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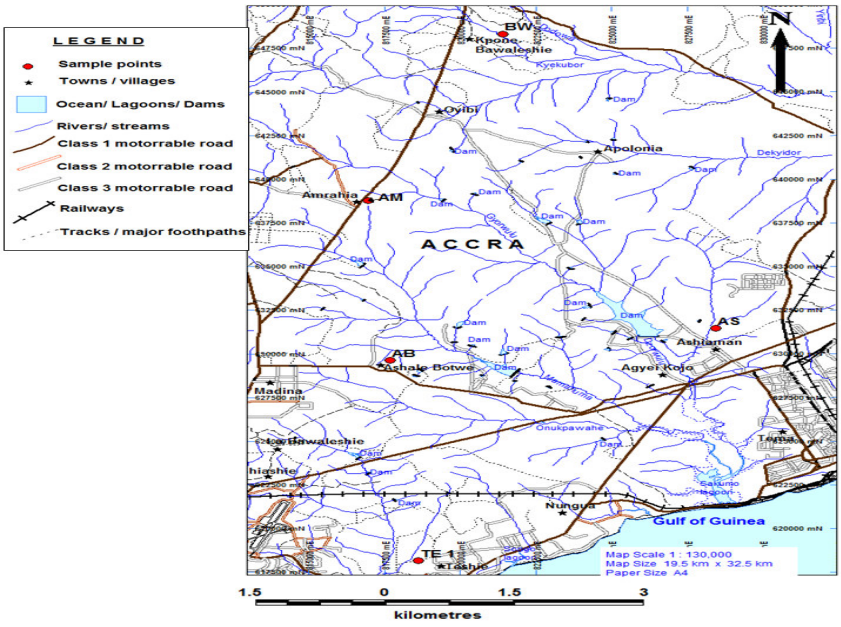
Health Risk Assessment of Organochlorine Pesticides Contaminations in Dairy Products from Selected Farms in Greater Accra Region-Ghana

D. Amoako, J.R. Fianko, S. Adu-Kumi, J.Pwamang J. Senu, E. O. Assibey, R. N. Odai, L. Kwarteng, W.K.Ahialey, B.K Augustt.
School of Nuclear and Allied Sciences, University of Ghana,
Department of Nuclear Sciences and Applications, Faculty of Science, P.O. Box LG 80, Legon-Accra, Ghana,
Environmental Protection Agency, Acccra-Ghana

Abstract:
The study was geared towards ascertaining the levels of synthetic pyrethroids and organochlorine pesticides residues in dairy products(milk, cheese and yoghurt) from selected farms in Greater Accra Region of Ghana. In all fifty (50) samples of dairy products (25 fresh cow milk, 9 cheese and 16 yoghurt) were analyzed. Detectable levels of organochlorine pesticides,OCPs(β-HCH, endrin, endosulfan, p'p'-DDT, heptachlor and methoxychlor) and Synthetic pyrethroids(permethrin, allethrin, cypermethrin, deltamethrin and cyfluthrin).
Ultrasonic extraction was employed and extract clean-up was done using silica gel and analyzed using a gas chromatograph (Agilent Model 6890 Gas Chromatograph) equipped with Ni-63 electron capture detector (ECD). . Milk samples were found to be the most contaminated with respect to the OCPs and the levels ranged between 0.0001µg/ml and 0.0407µg/ml. β-HCH was the highest OCP with concentration of 0.0407µg/ml while Cyfluthrin was the highest synthetic pyrethroids recorded in yoghurt sample (0.0318µg/ml).The levels of organochlorine pesticide residues detected in all the tissues were below the accepted Maximum Residue Limits (MRL), as adopted by the WHO/FAO Codex Alimentarius Commission (2005).
Keywords: dairy products, organochlorine pesticides, synthetic pyrethroid, health risk, Ghana, gas chromatography

INTRODUCTION

The drastic increase in population and technological advancement has significantly resulted in high production of synthetic chemicals and the subsequent release of contaminants into the environment. The extensive use of pesticides to control pest in farm animals has been in practice in Ghana for over 40years (Ntow *et al.*, 2005). Pesticides are extremely important because of their potential impact on human health and agriculture production. Without pesticides the quality and quantity of food production will diminish. It has been used to meet the food security and survival from disease vector organisms. Recently, attention has been drawn to the significant high amount of residues of synthetic pesticides (OCPs) present in cow milk and invariably greater proportion also get into human milk. Humans are on top of the food chain and they accumulate these lipophilic chemicals in their body fat mainly through intake of contaminated food (Ahlborg *et al*., 1992) There is empirical evidence of higher concentrations of OCPs residues in fatty foods including milk (Leng *et al.,* 2009).. OCPs residues bio-accumulates in the fatty tissues of exposed animals and humans, and may be responsible for a wide variety of health effects.The Organochlorine pesticides (OCPs) constitute about 35% of pesticides used in organized farms and kraals in Ghana.(Awumbila, B., and Bokuma, E., 1994). The increased higher application of pesticides has resulted in food contaminations (Wilson *et al.,* 2007). Earlier studies in Ghana indicated the presence of pesticide residues in water, sediment, vegetables, fruits, fish and soil at locations unknown for pesticide usage (Aboagye, 2002: Amoah *et al.*, 2006; Mensah *et al.*,2004; Osafo *et al*., 1998). Severe health effects are associated with exposure to pesticides in food. They are a major source of morbidity, mortality and increased risk of skin cancer, destruction of neurological cellular functions, chronic neurotoxicity, bladder and lung cancer even at very low concentrations (Mensah *et al.,* 2004; Sun *et al.*, 2006).



MATERIALS AND METHOD

Study Area: The study area is located in the Greater- Accra Region of Ghana and lies between latitude $5^0$33'00 "N and longitude $0^0$12'00 "E. (Fig 3.1). There are three broad vegetation zones in the area, which comprise shrub land, grassland and coastal lands. The average annual rainfall is about 730 mm, which falls primarily during the two rainy seasons (first season May-July and second season August-October). The mean monthly temperature ranges from 24.7°C in August (the coolest) to 28°C in March (the hottest) with annual average of 26.8°C. The predominant wind direction in the area is from the WSW to NNE sectors with maximum wind speed record of 107.4 km/hr (58 knots). The geology of the study area consists of Precambrian Dahomeyan schists, granodiorites, granites gneiss and amphibolites to late Precambrian Togo series comprising mainly quartzite, phillites, phylitones and quartz breccias. It is muddy, undulating, flatland in some areas and other parts hilly.

Chemicals and Reagent: Organic solvents were purchased from Dr Ehrenstorfer Augsberg, Germany. All solvents used were of high purity for high-performance liquid chromatography (HPLC): ethanol (Absolute), anhydrous sodium sulphate, dichloromethane, Acetonitril and hexane were used for sample extraction. Silica gel was used for sample clean-up (70-230 mesh cleaning agent)

Preparation of Silica gel: 150g of 70 to 100 mesh silicagel was put into a glass beaker and later placed in an oven at 120^{o}C overnight. It then cooled and stored in a dessicator, 2g of the activated silica gel was weighed and poured into a column which has been plugged with glass wool followed by 2g of anhydrous sodium sulphate.

Equipments: Sonicator, column chromatography, rotary evaporator Buchi RE-200 equipped with Buchi B740 re-circulating water chiller and Buchi V700 vacuum pump (BÜchi Labortechnic AG Postfach, weighing balance, gas chromatography (Agilent Model 6890) equipped with 63Ni electron capture detector (ECD), centrifuge, weighing balance, pulveriser.

Sampling: Two hundred and seventy six (276) lactating cows from different geographical locations within the study area (Amrahia(AM), Ashaley Botwe(AB), Ashaiman(AS), Bawaleshie(BW) and Teshie(TE) were used for the study. In all, fifty(50) dairy products samples were collected, and this was made up of nine (9) locally manufactured cheese(wagashe), twenty five (25) cow milk and sixteen (16) yoghurt samples.

Fresh cow milk samples were manually and randomly collected from healthy lactating cow on the farm at about 6 o'clock in the morning following sampling protocol as described by Ennaceur *et al.,*2007. The individual cow milk from a kraal was pooled into cleaned container and mixed thoroughly. About 50 ml of the milk were then transferred into well conditioned and labelled 100 ml glass bottles, sealed with aluminum foil and tightly covered with their lids. Yoghurt and cheese samples were collected fresh from the manufacturers before packaging. Conditioned glass bottles were used for the yoghurt samples, while the cheese samples were wrapped in aluminum foil. The samples were carried on ice in an ice cooler from the field to the laboratory and stored in a refrigerator at -20^{0}C prior to analysis.

Sample Extraction: The stored milk and yoghurt samples were left to defrost at ambient temperature and homogenized while the cheese samples were pulverized using mechanical pulveriser. The pulverised cheese samples were then freeze dried for a maximum of 72 hours. 20 g of freeze- dried cheeses samples, 10mL each of milk and yoghurt samples were used for the extraction process. 20 g of anhydrous sodium sulphate was added to

the cheese samples prior to the extraction. To each sample in different extraction bottles were added 26 ml of n-hexane/acetonitrile/ ethanol (20: 5: 1 v/v) mixture after which they were shaken gently to obtain a uniform mixture. The sample mixtures were then put into a sonicator at a frequency of 50 Hz for 1hour after which they were allowed to separate into the various layers. The organic phase was decanted into a previously weighed round bottom flask and covered with aluminium foil. The extraction process was repeated three times and the combined organic phase for each sample concentrated to about 5 ml using rotary evaporator. The organic phase was subsequently subjected to a clean-up process. The pesticides trapped in the cartridges were eluted with 6 ml (2 x 3 ml) ethyl acetate. The sample extract was concentrated using the rotary evaporator aided with a water chiller to 2 ml for GC analysis.

Sample Clean – up

The extracts of each sample were subjected to a clean – up process using a 25 cm chromatographic column whose internal diameter was 1 cm. The column was packed with 2 g activated silica gel and topped with 2 g anhydrous sodium sulphate and conditioned with 10 ml hexane. Then each extract was percolated through the column and eluted with 30 ml (3 x 10 ml) dichloromethane and n-hexane mixture (1: 9 ; v/v). The eluate was evaporated in a rotary evaporator to near dryness (0.5 ml) and recovered using 2 ml ethyl acetate for GC analysis.

Analysis of Pesticide: All samples were analyzed in a gas chromatograph (Agilent Model 6890 Gas Chromatograph) equipped with Ni-63 electron capture detector (ECD) and PTE-5 30 m-0.32 mm id, 0.32 mm film thickness capillary column at Ghana Standard Authority. Extracts of samples were interspersed with analytical standards of interest, placed on autosampler with standards at the start, between every 15 samples and the last of the GC sample run. The pesticide residue and PCB components in the samples were identified by comparing their retention times with those of the standard of the pesticides and PCBs. The identity of the OCP and PCB compounds in dairy products was confirmed by a second HP1 fused silica column 30 m-0.32 mm id, 0.25 mm film thickness. Quantification was based on comparison with calibration curves in the concentrations of 0.01 µg/ml, 0.02 µg/ml, 0.0030 µg/ml and 0.005 µg/ml for the pesticides. The gas chromatograph's conditions were as follows: injector temperature, 250 ^{0}C; injector mode, splitless; oven temperature programmed as follows 50^{0}C initial (2 min) to 160^{0}C at 5^{0}C/min and to 260^{0}C at 2^{0}C/min, held for 10 min. Electron capture detector temperature 300^{0}C, injector volume 2.0 µl. The carrier gas was nitrogen with a flow rate of 1.5 ml/min.

RESULTS AND DISCUSSIONS

Table 1.1 Levels of OCPs residues(µg/ml) in cow milk

OCPs	MRL	MEAN	RANGE	SD
β -HCH	0.01	0.0396	0.0001- 0.0016	$9.16X10^{-4}$
Endrin	0.05	0.0125	0.0001-0.0138	$5.3X10^{-4}$
Heptachlor	0.01	LD	<0.0001	LD
Endosulfan	0.05	0.0168	0.0001- 0.0168	0.00027
Dieldrin	0.20	0.00075	0.0001- 0.0002	$2.6X10^{-5}$
p'p'-DDE	0.05	LD	<0.0001	LD
p'p'-DDT	1.00	0.002	<0.0001	LD
p'p'-DDD	0.05	LD	0.0001- 0.0002	0.000026
γ Chlordan	0.05	LD	<0.0001	LD
Methoxychlor	0.05	0.0655	0.0328-0.0880	$9.8X10^{-4}$

Table 2.0 Levels of OCPs residues(µg/ml)in Yoghurt

OCPs	MRL	MEAN	RANGE	SD
β -HCH	0.01	0.0279	0.0084-0.0407	$1.15X10^{-3}$
Endrin	0.05	0.0023	0.0014 - 0.0064	$5.4X10^{-4}$
Heptachlor	0.01	0.0036	0.0001-0.0005	$3.7x10^{-4}$
Endosulfan	0.05	0.0018	0.0001-0.0029	$8.8x10^{-5}$
Dieldrin	0.20	0.006	0.0001-0.0121	$2.8X10^{-4}$
p'p'-DDE	0.05	0.0004	0.0001-0.0042	$2.6x10^{-4}$
p'p'-DDT	1.00	0.0004	0.0001-0.0006	$2.86x10^{-4}$
p'p'-DDD	0.05	0.0002	0.0001-0.0002	0.000026
γ Chlordan	0.05	LD	< 0.0001	LD
Methoxychlor	0.05	0.0564	0.0032-0.0107	$2.6X10^{-4}$

Table 3.0 1 Levels of OCPs residues(µg/ml) in Local Cheese

OCPs	MRL	MEAN	RANGE	SD
β -HCH	0.01	0.00205	0.0001- 0.0016	$1.2X10^{-3}$
Endrin	0.05	0.00025	< 0.0001	$3.6X10^{-5}$
Heptachlor	0.01	LD	0.0001-0.0003	LD
Endosulfan	0.05	0.00045	<0.0001	$2.8x10^{-4}$
Dieldrin	0.20	0.00125	0.0001-0.0034	$1.2X10^{-3}$
p'p'-DDE	0.05	0.0011	<0.0001	$2x10^{-4}$
p'p'-DDT	1.00	LD	<0.0001	LD
p'p'-DDD	0.05	LD	<0.0001	LD
γ Chlordan	0.05	0.0036	0.0001- 0.0012	0.0001
Methoxychlor	0.05	0.00163	0.0001- 0.0078	$2.7X10^{-4}$

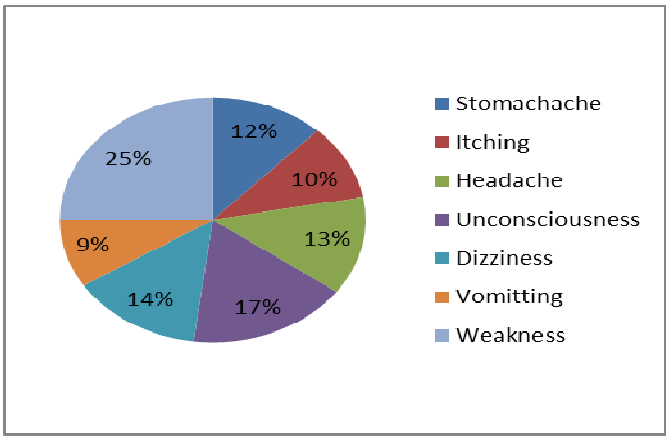


Fig. 1.0: Pesticides exposure symptoms among farmers

Table 4.5: Estimated dose values and Hazard indices of organochlorine pesticides residue exposure in milk from the study area

	RfD	Estimated Dose (µg/ml/day)			Hazard Index (HI)		
OCPs		**0-1yr**	**1-11yr**	**Adult**	**0-1yr**	**1-11yr**	**Adult**
β-HCH	0.003	0.0375	0.0125	0.0054	12.5	4.2	1.8
Endrin	0.20	0.0114	0.0039	0.0017	0.06	0.02	$8.5x10^{-3}$
Heptachl	0.0001	$8.4x10^{-5}$	$2.8x10^{-5}$	$1.2x10^{-5}$	0.84	0.28	0.12
Endosulf	0.006	0.0142	$4.8x10^{-3}$	$2.1x10^{-3}$	2.4	0.8	0.35
Dieldrin	0.005	$6.8x10^{-4}$	$2.3x10^{-4}$	$9.7x10^{-5}$	0.14	0.05	0.02
P'P'DDE	0.50	$8.5x10^{-5}$	$2.8x10^{-5}$	$1.2x10^{-5}$	$1.7x10^{-4}$	$5.6x10^{-5}$	$2.4x10^{-5}$
P'P'DDT	0.50	$8.5x10^{-5}$	$2.8x10^{-5}$	$1.2x10^{-5}$	$1.7x10^{-4}$	$5.6x10^{-5}$	$2.4x10^{-5}$
P'P'DDD	0.50	$1.7x10^{-4}$	$5.7x10^{-5}$	$2.4x10^{-5}$	$3.4x10^{-4}$	$1.1x10^{-4}$	$4.8x10^{-5}$
Chlord	0.0005	$8.5x10^{-5}$	$2.8x10^{-5}$	$1.2x10^{-5}$	0.17	0.06	0.02
Methoxy	0.005	0.0746	0.0249	0.01066	13.9	4.98	2.1

RESULTS AND DISCUSSIONS

As indicated on Table 1, 2 and 3, the mean concentrations of organochlorine pesticides residue analysed in dairy products. It was so conspicuous that the level of methoxychlor and HCH in milk samples were higher than the yoghurt and cheese simply because they are lipophilic and bioaccumulate more in fatty medium. An average of 0.002µg/kg of DDT(Accra-Ghana) was recorded in milk samples was far lower than those recorded for milk from places such as Kumasi(Ghana) 12.53µg/ml, Kenya 6.99mg/kg, Nigeria 3.83mg/kg, Ethiopia 7.75mg/kg and India 6.55mg/kg (FAO, 1986). This can be attributed to the high usage of OCPs in those areas. The drastic reduction in the level of DDT in the samples clearly confirms the fact that, in recent times the use of organochlorine pesticides is gradually phasing out.(UNEP, 2002). The mean concentration of HCH (0.0396µg/ml) and methoxychlor (0.0655µg/ml) in milk exceeded the maximum residue limit recommended by WHO. However, the level of endrin (0.0125µg/ml), endosulfan (0.0168µg/ml), dieldrin (0.00075µg/ml) and DDT (0.002µg/ml) in milk were all below the maximum residue limit. It was also discovered that heptachlor, p'p'-DDE, p'p'-DDD and chlordane were all below the limit of detection.

Similarly, for the yoghurt samples, the level of methoxychlor (0.0564µg/ml) and HCH (0.0279µg/ml) exceeded the maximum residue limit due to their high application and persistence in the environment.

Organochlorine pesticides such as endrin, heptachlor, endosulfan, dieldrin and DDT were all below the detection limit. This clearly indicates that, the manufacturing process of the yoghurt eventually led to the degradation of some of these OCPs.

For the cheese samples almost all the mean concentrations of the OCPs were less than their expected maximum residue limit except heptachlor, p'p'-DDD and p'p'-DDT whose level were below limit of detection.

From figure 1.0, the data obtained from the survey indicated that a very high proportion of farmers and farm workers were at high risk of pesticide poisoning from occupational exposure. About 90% of farmers did not wear protective devices nor applied safety measures during pesticide mixing and application. Farmers were generally less aware of the potentially adverse impacts of pesticide deposition on the environment. Pesticide exposure may be exacerbated by the fact that a good proportion of these agricultural workers eat or drink during pesticide application. Some pesticides have been found to cause infertility, sterility and birth defects; others have been linked to allergies, hematologic disorders, mutagenicity and cancer (; Mensah *et al,* 2004; Ntow, 2005).
Table 4.0 presents the health risk estimation, to assess the risk of OCPs usage to farmers and consumers, the relation below was used:

Life Exposure Dose = $\frac{\text{Residue conc. in food of interest X food consumption rate}}{\text{Body weight}}$

Hazard index = Estimated dose/reference dose

A hazard index HI <1 is considered to have an unlikely adverse health effect, while HI > 1 is said to have probable adverse health effect on consumers (USEPA, 2002) . Data analysis of health risk estimates indicated that γ-chlordane, endrin p'p'-DDT, DDE, heptachlor, dieldrin and DDD do not pose a direct hazard to human health, although present in milk samples. However, β-HCH (0.0375µg/ml), and methoxychlor (0.0746µg/ml) levels exceeded the reference doses 0.003 and 0.005 respectively in children between the ages of 0 -1 year, 1 -11 years and adults while endosulfan (0.0142µg/ml) levels in infants (0 -1years) also exceeded the reference dose(0.006) indicating a great potential for systemic toxicity in all age groups especially children who are considered to be the most vulnerable population subgroup.

CONCLUSION

It is clear from the results of the study that, substantial amounts of pesticides were inappropriately used by these farmers leading to several clinicopathological conditions including nausea, vomiting, blurred vision, abdominal cramps, unconsciousness, itching, stomachache, dizziness, diarrhoea and headache.It was evident that organochlorine pesticides such as methoxychlor, endosulfan and HCH posed great potential systemic toxicity. Other OCPs like heptachlor, chlordane, p'p'-DDT, p'p'-DDE, p'p'-DDD. Endrin and dieldrin were all below the reference doses and are unlikely to cause adverse health effects.

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