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Occurrence of paraquat residues in some Nigerian crops, vegetables and fruits

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Pesticides constitute the major source of potential environmental hazard to man and animal, as they are present and concentrated in the food chain. Paraquat (1,1¹-dimethyl-4,4¹-bipyridylium dichloride) is one of the most highly toxic herbicide to be marketed over the last 60 years. Although, Paraquat (PQ) has been banned or severely restricted in most countries, its use continues in some, especially in Nigeria. Therefore, this study investigated possible occurrence of PQ in some commonly consumed vegetables, crops and fruits in Abeokuta using spectrophotometric method. This study was conducted on 150 samples of different kinds of crops, vegetables and fruits (harvested from Fadama farmland of the University of Agriculture, Abeokuta) to assess the presence and levels of PQ residues. PQ residues was found to present at 0.13±0.02, 0.27±0.02, 0.06±0.01, 0.10±0.03, 0.15±0.03, 0.09±0.02, 0.09±0.02, 0.04±0.01 and 0.05±0.01 ppm in *Talinum triangulare*, *Corchorus olitorius*, *Amaranthus caudatus*, *Cratylia argentea*, *Capsicum frutescens*, *Lycopersicum esculentum*, *Raphanu sativus*, *Zea may* and *Dioscorea alata*, respectively. Paraquat residues were not detectable in *M. paradisiaca* and *C. papaya* using this method. The method achieves mean recovery of over 80% and is repeatable with overall coefficient of variation of 8.0% (n=10) at 0.05-1.0 ppm fortification level. All residue levels detected were within the PQ tolerance or maximum pesticide limits.

Key words: Occurrence, Paraquat residues, Nigerian, crops, vegetables, fruits.

INTRODUCTION

One of the major task facing control agencies in most of the developing and developed countries is monitoring for pesticide residues in foods. Pesticide residues monitoring program is important to enforce compliance with any legislated national and international maximum residue limits. Monitoring data are normally used to assess the dietary exposure of pesticide residues from food (Anderson and Poulsen, 2001; Camoni et al., 2001; European Commission, 2006).

Paraquat (PQ) was invented in England in 1956 and has been continuously used for agriculture all over the world because its splendid herbicidal effects have been producing large economic gains. It is used to control weeds and grasses in many agricultural and non-agricultural areas. For instance, it is used for pre-plant or

pre-emergence on vegetables, grains, potatoes and peanut areas; post emergence around fruit crops and soybeans during the dormant season on clover and other legumes. Paraquat products have been classified as restricted pesticides and even banned in some country (US EPA, 2001). More so, the occurrence of agro-chemical residues in foodstuffs, crops, vegetables, milk and milk products have been reported by different authors in many countries (Antonio and Manuela, 1995; Mohamed and Saad, 1995; Kinyamu et al., 1998; Rusibamayila et al., 1998; Osfor et al., 1998; PAN Europe, 2005; Codex Alimentarius, 2006).

On several occasions, incidents of poisoning after consuming these plants and animal products have been reported. These incidents were attributed to grower's misuse of the pesticides or to negligence in observing a safety interval after harvest. It has been reported that people were exposed to paraquat residues through diet (Selisker et al., 1995; Zeneca Agricochemicals, 1993). Determining the levels of herbicides present in plants and

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plant products has great relevance because these values are convenient indicators of environmental contamination by the herbicides. The present study was undertaken to evaluate quantitatively the paraquat residue levels in some vegetables, fruits and crops commonly consumed in Abeokuta, Nigeria, in order to assess the possible predisposition of human to this herbicide and its associated health risks such as Parkinson's disease, Alzheimer's disease and Amyotrophic lateral sclerosis (Grandjean and Landrigan, 2006).

MATERIALS AND METHODS

Randomly selected samples of different kinds of vegetables, crops and fruits namely *Raphanus sativus* (Radish), *Zea mays* (Agbado, Maize), *Lycopersicon esculentum* (Tomato), *Talinum triangulare* (Gbure, Water leaf), *Chochorus olitorius* (Ewedu, Nalta jute), *Amaranthus caudatus* (Efo tete, Tassel flower), *Celocia argentea* (Efo soko, Cockscomb), *Capsicum frutescens* (Ata wewe, Chilli pepper), *Dioscorea alata* (Isu ewura, Water yam), *Musa paradisica* (Ogede agbagba, Plantain) and *Carica papaya* (Ibepe, Pawpaw) used in this studies were harvested from the Fadama Farm of the University of Agriculture, Abeokuta, on which paraquat had been previously used (application rate of 2.2 Kg PQ/ha) as pre-emergence herbicides.

The control samples were obtained from the subsistence farmer's farmland on which there was no former history/record of PQ usage. PQ formulated as paraquat dichloride (Syngenta, Zwiterland) was purchased from one of the distributor (C.ZARD, Nig Ltd.). Sodium dithionite, calcium carbonate and sodium hydroxide were purchased from Aldrich Chemicals, sulphuric acid (analytical reagent grade) purchased from BDH Ltd. Spectrophotometer (Jenway, Model 6405 uv/vis) and centrifuge (JOL-802 Finlab, U.K, model TDL 80-2) were part of the apparatus used.

Preparations of samples

Randomly selected samples of each kinds of crops, fruits and vegetables aforementioned, harvested from a 'homogeneous lot' (same plantation, same paraquat treatment and same harvest date) on the Fadama farmland were thoroughly washed and rinsed with deionised water, copped, blended, homogenized and centrifuged at 5000 rpm for 30 min. The resulting supernatant was used for the analysis. Examination gloves (Top glove SDN BHD, Selangor D.E, Malaysia) were worn throughout the course of the experiment.

Extraction of paraquat residues

An extraction procedure adapted from Van Emon et al. (1987) as described by Selisker et al. (1995) was employed. Representative analytical sub-samples (2.5 g) were weighed into 25 ml calibrated polypropylene tubes followed by addition of concentrated tetraoxosulphate (VI) acid (2.5 ml 6 N H₂SO₄), closed and sonicated. The volume was made up to 5.0 ml with 6 N H₂SO₄, shaken for about 10 min in an orbital shaker. The mixture was then centrifuged at 5000 rpm for 10 min. The supernatant was carefully removed and kept at 4°C until used.

Spectrophotometric determination of PQ residues

The determination of PQ residues in the extracted samples was

carried out as described by Rai et al. (1997). 20 µl of the aforementioned supernatant was mixed with 4.9 ml of 0.01 M sodium acetate buffer, pH 5.0. This was followed by the addition of 2.0 ml 1% (w/v) aqueous sodium dithionite and 1 ml of 0.1 M sodium hydroxide. The mixture was allowed to stand for about 2 to 5 min and paraquat residues were quantified by measuring the absorbance at 600 nm. The amount of PQ residues was then estimated from a standard calibration curve plotted using commercially available PQ as standard, as seen in Figure 1. To examine the efficacy of extraction, three samples of each vegetable, crop and fruit were spiked with known concentration of PQ (0.01 to 0.5 ppm) and extraction was performed as described earlier and the mean percentage recovery level determined.

RESULTS AND DISCUSSION

The result of the levels of PQ residues determined from each sample analyzed is shown in Table 1. Among the samples analyzed, *Z. mays* and *C. olitorius* had the least (0.04 ppm) and highest (0.27 ppm) levels of PQ residues, respectively. The observed differences could be explained on the basis of different shape and morphology of these plants. The highest PQ level detected in *C. olitorius* could be attributed not only to the nature of its foliage system which could probably be responsible for the retention of this compound but also to the high fat content nature of the plant. PQ had been reported to be lipophobic, it is therefore not surprising to note that *Z. mays* whose seeds is majorly carbohydrate had the least amount of PQ residues. The highest level of PQ residues obtained in these studies was quite below that obtained in potatoes (0.5 ppm) in the work of Yuk et al. (1993). Also, the amount of PQ residues detected in *Z. mays* in this study (0.04 ppm) was not in agreement with the report of Plant Protection Ltd. (1986), where mean PQ level of 0.08 ppm was detected in maize. The differences may be attributed to the difference in the level of sensitivity of the method used. Codex online details for PQ reported that the maximum residue limits (MRLs) for PQ in leafy vegetables, maize, soya bean fodder, root and vegetables were 0.07, 0.05, 0.5 and 0.05 mg/kg, respectively (Codex Alimentarius, 2006). Costenla et al. (1990) also reported that PQ residues in coffee berries and bean in Costa Rica were at or below the limit detection of 0.02 mg/kg.

The European Union (EU) monitoring report on pesticide residues in food shows a frequency of samples with residues above MRLs of 5.5% and a frequency of samples with residues at or below the MRLs of 4.4%. Methomyl, methiocarb, dimethoate and bromopropylane were reported to be among substances found exceeding the MRLs. High level of exceedances were observed in grapes (5%), cucumber (3%) and aubergines (3%) (PAN Europe, 2005; European Commission, 2006). The percentage recovery of about 80, 85, 85, 86, 89, 85, 88, 85, 88 and 84% for *T. triangulare*, *C. olitorius*, *A. caudatus*, *C. argentea*, *C. frutescens*, *R. sativus*, *Z. mays*, *L. esculentum*, *D. alata*, *M. paradisica* and *C. papaya* respectively was discovered in these samples. One could

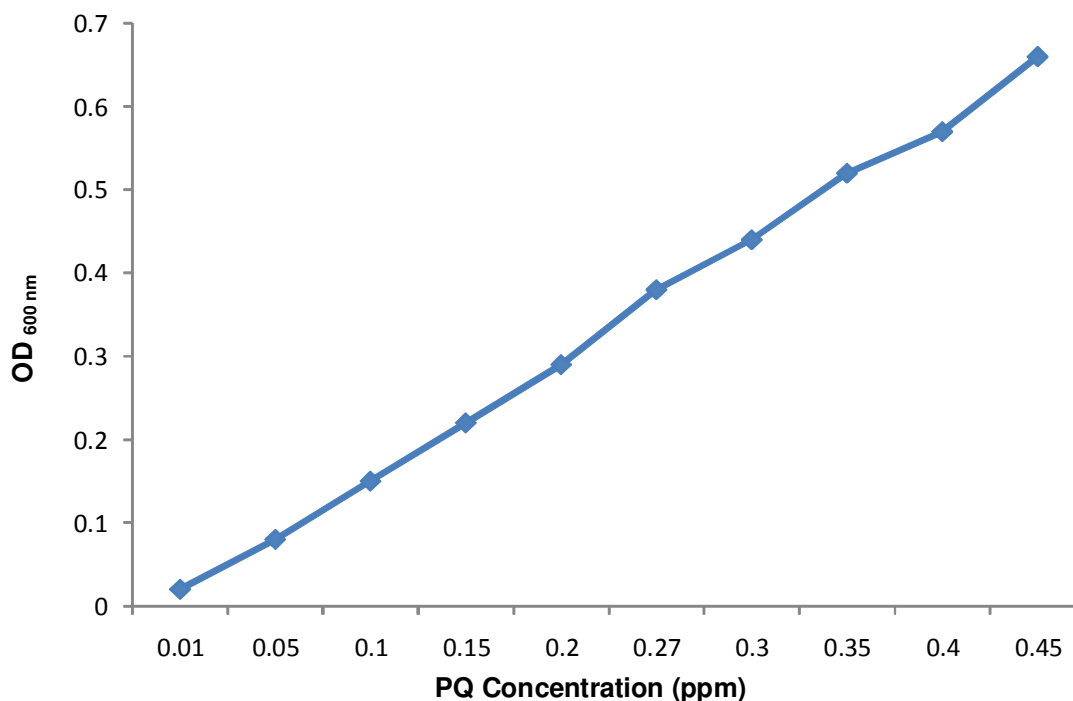


Figure 1. Calibration curve for paraquat residue concentration determination.

Table 1. Paraquat residues in some vegetables, crops and 1 fruits.

Sample	Residues (ppm) mean±SEM
<i>T. triangulare</i>	0.13±0.02
<i>C. olitorius</i>	0.27±0.02
<i>A. caudatus</i>	0.06±0.01
<i>C. argentea</i>	0.10±0.03
<i>C. frutescens</i>	0.15±0.03
<i>L. esculentum</i>	0.09±0.02
<i>R. sativus</i>	0.09±0.02
<i>Z. mays</i>	0.04±0.01
<i>D. alata</i>	0.05±0.01
<i>M. paradiscicica</i>	ND
<i>C. papaya</i>	ND

ND, Not detected; n = 15 (where n is the number of each kind of individually randomly selected samples analyzed).

have thought that *C. papaya* and *M. paradiscicica* would had the highest content of PQ residues, which could have arose from continuous accumulation due to their perennial nature. However, PQ residues in these plants were not detectable using the aforementioned methodology.

The present preliminary results revealed that in all the randomly selected samples tested, PQ residues detected were below the maximum residues limits (MRLs) of 0.5 mg/Kg set by the UK pesticides levels in crop foods and feedstuffs (Regulation, 1994; Statutory Instrument, 1985).

This is also in agreement with the report of Terry et al. (2002) that there was very little exposure to PQ for the consumers of treated crops as the vast majority of PQ uses do not result in detectable residues (>0.5 mg/kg) in food stuffs. Therefore, the consumption of these plant products does not seem to be a serious risk for consumer's health. On the other hand, we cannot rule out or forget the possible long-term effects of accumulation of this chemical in the body which may be deleterious. Thus, this calls for further investigations in this view.

To the best of our knowledge, this is the first reported notes on the occurrence of PQ residues in some Nigerian crops, vegetables and fruits using spectrophotometric method; work are still in progress on the use of high performance liquid chromatographic method which might offer faster, concise and possibly specific determinations.

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