HUMAN HEALTH RISK ASSESSMENT OF ORGANOCHLORINE PESTICIDES IN SOME FOODS GROWN IN NIGERIA

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Introduction
Pesticides such as OCPs are widely used in agricultural practices to improve agricultural yield, and so are of major eco-toxicological and public health risk concerns. Despite the health risks, application of these substances is increasing due to increasing population and high demands of farm produce. A developing country such as Nigeria in West Africa, with increasing population of more than 160 million employs the use of pesticides in the mass production of foods and agricultural produce to meet up the nation’s food demand. Lagos State is Africa’s biggest city and the fastest growing metropolis in the world with a population of about 20 million people therefore most of the food produced/grown in the northern and other parts of Nigeria end up there. Pesticides residues in food have been responsible for several cases of food poisoning and deaths recorded in Nigeria [1,2]. There have been studies on OCPs in some Nigerian grains which revealed the presence of Lindane, Diazinon and Aldrin in the pre storage samples [3]. Studies of pesticide residue in spinach lettuce, onions, cabbage and tomatoes in Nigeria also revealed that the amount of pesticide residues in the vegetables were above the limits. The world health organization has reported that roughly three million cases of pesticides poisoning occur annually, thus resulting in 220,000 deaths worldwide [4]. This paper presents the level of OCPs in some common fruits, vegetable and from local markets in Lagos State and also the first assessment of the risk involved in the consumption of these foods.

Materials and methods
Reagents and materials
OCP standards were obtained from Supelco (Bellefonte, PA, USA). Dichloromethane (DCM), ethylacetate, n-hexane and sodium sulphate anhydrous were bought from Sigma Aldrich, Inc. Germany (purity between 98-99 %). Solid phase extraction (SPE) catridges (Varian EnvirElut for pesticides) were purchased from (Varian Inc. USA)

Sampling
Samples of water melon (Citrullis lanatus), carrot (Daucus carota), cucumber (Cucumis sativus), cabbage (Brassica oleracea),lettuce (Lactuca sativa), wheat (Triticum spp),millet (panicum spp), sorghum (Sorghum bicolor), beans (Phaseolus spp), maize (Zea mays),tomato (Lycopersicon esculentum),chilli Pepper (Capsicum frutescens), cameroon pepper (Piper nigrum), green bell pepper (Capsicum annum), scotch Bonnet (Capsicum chinese) cowpea (Vigna unguiculata), were purchased from local wholesale markets in Lagos. The samples were collected and transported to the laboratory using standard sampling procedure [5]. The samples were milled/blended, homogenized and stored at a temperature of < 4ºC, prior to extraction.

Ultrasonic extraction and clean-up and GC-ECD analysis
An aliquot of 5.0 g of sample was weighed into 50 ml conical flask and 2.5 g of anhydrous sodium sulphate was added. The mixture in the conical flask was extracted with 20 ml of ethyl acetate and shaken at 270 rpm for 5 mins, sonicated for 20 mins at 40 ºC, after which it was allowed to stand for 5 mins and centrifuged for 5 mins at 2500 rpm. The supernatant was concentrated to about 1 ml under a gentle stream of nitrogen gas. The sample extract was loaded on the pre-conditioned SPE column, and eluted with a solvent mixture of n-hexane: DCM (3:2). The eluate was
concentrated and reconstituted to 1 ml using n-hexane. Quantification was done using a gas chromatograph (Agilent 7890A) equipped with an electron capture detector. Analytes were separated with an HP 5 column (30 m x 0.25 mm x 0.25 µm). Nitrogen was used as the carrier gas and the total run time was 24 mins.

Risk assessment
The Health Risk Index (HRI) was calculated based on the levels of the OCP residues found in the food samples. Estimated daily intakes (EDI) were determined and compared with the established acceptable daily intake (ADI) [6-8]. Calculations were performed for adults and children (age 2 - 5 years) [9].

\[
EDI = \frac{F \times C_r}{\text{mean body weight}}
\]

Where F = food consumption data, C_r is the concentration of the residue in the food sample

\[
HRI = \frac{EDI}{ADI}
\]

Results and discussion
The concentration of the 13 OCPs determined in the studied foods are shown in Tables 1 and 2.

Table 1: Result of analyses for concentration of 13 OCPs in Grains (Cereals and Pulses) (ng/g)

<table>
<thead>
<tr>
<th>Pesticide</th>
<th>Cereals</th>
<th>Pulses</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Millet</td>
<td>Maize</td>
</tr>
<tr>
<td>1 Alpha-BHC</td>
<td>1.25</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td>2 Beta-BHC</td>
<td>&lt;0.75</td>
<td>1.69</td>
</tr>
<tr>
<td>3 Lindane</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
</tr>
<tr>
<td>4 Chlorothalonil</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
</tr>
<tr>
<td>5 Delta-BHC</td>
<td>&lt;0.03</td>
<td>&lt;0.03</td>
</tr>
<tr>
<td>6 Heptachlor</td>
<td>&lt;0.3</td>
<td>1.38</td>
</tr>
<tr>
<td>7 Aldrin</td>
<td>&lt;0.3</td>
<td>&lt;0.3</td>
</tr>
<tr>
<td>8 Heptachlor-epoxide (B)</td>
<td>1.06</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td>9 P,P'-DDE</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td>10 Endosulfan I</td>
<td>&lt;0.09</td>
<td>&lt;0.09</td>
</tr>
<tr>
<td>11 P,P'-DDD</td>
<td>0.73</td>
<td>0.64</td>
</tr>
<tr>
<td>12 Dieldrin</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>13 P,P'-DDT</td>
<td>&lt;0.3</td>
<td>&lt;0.3</td>
</tr>
</tbody>
</table>
### Table 2: Result of analyses for concentration of 13 OCPs in vegetables and fruits (ng/g)

<table>
<thead>
<tr>
<th>Pesticide</th>
<th>Cabbage</th>
<th>Cameroonian Pepper</th>
<th>Green Pepper</th>
<th>Chilli pepper</th>
<th>Carrot</th>
<th>Lettuce</th>
<th>Tomato</th>
<th>Scotch Bonnet</th>
<th>Watermelon</th>
<th>Cucumber</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alpha-BHC</td>
<td>&lt;0.5</td>
<td>0.82</td>
<td>0.73</td>
<td>0.67</td>
<td>0.58</td>
<td>0.82</td>
<td>&lt;0.5</td>
<td>0.71</td>
<td>0.7</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td>Beta-BHC</td>
<td>1.64</td>
<td>1.8</td>
<td>1.72</td>
<td>1.78</td>
<td>0.86</td>
<td>1.75</td>
<td>1.66</td>
<td>1.76</td>
<td>1.8</td>
<td>&lt;0.75</td>
</tr>
<tr>
<td>Lindane</td>
<td>0.22</td>
<td>0.23</td>
<td>&lt;0.2</td>
<td>0.21</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
</tr>
<tr>
<td>Chlorothalonil</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
<td>0.34</td>
</tr>
<tr>
<td>Delta-BHC</td>
<td>&lt;0.03</td>
<td>&lt;0.03</td>
<td>&lt;0.03</td>
<td>&lt;0.03</td>
<td>&lt;0.03</td>
<td>&lt;0.03</td>
<td>&lt;0.03</td>
<td>&lt;0.03</td>
<td>&lt;0.03</td>
<td>&lt;0.03</td>
</tr>
<tr>
<td>Heptachlor</td>
<td>0.57</td>
<td>&lt;0.3</td>
<td>&lt;0.3</td>
<td>&lt;0.3</td>
<td>&lt;0.3</td>
<td>&lt;0.3</td>
<td>&lt;0.3</td>
<td>&lt;0.3</td>
<td>&lt;0.3</td>
<td>0.73</td>
</tr>
<tr>
<td>Aldrin</td>
<td>1.07</td>
<td>1.96</td>
<td>1.94</td>
<td>1.96</td>
<td>1.22</td>
<td>1.9</td>
<td>1.9</td>
<td>1.92</td>
<td>&lt;0.3</td>
<td></td>
</tr>
<tr>
<td>Heptachlor-epoxide (B)</td>
<td>&lt;0.50</td>
<td>0.58</td>
<td>&lt;0.5</td>
<td>0.58</td>
<td>&lt;0.50</td>
<td>&lt;0.50</td>
<td>&lt;0.50</td>
<td>&lt;0.50</td>
<td>0.56</td>
<td>&lt;0.50</td>
</tr>
<tr>
<td>PP'-DDE</td>
<td>86.1</td>
<td>123</td>
<td>11.9</td>
<td>123</td>
<td>115</td>
<td>119</td>
<td>10.2</td>
<td>119</td>
<td>123</td>
<td>41.7</td>
</tr>
<tr>
<td>Endosulfan I</td>
<td>0.17</td>
<td>0.29</td>
<td>0.27</td>
<td>0.29</td>
<td>&lt;0.09</td>
<td>0.28</td>
<td>0.16</td>
<td>0.29</td>
<td>0.29</td>
<td>&lt;0.09</td>
</tr>
<tr>
<td>P,P'-DDD</td>
<td>&lt;0.25</td>
<td>0.38</td>
<td>&lt;0.25</td>
<td>0.38</td>
<td>&lt;0.25</td>
<td>0.26</td>
<td>&lt;0.25</td>
<td>0.29</td>
<td>0.37</td>
<td>&lt;0.25</td>
</tr>
<tr>
<td>Dieldrin</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>0&lt;.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>P,P'-DDT</td>
<td>&lt;0.3</td>
<td>0.49</td>
<td>&lt;0.3</td>
<td>&lt;0.3</td>
<td>&lt;0.3</td>
<td>&lt;0.3</td>
<td>&lt;0.3</td>
<td>&lt;0.3</td>
<td>&lt;0.3</td>
<td>&lt;0.3</td>
</tr>
</tbody>
</table>

Concentrations of the various OCPs varied from below their limit of quantification (LOQ) to high levels. α-BHC (an OCP) in cereals had concentrations between <0.5 and 1.25 ng/g while beans and cowpeas had concentrations of 21 and <0.5 ng/g respectively. The highest concentration of β-BHC (beta-BHC) in this study was found in wheat (3.12 ng/g) followed by Sorghum (3.09 ng/g) and then beans (3.04 ng/g). The concentration of aldrin in cereals ranged between < 0.3 (millet and maize) and 3.45 ng/g (wheat) while of the pulses, (beans in this case), also had a high concentration of 3.5 ng/g. Sorghum had a very high concentration of PP’DDE (233 ng/g) though the level in other cereals where below their LOQs of 0.5 ng/g. The pulses also had high levels of PP’DDE such as 106 ng/g and 110 ng/g for beans and cowpeas respectively. Generally the levels were found to be lower in vegetables and fruits than in grains. Alpha–BHC in vegetables had concentrations between <0.5 and 0.73 ng/g while water melon and cucumber (fruits) had concentrations of 0.7 and <0.5 ng/g respectively. Concentrations of beta-BHC for vegetables and fruits in this study were between <0.75 and 1.8 ng/g. Lindane concentration for vegetables and fruits were relatively low, and varied between <0.2 and 0.23 ng/g. Chlorothalonil, delta-BHC and heptachlor all had concentrations below their LOD with the exception of cucumber which had a concentration of 0.34 ng/g of chlorothalonil, cabbage and cucumber which had concentrations of 0.57 and 0.73 ng/g respectively for heptachlor. The concentration of aldrin in vegetables ranged between 0.7 (tomatoes) and 1.96 ng/g (cameroun pepper) while in watermelon and cucumber the concentration were 1.92 and <0.3 ng/g respectively. PP’-DDE of all the OCPs determined had relatively higher concentrations consistently in all the samples in this study. The concentration range for PP’-DDE in vegetables were between 10.2 and 123 ng/g while in the two fruits studied; water melon and cucumber had concentrations of 123 and 41.7 ng/g respectively.

Based on this research and other researches carried out in Nigeria on the levels of OCPs in foods [10-12], the concentrations of OCPs found were lower than concentrations from other parts of the world. Also, the OCP levels in
this study were lower than in previous studies from Nigeria. This may be as a result of improved monitoring by regulatory agencies and the preference for the organophosphate and organocarbamate pesticides in farming practices in Nigeria. The list of commonly used pesticides in Nigeria is made up of predominantly carbamates and phosphates only a few organochlorine pesticides such as lindane, DDT, Heptachlor and aldrin were mentioned by Ita [13]. Secondly organic farming where little or no chemical is used in farming is still being practiced by subsistent farmer who make up a high percentage of farmers in Nigeria. 

Risk assessment showed HRI to be < 1 in almost all the cases with the exception of P,P'-DDD in fruits when consumed by children, which had an health risk index of 1.04. This may be because of the low body weight of children and thus there may be need for close monitoring of this particular residue in fruits consumed by children. For the adults, the HRI was observed to be < 1 in all the cases and the foods studied are considered to pose no risk. This may mean that the OCP residues under investigation are under control in the foods.

Acknowledgement
Authors wish to thank Pure Earth (blacksmith Institute) for financial support to write up the research work.

References
4. Adedjei OB and Okocha RO (2012).Advances in Environmental Biology, 6(8) 2344-2351