesticides in fruits and vegetables using gas and liquid chromatography and mass spectrometric detection. J. AOAC Int. 88, 615–629.
Manirakiza, P., Akinbamijo, O., Covaci, A., Pitonzo, R., Schepens, P., 2003. Assessment of organochlorine pesticide residues in West African city farms: Banjul and Dakar case study. Arch. Environ. Contam. Toxicol. 44, 171–179.
Mansour, S.A., Belal, M.H., Abou- Arab, A.A.K., Ashour, H.M., Gab, M.F., 2009. Evaluation of some pollutant levels in conventionally and organically farmed potato tubers and their risks to human health. Food Chem. Toxicol. 47, 615–624.
Martinez, M.P., Angulo, R., Pozo, R., Jodral, M., 1997. Organochlorine pesticides in pasteurized milk and associated health risks. Food Chem. Toxicol. 35, 621–624.
Mwevura, H., Othman, O.C., Mhehe, G.L., 2002. Organochlorine pesticide residues in edible biota from the coastal area of Dar Es Salaam City. West. Indian Ocean J. Mar. Sci. 1, 91–96.
Nakata, H., Kawazoe, M., Arizono, K., Abe, S., Kitano, T., Shimada, H., 2002. Organochlorine pesticides and polychlorinated biphenyl residues in foodstuffs and human tissues from China: status of contamination, historical trend and human dietary exposure. Arch. Environ. Contam. Toxicol. 43, 473–480.
Odhiambo, J.O., Qi, S., Xing, X., Zhang, Y., Muhayimana, A.S., 2009. Residues of organochlorine pesticides in vegetables from Deyang and Yanting areas of the Chengdu economic region, Sichuan. Province, China. J. Am. Sci. 5, 91–100.
Osibanjo, O., Bouwman, H., Bashir, N.H.H., Okond'Ahoka, J., Choong Kwet Yve, R., Onyoyo, H.A., 2002. In: Regionally Based Assessment of Persistent Toxic Substances. Sub-saharan Africa Regional Report, vol. 6. UNEP Chemicals, Geneva, pp. 56–61.
Osman, K.A., Al-Humaid, A.L., Al-Rehiayani, S.M., Al-Redhaiman, K.N., 2011. Estimated daily intake of pesticide residues exposure by vegetables grown in greenhouses in Al-Qassim region, Saudi Arabia. Food Control 22, 947–953.
PAN, 2010. PAN Pesticide Database, 20.03.2011. Available from: http://www.pesticideinfo.org.
Rawn, D.F.K., Judge, J., Roscoe, V., 2010. Application of the QuEChERS method for the analysis of pyrethrins and pyrethroids in fish tissues. Anal. Bioanal. Chem. 397, 2525–2531.
Sverdrup, L.E., Nielsen, T., Krogh, P.H., 2002. Soil ecotoxicity of polycyclic aromatic hydrocarbons in relation to soil sorption, lipophilicity and water solubility. Environ. Sci. Technol. 36, 2429–2435.
USEPA, 1996. Integrated Risk Information System. Off. Health. Environ. Assess., US Environmental Protection Agency, Washington, DC.
USEPA, 2011. Exposure Factor Handbook, EPA/600/R-090/052 F. US Environmental Protection Agency, Washington, DC.
Usman, M.T., Iqubal, S.N., Rehman, S., Hazhad, M., 2009. A quantitative analysis for the toxic pesticide residues in marketed fruits and vegetables in Lahore, Pakistan. Biomedica 25, 171–174.
Vorster, H.H., Batham, J.B., Venter, C.S., 2013. An introduction to the revised food – based dietary guidelines for South Africa. S. Afr. J. Clin. Nutr. 26 (3), 1–164.
Walker, K., Vallero, D.A., Lewis, R.G., 1999. Factors influencing the distribution of lindane and other hexachlorocyclohexanes in the environment. Environ. Sci. Technol. 33, 4373–4378.
Yamaguchi, R., 2015. Food consumption and preferences of the Bongando people in the Democratic Republic of the Congo. Afr. Study Monogr. 51, 37–55.