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Pesticides residue analysis in yam from selected markets across Ghana and Belgium: an evaluation of the QUECHERS method

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Abstract

Background: In recent years, concerns have been raised in Ghana regarding the use of pesticides in yamproduction to the extent that it is feared that pesticides residues may be found in the yam tuber which isconsumed by many Ghanaians. This present study, therefore, was designed to assess the level of pesticides residues in yam bought from across Ghanaian markets i.e. production for local consumption and from Belgium grocery shops (export production from Ghana) using the Quick, Easy, Cheap, Efficient, Rugged and Safe (QuEChERS) method coupled with LC-MS/MS. A total of 180 yam samples, including 150 from Ghana and 30 from Belgium were collected and pesticides residues were analyzed using a multi-residue method.

Results: A total of 25 pesticides were screened in the yam samples and 11 of them were detected. Theresults indicated that about 46% of the samples contained one or more of the 11 detected pesticides in arange of 0. 000014 mg/kg up to 0.0146 mg/kg. The three most detected pesticides in this study were fenpropimorph, cadusafos and fenitrothion, occurring in 179, 171 and 126 samples respectively. All the detected pesticides were below their respective EU maximum residue limits (MRL).

Conclusion: By these results, it can be said that, the residues of the monitored pesticides found in yam arevery low and are unlikely to pose a negative human health effect.

Keywords: Pesticides, Residues, Yam, Ghana, Human health. Maximum residue limit (MRL)

Background

The effort of the global community over the years at producing enough food to meet the demand for food that has tripled over the last 50 years (Bodirsky et al. 2015) has brought about new incentives and policies in agriculture. Key among the new incentives is the gross liberalization of the pesticides trade in both developed and developing countries to make pesticides affordable and accessible to famers. Because of these policy shifts, farmers who hitherto did not use pesticides, now use them and certain sectors of national agriculture which in the past were not known to be associated with pesticides, now use pesticides. A typical example is the case of Ghana where in the past pesticides use was restricted to a few crops such as cocoa in southern Ghana, cotton in northern Ghana and fruits and vegetables in both southern and northern Ghana, which has been extended to many other areas today (Ntow et al. 2009) including the production of yam.

Yam is a major food crop grown in many regions of Ghana and usually by small holder farmers (Anaadumba 2013). A few decades ago, the crop was cultivated using rudimentary practices, but today farmers use modern farming technologies including herbicides due to several factors. These factors include 'in particular' the commercialization of farming, dwindling labour force in the yam production areas and increasing weed pressure due to climate variability and overcultivation of the soil.

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The main herbicides used by the yam farmers are glyphosate and atrazine. Although, the farmers maintain the believe that the use of the pesticides help them to increase their production, there is public concern about the human health impacts of these products as there could be residues of the products in the yam that they consume (Cha et al. 2014). Of the numerous studies that have been conducted in Ghana on pesticides residues in food commodities (Asiedu 2013; Bempah and Donkor 2011) no study has yet been carried out on yam. Indeed, the study of Adeyeye and Osibanjo (1999) in Nigeria found residues of aldrin, dieldrin and DDT in yam, but not any herbicide. The present study therefore, was designed to investigate the hypothesis that there are pesticides residues in yam produced in Ghana with the objectives: (1) to conduct multiple pesticides residue analysis (LC-MS/MS) in yam from Ghanaian markets (local production) and from Belgian shops (export production) using the Quick, Easy, Cheap, Efficient, Rugged and Safe (QuEChERS) method and (2) to compare residue levels with the acceptable international food safety limits (MRL).

Methods

Sampling

A total of 180 yam samples were collected. Out of this number, 150 samples were collected in Ghana and 30 samples were collected in Belgium.

Sampling and sample preparation in Ghana

The Ghana samples were collected from five regions and from eight markets. During the sampling, samples were collected from one market each in the Northern region and Brong Ahafo region and from two markets each from the Ashanti, Greater Accra and Western regions. These markets (Fig. 1) include: Aboabu Central Market in Tamale (Northern region), Kintampo Yam Market (Brong Ahafo region), Moro Market and Ejisu Market in Kumasi (Ashanti region), Anaji Market and Market Centre in Takoradi (Western region) and Ashaiman Market and Konkomba Market (Greater Accra region). Sampling was done every week for six weeks between June and July 2016. A total of 30 samples were collected per regional market over the six-week period. During sampling yam retailers were interviewed about the

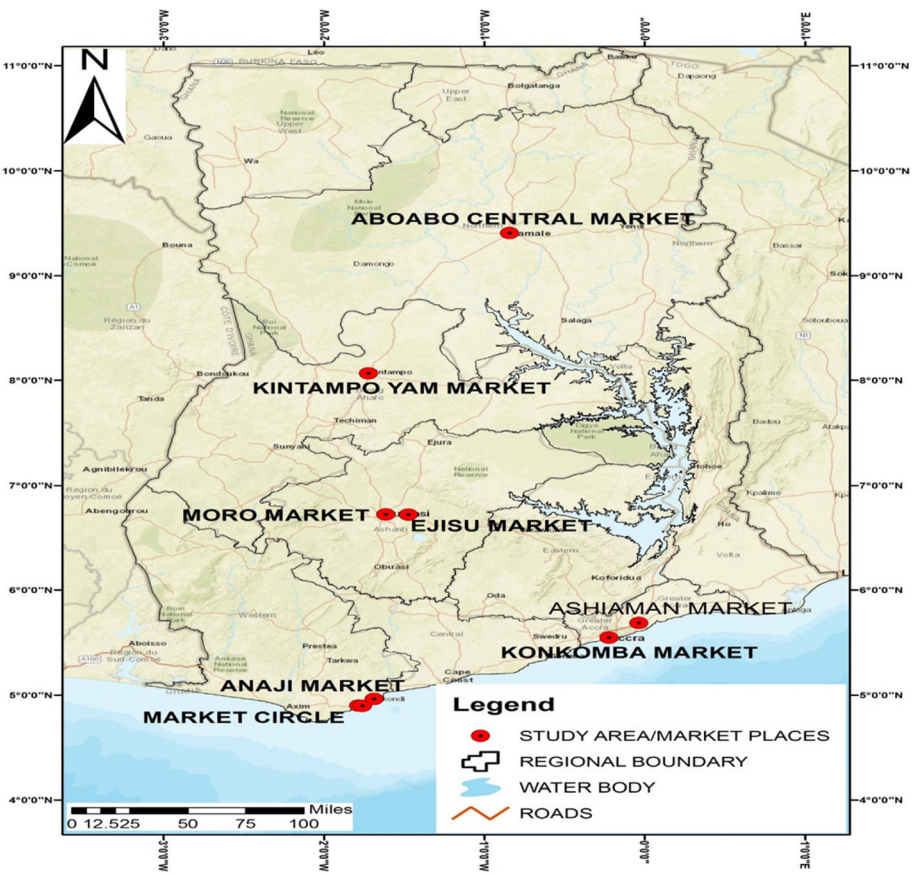

Fig. 1 Study area of the Ghana yam market survey (Alex Owusu, University of Ghana)

source of the yam they sell. The retailers indicated that they bought the yam from bulk sellers in the market who have the financial opportunity to go to the hinterlands with big trucks to buy yam directly from farmers and from local retailers. From this, it was realized that yam sold in the city markets are not originating from one source, but from multiple sources. After sampling, 50 g of each sample was ground using a blender. After blending of each sample the blender was cleaned thoroughly to prevent cross contamination. The blended yam was filled into 50 ml laboratory tubes, each of which was cupped, wrapped with a cello tape and kept into a transparent rubber bag. At this stage samples from each market were neatly wrapped into a larger and stronger rubber bag and frozen before being transported to the laboratory of Crop Protection Chemistry at Ghent University, Belgium. From there it was stored at – 20 °C until extraction and analysis.

Sampling and sample preparation in Belgium

The Belgium samples were collected from five shops spread across the city of Ghent in Belgium. These shops include; Jazwal Enterprise, Foreign Shop, Asian/African Shop, Africa/Caribbean Shop and Special Exotic Shop. Sampling in Belgium, like in Ghana was done within six weeks, but between January and February 2017. During the six weeks, one sample was collected from each of the five selected shops. During sampling, the shop owners were interviewed about the countries from which the yam they sold came from. The countries from which these shop owners imported yam include: Ghana, Cameroon and Nigeria. However, during the sampling period all the yams in the shops sampled were from Ghana. The samples were processed in a similar manner like those in Ghana, but without cello tapes and further wrapping. They were stored in a freezer at – 20 °C until extraction and analysis.

Reagents and materials

Laboratory reagents of high purity were used. Acetonitrile (analytical grade) was obtained from VWR PRO-LABO Suppliers and high-performance liquid chromatography (HPLC) grade water and acetone were supplied by ALLtech. Analytical grade salts (Table 1) including; magnesium sulfate anhydrous (MgSO4), sodium citrate tribasic dihydrate ($C_6H_2Na_3O_7$ $2H_2O$), sodium hydrogen citrate sesquihydrate ($C_6H_6Na_2O_7$ $1.5H_2O$) and sodium chloride (NaCl) to remove remaining water in organic solvents were supplied by Thermo Fisher Scientific Suppliers. Polypropylene centrifuge tubes (50 mL) were obtained from Thermo Fisher Scientific Suppliers.

Pesticides analytical standards

Pesticides analytical standards (Table 2) which were used in recovery experiments to validate the QuEChERS method on yam, were supplied by Supelco and delivered by Sigma-Aldrich Logistics. Before settling on these pesticides, a list of pesticides from the Ghana updated pesticides register was made. These were common pesticides on the Ghanaian market with the potential to be used on yam. However, after an initial assessment of the analytical equipment (Waters ACQUITY UPLC, Xevo TQD mass spectrometer) on the 82 pesticides on raw yam samples, it was observed that some of the pesticides could not be handled by LC-MS/MS in one analytical run with a high sensitivity and appropriate recovery, hence the list was reduced to 25.

Analytical equipment

Chromatographic separation of analytes was done by LC-MS/MS analysis on a triple quadrupole system with ESI (Waters ACQUITY UPLC, Xevo TQD mass spectrometer). Conditions and parameters of the analytical equipment are provided in Table 3.

Analytical method validation

The analytical procedure based on the QuEChERS method was validated for yam before being used in this study. In the validation process, the limit of detection (LOD) and the limit of quantification (LOQ) were determined by preparing matrix spikes at a low level near the expected detection limit. In this study, a uniform volume of 100 μL (0.0007 mg/L) for all the pesticides (Table 2) was spiked into the yam in eight

Table 1 Reagents and Materials and their respective analytical purities

No	Reagent	Purity (%)	Suppliers
1	Acetonitrile	99.9	VWR PRO-LABO
2	Acetone	99.0	ALLtech
3	Water (Milli Q)	100.0	ALLtech
4	Magnesium sulfate anhydrous (MgSo4)	99.5	Thermo Fisher
5	Sodium chloride (NaCl)	99.0	Thermo Fisher
6	Sodiumcitratetribasic dihydrate ($C_6H_2Na_3O_7$ $2H_2O$)	99.0	Thermo Fisher
7	Sodiumhydrogencitrate sesquihydrate ($C_6H_6Na_2O_7$ $1.5H_2O$)	99.0	Thermo Fisher

Table 2 Pesticides Analytical Standards (suppliers, Sigma-Aldrich and purity, 99%)

No	Pesticide analytical standard	LC-MS/MS Conditions for Analysis					
		Parent	CV(V)	Product 1	CE (eV)	Product 2	CE (eV)
1	acetamiprid	222.0	28	126.0	20	56.1	15
2	azoxystrobin	404.0	22	372.0	15	329.0	30
3	bentazone	241.1	15	199.1	12	107.2	26
4	butachlor	312.2	20	57.3	22	238.2	12
5	cadusafos	271.1	22	159.0	16	131.0	22
6	carbendazim	192.1	27	160.1	18	132.1	28
7	carbofuran	222.1	28	165.1	16	123.0	16
8	chlorpyriphos	349.9	30	97.0	32	198.0	20
9	difenconazole	406.0	40	251.1	25	111.1	60
10	diuron	233.0	28	72.1	18	46.3	14
11	dimethoate	230.1	18	125.0	20	199.0	10
12	diazinon	305.1	25	169.0	22	96.9	35
13	epoxiconazole	330.0	28	121.0	22	106.0	32
14	fenitrothion	278.0	32	109.1	20	79.1	32
15	fenpropimorph	304.2	44	147.1	28	57.2	30
16	imidacloprid	256.1	28	175.1	20	209.1	15
17	malathion	331.0	14	127.0	12	99.0	24
18	metalaxyl	280.1	20	220.1	13	192.1	17
19	pendimethalin	282.2	15	212.2	10	194.1	17
20	profenofos	372.9	30	302.6	20	127.9	40
21	propanil	217.9	34	161.9	16	127.0	22
22	propiconalzole	344.0	16	326.0	12	189.0	20
23	propoxur	210.0	15	111.0	16	168.0	10
24	pyraclostrobin	388.1	25	163.0	25	193.9	12
25	tryfloxystrobin	409.0	28	186.0	16	145.0	40

repetitions for the determination of the LOD and LOQ. The LOD and the LOQ were statistically determined based on the t^{S}_{99} *LLMV* method where $t_{99(n-1)} = 3$ (Corley 2003). The validity and precision of the method (analytical method efficiency) was determined with recovery tests. The recoveries were calculated based on the peak areas of the analytes, taking into account matrix and dilution effects (Butler et al. 2007; Corley 2003; Dankyi et al. 2015; González-Curbelo et al. 2011; Lesueur et al. 2008; Mekonen et al. 2014; Nguyen et al. 2008; Shrivastava and Gupta 2011). The linearity was determined by preparing a stock solution of pure standards of the pesticides studied and diluting them to produce a concentration range. The standard solution of the pesticides was run on LC-MS/MS under the set of chromatographic conditions to produce 9-point calibrations ranking from 0.0001 mg/L to 0.01 mg/L. The recovery tests were done by spiking a mixture of 25 pesticides (Table 2) into blank samples of yam.

QuEChERS method and analyses of recovery and samples

Pesticides residue determination in food commodities by the QuEChERS method is found to produce better recoveries compared with classical techniques of liquid-liquid extraction (Mekonen et al. 2014). The modified QuEChERS method, based on the procedure by the Association of Analytical Communities official method 2007.01 (Koesukwiwat et al. 2014; Mekonen et al. 2014; Neil et al. 2007) but without the cleanup phase was adopted for the extraction of the spiked samples and blank samples of yam. The cleanup phase was skipped because the yam tuber is a relatively clean product with low fat and pigment content (Udensi 2008; Kouassi et al. 1988; Muzac-Tucker et al. 1993; USDA, 2017). The QuEChERS method is found to give high-quality results for many pesticides (Wilkowska and Biziuk 2011). The procedure for spiking and extraction was executed in 9 distinct steps as presented in Table 4.

Table 3 Chromatographic conditions of the LC-MS/MS system

HPLC Instrument	Waters ACQUITY UPLC
Column	Waters HSS T3 (1.8 μm)
Injection volume	10 μL
Oven temperature	40 °C
Mobile phase A	Water + 10 mM ammoniumacetate
Mobile phase B	Acetonitrile + 0.1% formic acid
Flow	0.4 mL/min
Gradient	0–0.25 min 2% solvent B
	0–7 min linear gradient to 98% solvent B
	7–8 min 98% solvent B
	8–9 min linear gradient to 2% solvent
	9–10 min 2% solvent B
Detector	Triple quadrupole mass spectrometer
Spectrometer	None
Interface	Electrospray ionisation
Potential	5000 V
Temperature	500 °C
Scan type	MRM (Multiple Reaction Monitoring Mode)
Collision gas	Argon

Sample extraction after preparation was done in accordance with the same QuEChERS procedure adopted for the recovery tests for the analytical method validation as described in Table 4 except for the spiking step. With a total of 180 samples from both Ghana and the Belgium markets, 10 g was weighed from each sample into a 50 mL tube using the Sartorius analytical balance. After the weighing step, steps 3 to 9 of the QuEChERS method (Table 4) were executed.

Table 4 Procedure for Spiking and Extraction

Step	Description
1	10 g of blended yam samples were weighed in 50 ml centrifuge tubes on Sartorius analytical balance.
2	Blank samples were spiked with 100 μL of mixed standard of the 25 compounds involved in 8 replicates.
3	15 mL of acetonitrile containing 1% glacial acetic acid (*v*/v) was added in each sample by using a solvent dispenser.
4	Each tube was tightly cupped and shaken for 1 min to ensure contact between the solvent and the sample matrix.
5	6 g anhydrous MgSO4, 1.5 g NaCL, 1.5 g sodium citrate tribasic dihydrate ($C_6H_2Na_3O_7$ $2H_2O$ and 0.75 g sodium hydrogen citrate ($C_6H_6Na_2O_7$ $1.5H_2O$) were added and the sample was shaken for 5 min on a mechanical shaker at 300 rpm to enhance sample throughput.
6	The samples were centrifuged at 10,000 rpm for 5 min.
7	5 mL aliquot of extract was taken into a 10 mL test tube.
8	1 mL of the aliquot of extract in the 10 mL tubes was taken into 10 mL flask and diluted to 10 mL with water.
9	1 mL extract was then transferred from the 10 mL flask into an auto sampler vial for LC-MS/MS analysis.

Data analysis

The pesticides residue data were analyzed using SPSS version 19. One sample t-test was conducted to determine the differences among the markets with regards to the number of pesticides detected and the number of samples contaminated per market.

Results and discussion

Method validation results

The QuEChERS method as adopted in this study was validated based on the performance criteria set out by the European Commission Directorate General for Health and Food Safety. These include sensitivity/linearity, percentage recoveries as a measure of trueness or bias, precision (relative standard deviation), LOD and LOQ. With regards to the method sensitivity/linearity, the calibration curves generated for the 25 pesticides were linear over a concentration range of 0.0001 mg/kg

Table 5 Method validation results in Yam matrices: recovery %, relative standard deviation, LOD, LOQ and spiked concentration (0.0007 mg/kg)

Pesticide	Recovery (%)	RSD (%)	LOD (mg/kg)	LOQ (mg/kg)
Acetamiprid	84	9	0.0005	0.0015
Azoxystrobin	114	4	0.0003	0.0009
Bentazone	95	15	0.0007	0.0020
Butachlor	89	7	0.0004	0.0012
Cadusafos	105	9	0.0005	0.0014
Carbendazim	112	18	0.0007	0.0021
Carbofuran	98	6	0.0002	0.0007
Chlorpyrifos	90	12	0.0004	0.0011
Difenconazole	94	6	0.0002	0.0007
Diuron	79	18	0.0011	0.0032
Dimethoate	104	20	0.0010	0.0030
Diazinon	96	8	0.0004	0.0012
Epoxiconazole	103	9	0.0010	0.0031
Fenpropimorph	100	6	0.0002	0.0006
Imidacloprid	74	13	0.0007	0.0022
Malathion	101	7	0.0004	0.0013
Metalaxyl	103	14	0.0009	0.0026
Pendimethalin	107	12	0.0003	0.0009
Profenofos	72	9	0.0004	0.0013
Propanil	108	14	0.0005	0.0016
Propiconazole	95	5	0.0002	0.0007
Propoxur	95	7	0.0004	0.0012
Pyrachlostrobin	99	7	0.0004	0.0011
Tryfloxystrobin	105	5	0.0002	0.0007
Fenitrothion	112	14	0.0025	0.0074

LOD limit of detection, *LOQ* limit of quantification, *RSD* relative standard deviation (%)

to 0.01 mg/kg and showed a correlation coefficient (r^2) of more than 0.9955.

The method validation result is summarized in Table 5. The recovery studies revealed that the QuEChERS method is an efficient method for multi-residue analysis of the tested pesticides in yam. The recoveries of all the 25 pesticides analyzed were well within the 70% - 120% performance criteria (Bempah and Donkor 2011; Berrada et al. 2010; Gilbert-López et al. 2010; Lesueur et al. 2008; Lozowicka et al. 2015; Mekonen et al. 2014; Nguyen et al. 2008; Osman et al. 2010) These recoveries indicate that the method used is reproducible. In terms of accuracy and precision i.e. repeatability expressed in terms of relative standard deviation (RSD, %), the 25 pesticides gave RSD varying between 4% and 20% at the spiking level.

With regards to the LOD and LOQ, the results revealed that the LOD for the 25 pesticides varied between 0.0002 mg/kg and 0.0025 mg/kg whereas the LOQ varied between 0.0006 mg/kg and 0.0074 mg/kg. This is consistent with results of previous studies in which the LOD ranged between 0.0004 mg/kg and 0.048 mg/kg while LOQ ranged between 0.0012 mg/kg and 0.05 mg/kg (Lesueur et al. 2008; Nguyen et al. 2008; Soler et al. 2005). The obtained LOD and LOQ for the tested pesticides, did fulfil the 10 μg/kg threshold required to monitor organic farming food (Lesueur et al. 2008). This result compares favourably with previous studies in which the LOD was as high as between 20 μg/kg and 115 μg/kg and LOQ was up to 400 μg/kg (Blasco et al. 2004, 2005, 2006; Soler et al. 2005; Zrostlíková et al. 2003).

Pesticides residues in yam samples

Following the validation exercise to determine the effectiveness and efficiency of the QuEChERS method for multi pesticides residue extraction from yam, the 180 yam samples were analyzed for 25 pesticides based on an initial screening of available pesticides on the Ghanaian market and in the updated pesticides register of Ghana. The analyzed pesticides included eleven insecticides (fenitrothion, propoxur, imidacloprid, malathion, profenofos, carbofuran, acetamiprid, dimethoate, cadusafos, diazinon and chlorpyrifos), nine fungicides (metalaxyl, fenpropimorph, pyrachlostrobin, propiconazole, tryfloxystrobin, carbendazim, azoxystrobin, difenconazole and epoxiconazole) and five herbicides (propanil, pendimethalin, diuron, bentazone and butachlor). Only 11 of the analyzed pesticides (Table 6) including four fungicides (metalaxyl, fenpropimorph, propiconazole and carbendazim), five insecticides (fenitrothion, cadusafos, imidacloprid, profenofos and propoxur) and two herbicides (bentazone and pendimethalin) were found in one or more than one of the yam samples.

Since interactions with players along the yam value chain from the farmer in the village through the Ghanaian market to the shops in Ghent, Belgium, indicated that no post-harvest pesticide treatment is offered to yam for preserving it, these residues cannot be attributed to direct application of the pesticides to the yam tuber. However, since yam is cultivated in a mixed cropping system and rotated with other crops in Ghana, there seems to be an important way through which these compounds could contaminate the yam. This could be on-farm contamination through foliar uptake due to spray drift or root uptake due to crop rotation, depending on the environmental fate of the pesticides involved (EXTOXNET, 1993.; Nemeth-Konda et al. 2002; Wu et al. 2002; Yule and Duffy 1972; Zheng et al. 1994). The detected pesticides, except for fenitrothion, profenofos and bentazone which are reported to degrade rapidly in the soil, have moderate to high persistence in the soil (University of Hertfordshire, PPDB). Their DT50s in soil (Table 7) vary from 2.7 days up to 191 days. Among these pesticides, benazone, metalaxyl, propoxur and imidacloprid have a high solubility (7112 mg/L, 8400 mg/L, 1800 mg/L and 610 mg/L respectively) while profenofos, fenitrothion, pendimethalin, carbendazim and fenpropimorph have a low solubility (28 mg/L, 19 mg/L, 0.33 mg/L, 8 mg/L and 4.32 mg/L respectively). Cadusafos and propiconazole have a moderate solubility of 245 mg/L and 150 mg/L respectively. With regards to volatility, cadusafos is the only pesticide among the detected pesticides with high a volatility (119.6 mPa) while the others have a low volatility ranging between 4.0 × 10−07 mPa and 3.9 mPa (University of Hertfordshire, PPDB). Under optimum soil conditions, pesticides with a higher DT50 and a moderate to a high solubility, have the tendency to be absorbed by roots of crops growing in the field and subsequent crops in crop rotations (Doan Ngoc et al. 2015; Hwang et al. 2015; Kucharski et al. 2012). Pesticides with high volatility can be absorbed by the foliar of non-target crops through spray drift and can also be taken up by crop roots under dry soil conditions. One other possible way by which the contamination could arise is through contaminated surfaces due to storage and distribution practices (Ecobichon 2001; Gerken et al. 2001; Hassink et al. 2007). The concentration of the pesticides and the respective MRLs are presented in Table 6. The results show that about 46% of the yam samples contained one or more than one of the eleven detected pesticides. Among the 11 pesticides fenpropimorph was the most frequently detected pesticide, occurring in 179 out of the 180 samples. This was followed by cadusafos and fenitrothion occurring in 171 and 126 samples respectively. Next to these, propiconazole, metalaxyl, propoxur, bentazone and carbendazim, occurred in 38, 29, 19, 6 and 2 samples respectively. The rest, including imidacloprid, pendimethalin and profenofos, occurred in only 1 sample each. These results are

Table 6 Detected Pesticides in Analyzed Yam Samples Across Ghanaian and Belgian Markets

Pesticides	No of samples/30	EU MRL (mg/kg)	Min (mg/kg)	Average (mg/kg)	Median	95th percentile	Max (mg/kg)
Accra Market, Ghana							
metalxyl	1/30	0.05*	0.0003**	0.0003**	0.0003**	0.0003**	0.0003**
fenpropimorph	30/30	0.01*	0.00001	0.0001	0.00011	0.0002	0.003
propiconazole	4/30	0.01*	0.0003**	0.0003**	0.0003**	0.0003**	0.0003**
cadusafos	30/30	0.01*	0.00001	0.00014	0.00015	0.00019	0.0002
fenitrothion	10/30	0.01*	0.0003	0.0022	0.0016	0.0053	0.0065
Kintampo Market, Ghana							
propoxur	6/30	0.05*	0.00002	0.00003	0.00003	0.00004	0.00004
metalaxyl	3/30	0.05*	0.0003**	0.0003**	0.0003**	0.0003**	0.0003**
fenpropimorph	30/30	0.01*	0.00003	0.00018	0.00014	0.00043	0.00081
propiconazole	9/30	0.01*	0.00001	0.000018	0.00002	0.00003	0.00004
bentazone	1/30	0.03*	0.0002**	0.0002**	0.0002**	0.0002**	0.0002**
cadusafos	30/30	0.01*	0.00006	0.0001	0.00015	0.000095	0.00019
profenofos	1/30	0.01*	0.0005**	0.0005**	0.0005**	0.0005**	0.0005**
fenitrothion	14/30	0.01*	0.0003	0.0086	0.0087	0.0015	0.0016
Kumasi Market, Ghana							
propoxur	4/30	0.05*	0.0001**	0.0001**	0.0001**	0.0001**	0.0001**
metalaxyl	9/30	0.05*	0.00001	0.00002	0.00001	0.00007	0.0001
fenpropimorph	30/30	0.01*	0.00004	0.00017	0.00011	0.00055	0.0006
propiconazole	8/30	0.01*	0.0003**	0.0003**	0.0003**	0.0003**	0.0003**
bentazone	4/30	0.03*	0.00031	0.00083	0.0008	0.00014	0.00144
cadusafos	30/30	0.01*	0.00003	0.000072	0.00007	0.00011	0.00012
imidacloprid	1/30	0.5	0.0004**	0.0004**	0.0004**	0.0004**	0.0004**
fenitrothion	29	0.01*	0.0001	0.0019	0.0012	0.0062	0.0092
pendimethalin	1/30	0.05*	0.0003**	0.0003**	0.0003**	0.0003**	0.0003**
Takoradi Market, Ghana							
propoxur	2/30	0.05*	0.0001**	0.0001**	0.0001**	0.0001**	0.0001**
metalaxyl	2/30	0.05*	0.0003**	0.0003**	0.0003**	0.0003**	0.0003**
fenpropimorph	30/30	0.01*	0.00003	0.00012	0.0001	0.0003	0.0004
propiconazole	1/30	0.01*	0.0003**	0.0003**	0.0003**	0.0003**	0.0003**
cadusafos	24/30	0.01*	0.00003	0.00012	0.0001	0.0003	0.0004
fenitrothion	15/30	0.01*	0.0008	0.0034	0.0025	0.0096	0.0111
Tamale Market, Ghana							
metalaxyl	7/30	0.05*	0.0003**	0.0003**	0.0003**	0.0003**	0.0003**
fenpropimorph	29/30	0.01*	0.00001	0.00008	0.00004	0.00027	0.00041
propiconazole	3/30	0.01*	0.0003**	0.0003**	0.0003**	0.0003**	0.0003**
carbendazim	1/30	0.1*	0.0004**	0.0004**	0.0004**	0.0004**	0.0004**
bentazone	1/30	0.03*	0.0002**	0.0002**	0.0002**	0.0002**	0.0002**
cadusafos	27/30	0.01*	0.00005	0.000102	0.00009	0.00018	0.00019
fenitrothion	28/30	0.01*	0.0002	0.0025	0.0013	0.0068	0.0085
Ghent Market, Belgium							
propoxur	7/30	0.05*	0.00003	0.00004	0.0005	0.00006	0.00007
metalxyl	7/30	0.05*	0.0003**	0.0003**	0.0003**	0.0003**	0.0003**
fenpropimorph	30/30	0.01*	0.00005	0.00013	0.00013	0.00024	0.00033

Table 6 Detected Pesticides in Analyzed Yam Samples Across Ghanaian and Belgian Markets *(Continued)*

Pesticides	No of samples/30	EU MRL (mg/kg)	Min (mg/kg)	Average (mg/kg)	Median	95th percentile	Max (mg/kg)
propiconazole	13/30	0.01*	0.0001	0.000014	0.00001	0.00002	0.00002
carbendazim	1/30	0.1*	0.0004**	0.0004**	0.0004**	0.0004**	0.0004**
cadusafos	30/30	0.01*	0.00005	0.00009	0.000085	0.00012	0.00014
fenitrothion	30/30	0.01*	0.0009	0.0039	0.0032	0.0099	0.0146

MRL Maximum Residue Limit
**= *LOD value from validation*
*= *EU MRL default value*

consistent with previous studies in Ghana in which residues of propoxur and carbendazim were detected in crop produce at levels below the EU MRLs (Aboagye and E. 2002; Apau and Dodoo 2011; Samuel et al., 2012). Among the markets from which the yam samples were obtained, the market at Accra recorded the least number of pesticides found with only 5 pesticides, followed by Takoradi with 6 pesticides. The Tamale and Ghent markets recorded 7 pesticides each, while Kintampo and the Kumasi markets recorded 8 and 9 pesticides respectively. There was significant difference ($P < 0.05$) among the markets with regards to the number of samples contaminated by the pesticides. The Takoradi and Kintampo markets had the least number of samples contaminated (12 samples respectively). These were followed by the Kumasi, Tamale and Accra markets with 13, 14 and 15 samples respectively contaminated. The market in Ghent had the highest number of samples contaminated (17).

With regards to the concentration of the detected pesticides across the sample markets, there was significant difference ($P < 0.05$) among the markets. The differences notwithstanding, it was observed that the residues of the detected pesticides were very low. The concentration of each of the pesticides except fenitrothion was lower than 0.01 mg/kg. These levels of residues indicate contamination of the yam tubers through other sources other than treatment by pesticides.

Table 7 Properties of Detected Pesticides

Pesticide	DT50 Soil (days)	Solubility (mg/L)	Volatility (mPa)
bentazone	20	7112	0.017
carbendazim	40	8	0.098
cadusafos	38	245	119.6
fenitrothion	2.7	19	0.67
fenpropimorph	35	4.32	3.94
imidacloprid	174	610	4.0×10^{-07}
metalaxyl	36	8400	0.75
pendimethalin	182	0.33	3.34
profenofos	7	28	1.53
propiconazole	72	150	0.056
Propoxur	79	1800	1.3

DT50 Half-life of pesticides in soil

When compared with the EU MRL as provided by the European Commission, all the detected pesticides had their concentrations far below their respective MRL for yam. The MRLs as reported in Table 6, except for imidacloprid, are default values. This means that no study was conducted for them in yam hence the authorities decided to use default values of 0.01 mg/kg and 0.05 mg/kg as their default MRLs. This is consistent with previous studies in which pesticides were detected in a whole food basket including yam at concentrations below the MRLs (Adeyeye and Osibanjo 1999; Asiedu 2013; Bempah and Donkor 2011; Kolani et al. 2016; Yang et al. 2016). Other studies show similar results (Blasco et al. 2006; Lozowicka et al. 2015; Osibanjo and Adeyeye 1995; Su et al. 2003).

Besides the EU Commission MRL, the Codex Alimentarius MRL was another international food safety standard limits that the residues as observed in this study were supposed to be compared with. Unfortunately, at the time of the study there was no MRL for yam on the Codex Alimentarius maximum residue limit database.

Conclusion

The modified QuEChERS method has proved to be effective for the analysis of pesticides residues in yam. Eleven out of 25 pesticides monitored were detected in about 46% of the yam samples collected from Ghana and Belgium markets. Samples showed contamination of one or more of the eleven different pesticides. However, none of the pesticides detected in the yam samples exceeded the MRL set for yam by the European Commission Directorate General for Health and Food Safety. For now, the Ghana yam can be regarded as wholesome food commodity which may not pose any threat to human health. There were no codex alimentarius MRL values for yam. Hence, we recommend that codex alimentarius should establish maximum residue limits for yam. We also recommend that the government should provide enough resources to the regulatory authorities to do effective monitoring to ensure that pesticides are handled according to industry best practices. Specifically, education programmes on how to

avoid storage contamination and drift issues in mixed cropping systems should be instituted.

Abbreviations

CE: Collision Energy; CV: Cone Voltage; ESI: Electron Spay Ionization; EU: European Union; eV: Electric Volt; GETfund: Ghana Education Trust Fund; HPLC: High Performance Liquid Chromatography; LC-MS/MS: Liquid Chromatography Tandem Mass Spectrometry; MRL: Maximum Residue Limit; QuEChERS: Quick, Easy, Cheap, Efficient, Rugged and Safe; UPLC: Ultra Performance Liquid Chromatography

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Availability of data and materials

The data supporting our findings have been attached as Additional files.

Authors' contributions

Each of the authors made a significant contribution to the research. The corresponding author (Abukari Wumbei) has been involved from sample collection through sample preparation, extraction, drafting of the manuscript to the submission of the manuscript. David Senaeve and Michael Houbraken handled the analysis of the samples and contributed to the drafting of the manuscript. Pieter Spanoghe as the promoter of the research, provided the overall direction and guidance to the team right from the conception of the research to the submission of the manuscript. All authors read and approved the final manuscript.

Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Competing interests

We declare that none of us, the authors have any competing interests as far as the submission of this paper is concerned.

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