Food and Chemical Toxicology 46 (2008) 3703–3706

Contents lists available at ScienceDirect

Food and Chemical Toxicology

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

Dietary intake of organophosphorus pesticide residues through vegetables from Kumasi, Ghana

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ARTICLE INFO

Article history:
Received 17 May 2008
Accepted 22 September 2008

Keywords:
ADI
Gas chromatography
Hazard index
MRL
Organophosphorus pesticides
Vegetables

ABSTRACT

Contamination and health risk hazards of organophosphorus pesticides residues in vegetables were studied. Ethyl-chlorpyrifos, observed at an average level of 0.211 ± 0.010 mg kg^{-1} in 42% of tomato, 0.096 ± 0.035 mg kg^{-1} in 10% of eggplant and 0.021 ± 0.013 mg kg^{-1} in 16% of pepper was below the 0.5 mg kg^{-1} MRL. Dichlorvos was the most frequently detected residue in all the samples analyzed. Levels of malathion in tomatoes (0.120 ± 0.101 mg kg^{-1}) and pepper (0.143 ± 0.042 mg kg^{-1}) exceeded the MRL of 0.1 mg kg^{-1}. Health risks were found to be associated with methyl-chlorpyrifos, ethyl-chlorpyrifos, and omethioate in tomatoes and methyl-chlorpyrifos, ethyl-chlorpyrifos, dichlorvos, monocrotophos and omethioate in eggplant. Routine monitoring of these pollutants in food items is required to prevent, control and reduce the pollution and to minimize health risks.

1. Introduction

Organophosphate pesticides (OP) are widely used in agriculture and animal production for the control of various insect pests in many developing countries like Ghana. Most OP are only slightly soluble in water and high oil–water partition coefficients and a low vapour pressures (WHO, 1986). Majority of OP are liquids of comparatively low volatility, (except dichlorvos), and they all undergo degradation by hydrolysis, yielding non-toxic, water-soluble products. Toxic hazards of OP are therefore essentially short-term in contrast to that of the persistent organochlorine pesticides. Organophosphorus pesticides however have higher acute toxicities than chlorinated pesticides but they have an advantage of being more rapidly degraded in the environment. Their toxicological effects are mostly due to the inhibition of acetylcholinesterase in the nervous system, resulting in respiratory, myocardial and neuromuscular transmission impairment (Goh et al., 1990).

WHO/FAO (1990) estimated an annual worldwide total of 3 million cases of acute and severe pesticide poisoning with some 220,000 deaths. The majority of these cases of poisoning and deaths occur in the developing countries, although far greater quantities of pesticides are used in the developed countries (Bhanti et al., 2004). Recent data reveals that the largest proportion of human acute toxicity of pesticides is due to organophosphorus pesticides (Ecobichon, 2001).

Acute toxic effects of pesticides on animals and humans are fairly easily recognized, but the effects that result from long-term exposure to low doses are often difficult to distinguish. In particular, the effects of a regular intake of pesticide residues in food are hard to detect and quantify. An exposure or risk assessment is necessary in order to ascertain the effects due to regular intake of pesticide residues in food.

Several indices of residue levels can be used to predict pesticide residue intake. The Maximum Residue Limits (MRL) is one such index and represents the maximum concentration of a pesticide residue (mg/kg) that the Codex Alimentarius Commission recommends be legally permitted in food commodities and animal feeds. The Acceptable Daily Intake (ADI) which is the estimated amount of a substance in food (expressed on a body-weight basis) that can be ingested daily over a lifetime without appreciable health risk to the consumer could also be used to predict the dietary intake of pesticide residues. The estimated dietary intake of a pesticide residue in a given food is obtained by multiplying the residue level in the food by the amount of that food consumed. The Estimated Average Daily Intake (EADI) of pesticide residues should be less than its established ADI (WHO, 1997).

Ghanaians rely extensively on OP for pest control and disease vector eradication (Clarke et al., 1997). Some of these toxic chemicals are either completely banned or are allowed for restricted use only. Management and regulation of these chemicals in developing countries are, however, often inadequate due to lack of resources, weak import controls, poor storage and stock management, lack

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doi:10.1016/j.fct.2008.09.049

of training and education on appropriate pesticide use and widespread misuse of pesticides (Waichman et al., 2007). Due to high demand for farm produce and low perception of the toxic effects of pesticide residues in food (Amoah et al., 2006; Bhanti and Taneja, 2007) some farmers do not wait long enough for the residues to wash off after spraying before harvesting. Increased use of OP in agriculture has therefore resulted in the occurrence of residues and metabolites in food commodities.

Research data available have indicated the presence of organochlorine pesticide residues in dairy products, meat (Darko and Acquaah, 2007, 2008) fish, water, sediments (Darko et al., 2008) and in human blood and breast milk (Ntow, 2001) in Ghana. No published data is, however, available on the levels of OP residues in the biota. This work, therefore, seeks to provide the baseline information on contamination levels of OP pesticide residues in vegetables found on the Ghanaian market and to elucidate their hazard indices. Because pesticide residues in food constitute a significant health risk, their continuous monitoring and control in food items is of great importance.

2. Materials and methods

Pesticide residue grade of acetonitrile (99.5%) and ethylacetate (99.8%) were purchased from BDH. Organophosphorus pesticides standards (methyl-chlorpyrifos, ethyl-chlorpyrifos, dichlorvos, dimethoate, monocrotophos, omethioate, methyl-parathion and ethyl-parathion) were purchased from Ehrenstorfer GmbH (Augsburg, Germany) in sealed vials. Glassware were washed with detergent, rinsed with distilled water and acetone and were heated to 180 °C for 2 h. Standard solutions were prepared in ethylacetate and stored at 4 °C in a refrigerator.

A total of 50 samples each of tomatoes, eggplant, and pepper were collected randomly from Kumasi Central Market between the periods of May–July 2006 and December 2006–March 2007. Samples collected were immediately wrapped in aluminum foil, placed in an ice-chest kept at 4 °C and sent to the laboratory for analysis. In the laboratory, similar samples were wholly bulked together and ground in a waring blender to obtain a homogenous composite.

Two grams of each ground sample was weighed in a 10 mL screw-capped tube, 5 mL of acetonitrile was added and, after agitation in a rotatory shaker for 15 min, the acetonitrile layer was allowed to separate and then removed by decantation. Two other extractions were made. The combined acetonitrile phase was centrifuged for 2 min at 3000 rpm and the supernatant carefully transferred in a graduated vial. The extracts were concentrated to about 2 mL using a Buchi rotary evaporator operating at temperature of 30 °C at a reduced pressure (Bhanti and Taneja, 2007; Chun and Kang, 2003). Internal standard was added and the extract was made up to 2 mL with acetonitrile before GC injection.

A Shimadzu Gas Chromatograph, GC-9A, equipped with a flame photometric detector, CR-7A integrator, DB-1 (methyl polysiloxane) and DB-17 (50% phenyl, 50% methyl polysiloxane) wide-bore capillary columns (30 m × 0.53 mm ID × 1.5 μm film thickness) was used for the analyses. The gas chromatographic analysis was performed under the following conditions: detector temperature was 250 °C, injector temperature was 250 °C and column temperature was 200 °C (isothermal). Carrier gas was helium at a flow rate of 17 ml min^{-1}. One microliter (splitless) of sample was injected into the GC in the phosphorus mode (Saeed et al., 2005).

Untreated samples were fortified at 0.001 mg kg^{-1} by adding standard pesticide solutions. The samples were allowed to equilibrate for 30 min prior to extraction. After extraction and solvent evaporation, the samples were analyzed according to the proposed method. The recovery values were calculated from calibration curves constructed from the concentration and peak areas of the chromatograms obtained with standards of the OP (Table 1). Detection limits of the method were found by determining the lowest concentrations of the residues in each of the matrices that could be reproducibly measured at the operating conditions of the GC using a signal-to-noise ratio of three (Table 1). Blank analyses were also performed in order to check interference from the sample. All analyses were carried out in triplicates and the mean concentrations were calculated based on the number of samples that tested positive to each sample.

3. Results and discussion

The mean recoveries for the residues ranged from 88% for methyl-parathion in tomatoes to 105% for dichlorvos in eggplant (Table 1). These recovery values show that the method used is reproducible. Detection limits ranged from 0.001 mg kg^{-1} to 0.015 mg kg^{-1} indicates that the GC at its operation conditions was sensitive to the analytes (Araoud et al., 2007; Gilvydis and Walter, 1999). Repeatability studies yielded a relative standard deviation lower than 10% in all cases (Table 2).

Ethyl-chlorpyrifos was detected at an average concentration of 0.211 ± 0.010 mg kg^{-1} in 21 out of 50 (42%) of tomato samples analyzed. This level of ethyl-chlorpyrifos determined is less than the 0.5 mg kg^{-1} MRL set by the WHO (FAO/WHO, 1993). The average level of ethyl-chlorpyrifos measured in 10% of eggplant samples analyzed was 0.096 ± 0.035 mg kg^{-1} while it occurred at a mean of 0.021 ± 0.013 mg kg^{-1} in 16% of pepper samples.

Methyl-chlorpyrifos occurred in 30% of tomatoes and 8% of eggplant. It was however not detected in any of the pepper samples. The mean concentrations of methyl-chlorpyrifos obtained were 0.160 ± 0.091 mg kg^{-1} and 0.028 ± 0.014 mg kg^{-1} in tomatoes and eggplant, respectively. These levels observed are below the MRL of 0.5 mg kg^{-1} for tomatoes, 0.1 mg kg^{-1} for eggplant and 0.5 mg kg^{-1} for pepper.

Dichlorvos was the most frequently detected residue in all the samples. It occurred at a mean concentration of 0.022 ± 0.013 mg kg^{-1} in 48% of tomato, 0.151 ± 0.035 mg kg^{-1} in 42% of eggplant and 0.090 ± 0.063 mg kg^{-1} in 26% of pepper samples analyzed.

Malathion occurred in 32% of tomato sample at an average concentration 0.120 ± 0.101 mg kg^{-1}. In the eggplant, the level of malathion was 0.298 ± 0.089 mg kg^{-1} whilst it occurred at a mean concentration of 0.143 ± 0.042 mg kg^{-1} in pepper. Levels of malathion in tomatoes and pepper exceeded the MRL of 0.1 mg kg^{-1}.

Monocrotophos was detected in two samples each of tomatoes and eggplant at mean concentrations of 0.063 mg kg^{-1} ± 0.022 and 0.060 ± 0.022 mg kg^{-1}, respectively. It was however, not detected in any of the pepper samples analyzed.

Methyl-parathion was detected in five samples each of tomatoes and eggplant and in eight of pepper samples. The average concentrations of methyl-parathion were 0.021 ± 0.013 mg kg^{-1} in

Table 1
Mean recovery of blank samples spiked with various OP standards of samples examined in this study ($n = 5$)

	Tomatoes			Eggplant			Pepper		
	Recovery (%)	RSD (%)	LD (mg kg^{-1})	Recovery (%)	RSD (%)	LD (mg kg^{-1})	Recovery (%)	RSD (%)	LD (mg kg^{-1})
Methyl-chlorpyrifos	91	7	0.008	90	11	0.002	94	7	0.005
Ethyl-chlorpyrifos	94	4	0.005	94	6	0.006	93	1	0.002
Dichlorvos	89	3	0.003	92	9	0.001	91	6	0.005
Dimethoate	99	5	0.002	105	7	0.005	98	3	0.004
Malathion	96	2	0.001	94	3	0.005	97	2	0.005
Monocrotophos	102	4	0.001	99	5	0.005	96	8	0.003
Omethioate	98	4	0.009	96	8	0.008	95	5	0.005
Methy-parathion	88	6	0.006	90	6	0.006	96	10	0.004
Ethyl-parathion	93	3	0.008	92	4	0.005	91	2	0.002

RSD = relative standard deviation.
LD = limits of detection.

Table 2
OP pesticide levels detected in vegetable samples obtained from Kumasi market, Ghana

	MRL (mg kg^{-1})	Tomatoes ($n = 50$)				Eggplant ($n = 50$)				Pepper ($n = 50$)			
		Mean (mg kg^{-1})	SD	Range (mg kg^{-1})	(%)	Mean (mg kg^{-1})	SD	Range (mg kg^{-1})	(%)	Mean (mg kg^{-1})	SD	Range (mg kg^{-1})	(%)
Methyl-chlorpyrifos	0.5[a,c] 0.1[b]	0.160	0.091	0.044–0.524	30	0.028	0.014	0.015–0.084	8	–	–	–	–
Ethyl-chlorpyrifos	0.5[a]	0.211	0.010	0.171–0.251	42	0.096	0.035	0.065–0.236	10	0.021	0.013	0.001–0.039	16
Dichlorvos	NA	0.022	0.013	0.044–0.274	48	0.151	0.035	0.120–0.291	42	0.090	0.063	0.001–0.213	26
Dimethoate	1[c]	0.250	0.182	0.228–0.978	42	0.210	0.053	0.162–0.422	26	0.160	0.010	0.011–0.244	18
Malathion	0.1[a,c]	0.120	0.101	0.074–2.620	32	0.298	0.089	0.176–0.340	18	0.143	0.042	0.093–0.218	24
Monocrotophos	NA	0.063	0.011	0.019–0.107	12	0.060	0.022	0.040–0.148	2	–	–		–
Omethioate	NA	0.012	0.016	0.040–0.076	36	0.110	0.062	0.054–0.358	16	0.001	0.001	0.001–0.036	20
Methyl-parathion-methyl	NA	0.021	0.013	0.010–0.073	10	0.041	0.001	0.031–0.058	12	0.018	0.011	0.013–0.068	16
Ethyl-parathion	NA	0.081	0.034	0.026–0.217	16	0.061	0.021	0.042–0.145	10	0.089	0.005	0.061–0.264	12

LD = below detection.
SD = standard error of mean.
NA = MRL not available for commodities analyzed.
[a] MRL of OP in tomato.
[b] MRL of OP in eggplant.
[c] MRL of OP in pepper.

Table 3
Reported organophosphorus residues levels in Egyptian vegetables during 1997 (Dogheim et al., 2002)

	Tomatoes		Eggplant		Pepper	
	Mean (mg kg^{-1})	Range (mg kg^{-1})	Mean (mg kg^{-1})	Range (mg kg^{-1})	Mean (mg kg^{-1})	Range (mg kg^{-1})
Methyl-chlorpyrifos	0.16	0.09–0.47				
Ethyl-chlorpyrifos	0.20	0.23–0.26			0.47	0.04–1.30
Dimethoate			0.07	0.07–0.07	0.50	0.05–3.20
Malathion	0.31	0.31–031			0.90	0.05–0.13

tomatoes, 0.041 ± 0.001 mg kg^{-1} in eggplant and 0.018 ± 0.011 mg kg^{-1} in pepper samples. Ethyl-parathion was detected at mean concentrations of 0.081 ± 0.034 mg kg^{-1} in 16% of tomato samples, 0.061 ± 0.021 mg kg^{-1} in 10% of eggplant and 0.089 ± 0.005 mg kg^{-1} in 12% of pepper samples. These levels of ethyl-parathion and methyl-parathion observed are higher than the 0.006 mg kg^{-1} ethyl-parathion and 0.003 mg kg^{-1} methyl-parathion in vegetables recorded in a similar study in China (Bai et al., 2006). Levels of ethyl-parathion were higher than its metabolite, methyl-parathion in all the vegetable types. Similar trends were observed between ethyl-chlorpyrifos and methyl-chlorpyrifos, and also dimethoate and omethoate. This may be an indication that the residues detected are as result of current and/or continuous usage of the pesticides.

No MRL is yet established for dichlorvos, monocrotophos, omethioate, methyl-parathion and ethyl-parathion in vegetables (tomato, eggplant and pepper) analyzed.

Table 3 reports the levels of OP residues measured in vegetables surveyed from eight Egyptian markets in 1997 (Dogheim et al., 2002). Except for dimethioate in eggplant, all OP residues measured in that survey were generally higher than those reported in this work. Also, levels of all the residues (except for ethyl-parathion and methyl-parathion) obtained in this survey were higher than those obtained from a similar survey on Danish market during 2000–2001 (Poulsen and Andersen, 2003). This is the usual trend expected between samples from developed nations (like Denmark) and developing one (like Ghana).

Health risk indices of the residues were computed using the data obtained and food consumption assumptions. FAO (2003) quotes the per capita food consumption rate in Ghana as 13.56 kg yr^{-1}, 17.27 kg yr^{-1} and 0.12 kg yr^{-1}, respectively for tomatoes, eggplant and pepper.

Estimated Average Daily Intake (EADI) was found by multiplying the average residual pesticide concentration (mg kg^{-1}) by the food consumption rate (kg day^{-1}). Estimated the hazard indices were obtained by dividing the EADI (mg kg^{-1} day^{-1}) by their corresponding values of WHO/FAO acceptable daily intakes, ADI (WHO, 1997).

Table 4
Health risk assessment based on average daily intake of pesticide residues in vegetables

	WHO/FAO ADI (mg kg^{-1}day^{-1})	Tomatoes		Eggplant		Pepper	
		EADI (mg kg^{-1} day^{-1})	Hazard index	EADI (mg kg^{-1} day^{-1})	Hazard index	EADI (mg kg^{-1} day^{-1})	Hazard index
Methyl-chlorpyrifos	0.001	0.0060	5.960	0.0013	1.328	0.0000	0.000
Ethyl-chlorpyrifos	0.001	0.0079	7.860	0.0046	4.555	0.0000	0.007
Dichlorvos	0.004	0.0008	0.205	0.0072	1.791	0.0000	0.007
Dimethoate	0.01	0.0093	0.931	0.0100	0.996	0.0001	0.005
Malathion	0.02	0.0045	0.224	0.0141	0.707	0.0000	0.002
Monocrotophos	0.0006	0.0023	3.912	0.0028	4.745	0.0000	0.000
Omethioate	0.0003	0.0004	1.490	0.0052	17.397	0.0000	0.001
Methly-parathion	0.02	0.0008	0.039	0.0019	0.097	0.0000	0.000
Ethyl-parathion	0.005	0.0030	0.603	0.0029	0.579	0.0000	0.006

Table 4 contains the average daily intake values of the residues and their corresponding hazard indices in the three sample types. Health indices of methyl-chlorpyrifos (5.960), ethyl-chlorpyrifos (7.860), omethioate (1.490) in tomatoes were more than unity. Similarly, the health indices of methyl-chlorpyrifos (1.328), ethyl-chlorpyrifos (4.555), dichlorvos (1.791), monocrotophos (4.745) and omethioate (17.397) in eggplant were more than one. Thus, lifetime consumption of tomatoes and eggplant from Kumasi Market could pose some health risks due the levels of OP residues present in them. No health hazard was found associated with the consumption of pepper as the indices for all the residues in pepper were less than one.

The results underline that OP residues are present in vegetables on Kumasi Market and that routine monitoring of these pollutants in food items is required to prevent, control and reduce the pollution and to minimize health risks. This research has provided important information on OP residues contamination on vegetables from Kumasi for the first time.

Conflict of interest statement

The authors declare that there are no conflicts of interest.

Acknowledgement

The authors would like to express their profound appreciation to Prof. Kurunthachalam Kannan (Environmental Health Sciences, Wadsworth Center, State Department of Health, USA) and Dr. Maria Teresa Baeza Romero (School of Earth and Environment, University of Leeds, England), for their support in various forms towards execution of this project.

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