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Pesticide Contamination in Groundwater and Streams Draining Vegetable Plantations in the Ofinso District, Ghana

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1. Introduction

1.1 Ghana's geographical location and climate

Ghana, officially the Republic of Ghana and formerly the Gold Coast, is a West African country with a geographical location of 5°36′ N, 0°10′ E. It shares borders with Cote d'Ivoire to the west, Burkina Faso to the north and Togo to the east. To the south of the country is the Gulf of Guinea of the Atlantic Ocean. The climate is tropical equatorial ranging from the bimodal rainfall equatorial type in the south to the tropical unimodal monsoon type in the north. It is influenced by the hot, dry and dusty-laden air mass that moves from the north-east across the Sahara and by the tropical maritime air mass that moves from the south-west across the southern Atlantic ocean. The annual rainfall ranges from 1015 to 2300 mm with annual mean temperature and relative humidity of 30°C and 80% respectively (Ntow & Botwe, 2011). Ghana has a total land area of about 23,853, 900 ha and a population of about 24.2 million. The arable land covers an area of about 13,628,179 ha (approx. 57% of total land area) of which approximately 44% is under cultivation.

1.2 Economic importance of agriculture in Ghana

Agriculture is Ghana's most important economic sector, employing more than 60% of the labour force. Currently, agriculture contributes about 33% of Ghana's gross domestic product (GDP) and accounts for over 40% of export earnings. Ghana's agriculture is predominantly smallholder, traditional and rain-fed. The major agro-ecological zones in Ghana are Rain Forest, Deciduous Forest, Forest-Savannah Transition, Coastal Savannah and Northern (Interior) Savannah which comprises Guinea and Sudan Savannahs. The type of agricultural activity carried out in each zone is determined largely by rainfall. In the south, there is a major and a minor growing season due to the bimodal rainfall pattern in the Forest, Deciduous Forest, Transitional and Coastal Savannah zones whereas in the Northern Savannah, the unimodal rainfall pattern results in a single growing season. Within the agricultural sector, vegetable production plays an important socio-economic role, having developed from a mainly subsistence activity to a commercial activity. Vegetable production in Ghana typically occurs in intensely managed vegetable plantations characterized by an

extensive network of drainage systems through which surplus water may flow out (Ntow *et al.*, 2008). Vegetables cultivated in Ghana include tomato (*Lycopersicon esculentum*), eggplant (*Solanum melongena*), pepper (*Capsicum annum*) and onion (*Allium cepa*), although some regions are more efficient and specialised in the production of only one or two vegetable crops (Ntow, 2001).

1.3 Pesticide use in vegetable cultivation in Ghana

Vegetables generally attract a wide range of pests and diseases, and require intensive pest management (Dinham, 2003), which includes all aspects of the safe, efficient and economic use and handling of pesticides. In Ghana, pest and disease control practices in vegetable production involve the use of chemical pesticides. A total of 43 pesticides, comprising insecticides, fungicides and herbicides, have been found in use in vegetable farming in Ghana. Among these pesticides, the herbicides class of pesticides is the most used (44%), followed by insecticides (33%) and then fungicides (23%) (Ntow *et al.*, 2006). Although it is recognized that better management of pesticides results in high crop productivity while greatly reducing adverse environmental impacts, most of the local farmers lack adequate training in the proper application of pesticides. Pest and disease control therefore involves relatively high inputs of highly toxic chemical pesticides which are most of the time misapplied (Ntow *et al.*, 2006). The average pesticide application rate is estimated to be 0.08 litres active ingredient (a.i.) per hectare (Ntow *et al.*, 2008). Misapplication and intensive use of pesticides in vegetable cultivation can result in pesticide contamination of the environment.

1.4 Impacts of pesticide use in vegetable agro-ecosystems

Water pollution by pesticides has long been recognized as a major environmental impact associated with agriculture due to the potential adverse effects on aquatic life and on humans if contamination extends to drinking waters (Skinner *et al.*, 1997). Most vegetable farms in Ghana are sited a few meters from streams for easier access to water for irrigation purposes. The close proximity of streams to vegetable farms is of particular concern as there is high potential for pesticides to move offsite into surrounding streams via run-off through the extensive system of drainage canals that characterize these farms. Persistent pesticides, particularly the organochlorine group of pesticides, can be transferred to aquatic organisms at all trophic levels within the food chain due to their bioconcentration and bioaccumulation potential. Many organochlorine pesticides are known to mimic hormones and disrupt reproductive cycles of humans and wildlife (Colborn and Smolen, 1996) and therefore they can be detrimental to a wide variety of aquatic wildlife populations (Robinson, 1991). Even non-persistent pesticides, such as the pyrethroids, carbamates and organophosphate group of pesticides, can be highly toxic to aquatic life (Castillo *et al.*, 2006). Pesticides can also enter groundwater via seepage or soil percolation. Pesticides contamination of streams and groundwater also presents health threat to the rural communities as they depend on streams and groundwater for drinking and other domestic purposes.

Concerns over the adverse ecological and human health impacts of pesticides have led to the institution of very strict programs to control and monitor pesticide contamination in water sources in developed countries such as the United States and members states of the European Community (García de Llasera and Bernal-González, 2001). These programs have, however, not been implemented in most developing countries such as Ghana. Few studies

conducted in Ghana have focused on the organochlorine pesticides (Osafo & Frimpong, 1998; Ntow, 2001, 2005). However, pesticides from the organophosphate group, which are now commonly used in Ghana following the ban on persistent organochlorine pesticides, have not been determined in water quality studies. In this chapter, pesticide contamination in groundwater and streams draining vegetable plantations in the Ofinso District of Ghana are assessed and the ecotoxicological significance of the pesticides contamination evaluated.

1.5 Study area

The present study was conducted in the Ofinso District of the Ashanti Region of Ghana (Fig. 1). The Ofinso District is located in the extreme North-Western part of the Ashanti Region, with about half of its boundaries bordered by Brong Ahafo Region (in the north and west).
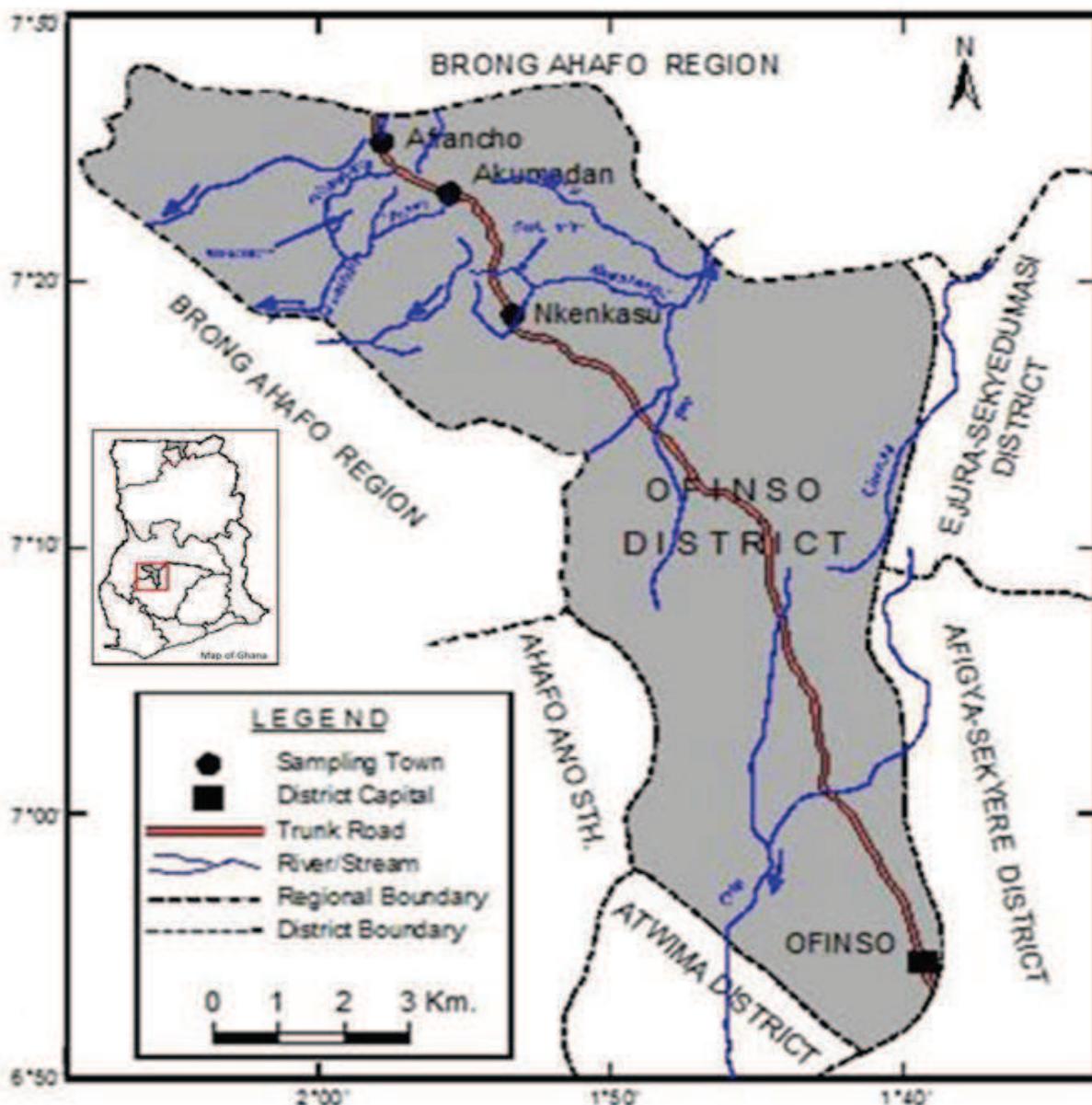

Fig. 1. Map showing the study area

It is bordered to the east by Ejura-Sekyedumasi District, to the south by Afigya Sekyere, Ahafo Ano South and Atwima Districts. The district has 126 settlements and a population of about 35,190 with New Ofinso as its capital. The district has five towns namely Abofour, Nkenkasu, Afrancho, Akumadan and New Ofinso. The study area is within the Ofin, Pru and Afram river basins. In the present study, vegetable plantations were selected from Akumadan, Nkenkasu, and Afrancho. Agriculture is the main economic activity in these areas with over 70% of the active population being farmers. The district is well known for the cultivation of vegetable crops. Other major crops cultivated include cassava, maize, plantain and cocoa. More than 23 different active ingredients formulated as insecticides, herbicides and fungicides have been used in the cultivation of vegetables in the district.

The five most frequently used insecticides include two organophosphates (chlorpyrifos and dimethoate), two pyrethroids (lambda-cyhalothrin and cypermethrin), and one organochlorine (endosulfan). Farmers use these highly toxic pesticides under primitive field conditions with insufficient protective equipment and training. Pesticide applications occur frequently, all year round, and are relatively intensive (500-1000 ml/ha). Pesticides are also sprayed in combinations, with many farmers (60%) spraying their crops on calendar basis, at 7-day intervals (Ntow *et al.* 2006). Streams within the catchments of vegetable farmlands are vulnerable to pesticide contamination as a result of spray drift and surface runoff (Maule *et al.*, 2007). The quality of these water resources is of critical interest as they serve as aquatic habitats and drinking water sources.

2. Methods

2.1 Sampling of stream water, sediment and groundwater

Twenty-one streams flowing in and/or around vegetable plantations, stream-bed sediments and 9 drinking water wells in the Ofinso District of the Ashanti Region of Ghana were sampled between February 2008 and January 2009 as part of a pesticide monitoring programme in vegetable agro-ecosystems in Ghana. Streams sampled included Akumadan, Nkenkasu and Afrancho (Fig. 1) which flow in and around vegetable farmlands. The other streams sampled in the district were ephemeral and these included Srani, Bosompong, Sukubrim, Siasu, Ankonom, and Naasu (not shown). For each stream, 1 L water samples were collected into 1-L glass amber coloured bottles with Teflon-lined caps from upstream, mid-stream and downstream. During the same period, stream-bed sediment samples of about 200 g were collected into wide-neck glass jars. Groundwater samples were extracted from drinking water wells located within farming communities at Akumadan, Nkenkasu, and Afrancho into 1-L glass amber coloured bottles with Teflon-lined caps. None of the wells sampled was in a farmed section of the study area. All the wells are shallow wells (< 15 m) and represent unconfined aquifers. The wells receive water from the soil and upper porous rock zones that characterise the Ofinso District. Prior to sampling, pumps were run for about 5 min to clear the casing of standing water and to bring in fresh water from the aquifer. During this period, field measurement parameters (e.g. temperature) were stabilised. The sampling bottles were rinsed with well water before taking the water samples. Three replicates were collected from each well. The samples were transported to the laboratory within 24 to 48 h on ice in clean ice chests and stored in the laboratory refrigerator at 4oC until analysed. The samples were extracted within 24 h of arrival at the laboratory. Field blanks were prepared with distilled water and were analysed only when

pesticide residues were detected in primary samples. Sampling was conducted throughout rainy and dry seasons and was not timed to applications of different pesticides or to rain events.

2.2 Chemical analysis
2.2.1 Sample extraction
The extraction and analyses of water samples were performed following the Association of Official Analytical Chemists 990.06 and 970.52 methods as described by Ntow *et al*. (2008). Briefly, water samples were extracted sequentially three times with 25 mL *n*-hexane each time. The extract was dried with anhydrous sodium sulphate and concentrated down to 10 mL by means of ultrasonic bath type concentrators (Turbo Vap II). Extract clean up was done, using a chromatographic column, packed with florisil, previously activated for 3 h in an oven at 130ºC, and anhydrous sulphate (all rinsed with petroleum ether). The extract was transferred to the column. Three fractions were obtained after elution with 6, 15, 50% ethyl ether in petroleum ether. Maximal flux rate of elution was 5 mL/min. Each eluate was evaporated and the extracts (re-dissolved in 1.5 ml *n*-hexane and made up to 2 ml with more *n*-hexane) were injected into a gas chromatographic system for identification and quantification of the pesticides.

Extraction and analysis of sediment samples followed the method described by Ntow *et al*. (2008). Briefly sediment samples were well mixed to obtain a homogeneous sample and then transferred into a pan to air-dry at ambient temperature until a constant weight was obtained. The samples were later ground in a mortar into fine powder such that they could pass through 2 mm sieve. Five grams (dry weight) of the sediment samples were soxhlet extracted in methanol, and cleaned up in florisil in the same way as described above for water. Sampling protocol and analytical procedures were subjected to quality control through field and laboratory blanks and spiking of samples with pesticide standards.

Laboratory glassware used in the sampling and analyses were cleaned as described by Ntow (2001). Pesticide grade solvents used for the analyses were *n*-hexane (>99%) and acetone (>99.9%) (Sigma, Munich, Germany); methanol (99.8%) and petroleum ether (BDH; VWR International, UK); dichloromethane and ethyl ether (Fluka; Munich, Germany). Deionised water was used from a Milli-Q water purification system (Millipore, Bedford, MA, USA) for blanks, sediment extraction, and spiked samples. Pesticide standards (> 98% purity) were obtained from Dr. Ehrenstorfer (Augsburg, Germany). Standard mixtures were prepared from individual pesticide stock solutions (50-100 mg in 100 ml acetone) and then diluted to working calibration standards at three concentration levels with acetone/cyclohexane (pesticide grade) mixture (1:9).

2.2.2 Pesticide residue analysis
Measurement of pesticide compounds in water and sediment samples was performed on a GC-MS (Agilent 6890 Series GC System) coupled with an Agilent 5973N mass selective detector-electron impact ionization; and fused capillary column (HP-5MS) packed with 5% Phenyl Methyl Siloxane (30 m * 0.25 mm I.D and film thickness 0.25 µm), which was operated in the selected ion-monitoring mode at the following conditions: injection port 250ºC (splitless, pressure 22.62 psi; purge flow 50 mL/min; purge time 2.0 min; total flow 55.4 mL/min). Column oven: initial 70ºC, held 2 min, programming rate 25ºC/min (70 to 150ºC); 10ºC/min (150 to 200ºC); 8ºC/min (200 to 280ºC) and held 10 min at 280ºC. The

carrier gas was nitrogen at 15 psi; detector make-up, 30 mL/min. The injection volume was 1 μL (Agilent 7683 Series injector). Selection of analysed pesticides was done on the basis of pesticide use information provided by Ntow *et al.* (2006). The pesticides analysed included α- and β-endosulfan, endosulfan sulphate, dieldrin, dichlorodiphenyltrichloroethane (p,p'-DDT), dichlorodiphenyldichloroethylene (p,p'-DDE) and chlorpyrifos. For quality control of gas chromatographic conditions, a checkout procedure was performed before sample analysis in which a standard mixture with α-endosulfan content of 400 ng/L was used. Calibration was carried out when the concentration of α-endosulfan in standard mixture deviated significantly from 400 ng/L. Also the linearity of detector response was checked with five standard solutions of concentration 200 - 1000 ng/L. The correlation coefficient, r, obtained was ≥ 0.94. Recovery of the different pesticides ranged between 79% and 104% and their detection limits varied between 0.001 and 0.01 μg/L. The residues are expressed as μg/L (ppb) for surface water and μg/kg dry weight (ppb) for sediment. Because most of the pesticides analysed by GC/MS had a method detection limit at or below 0.01 μg/L, the reporting limit was chosen as 0.01 μg/L for these compounds. This reporting limit was used in calculating incidences of occurrence. A pesticide that has been identified but not quantified is indicated as below the detection limit.

2.2.3 Physicochemical analysis

The pH and temperature of samples were determined in situ using a pH meter. The pH meter was first calibrated with standard pH buffers before immersing the probe into the water or sediment. Temperature was measured concurrently. Total suspended solids and turbidity in water were measured using a turbidity meter (2100P Turbidimeter, Hach Company, Loveland, CO, USA). Calibration of the turbidity meter was done by filtering some water samples through pre-weighed Whatman GF/F (0.45 μm pore-size) glass microfiber filters which were then dried at 60°C for 48 h and re-weighed to determine TSS. Water content (expressed as weight fraction of water) was determined by first weighing wet sediment samples, then oven-drying the sediment samples at 105°C until constant weight, and obtaining the weight difference. Total suspended solids and turbidity were measured concurrently (Ntow *et al.*, 2008). Total organic carbon was obtained from the percentage organic matter in the sediments as percentage loss-on-ignition after drying 1.0 g of the sediment samples (previously acidified for the removal of carbonates) at 550°C in a furnace (Mwamburi, 2003).

2.3 Statistical analysis

A paired Student's *t* test was performed to analyze significant differences between pesticide residue levels in stream water and stream-bed sediment. One-way analysis of variance (ANOVA) was performed to analyze significant differences in pesticide residue levels in water and sediment from different sites. Pearson correlation analysis was performed to determine the relationship between the levels of pesticide residues and sediment characteristics (total suspended solids and total organic carbon) at the 95% confidence level ($p < 0.05$)

2.4 Ecotoxicological significance of measured pesticides in stream water

The effects of pesticides on water quality are commonly assessed by comparing the observed concentrations of individual pesticide compounds in the aquatic system with criteria that have been established to protect the health of aquatic organisms (Castillo *et al.* 2000; Hoffman *et al.* 2000). By comparing the pesticide concentrations in this study with the

toxicity values listed in Table 1, the acute and chronic risk ratios were calculated for the water samples. A ratio of 1 means the individual pesticide has reached its criteria concentration in the streams. Risk for acute toxicity is based on the highest pesticide concentration found compared to the LC_{50} (Table 1). Risk for chronic toxicity is calculated based on the average concentration of all positive observations and the water quality criteria (Table 1).

Pesticides	Main use	Lowest LC_{50} for crustaceans or fish (μgL^{-1}) (EXTOXNET 1996)	Water-quality criterion (μgL^{-1}) (USEPA 1999)
α-Endosulfan	Insecticide	1.20	0.056
β-endosulfan	Insecticide	1.20	0.056
Endosulfan sulphate	Insecticide	1.20	0.056
Dieldrin	Insecticide	-	0.056
Chlorpyrifos	Insecticide	0.01	0.041
p,p′-DDE	Insecticide	0.18	0.001
p,p′-DDT	Insecticide	0.18	0.001

Table 1. Reference toxicity values for pesticides analyzed

3. Results and discussion

3.1 Physicochemical characteristics of water and sediment samples analyzed

The physicohemical characteristics of groundwater, stream water and sediment samples analyzed are presented in Table 2.

Physicochemical parameter	Groundwater	Stream water	Sediment
pH	5.8 - 6.4	6.6 - 8.3	5.6 - 6.8
Temperature (^{o}C)	21.4 - 22.7	23.2 - 27.4	-
Total suspended solids (mg/l)	0	5.8 - 20.6	-
Turbidity (NTU)	0.74 - 2.93	2.2-32.5	-
Moisture content (%)	-	-	18.0 - 26.3
Total organic carbon (%)	-	-	2.1 – 13.6

Table 2. Physicohemical characteristics of groundwater, stream water and sediment samples analyzed

The pH and turbidity of groundwater were within acceptable levels for human consumption. The pH, temperatures, levels of total suspended solids and turbidity of stream water were also suitable for aquatic life.

3.2 Pesticide residue levels in groundwater

Pesticide residues were not detected in all the groundwater samples analyzed (Table 3). The non-detection of pesticide residues in groundwater could be due to their high adsorption to soil particles which does not facilitate their infiltration into groundwater. This is an indication that groundwater consumption may not contribute to community exposure to these pesticides.

Pesticide components	Groundwater (n =81)		Stream water (n = 192)		Sediment (n = 180)	
	Mean ± SD (μgL^{-1})	I.R (%)	Mean ± SD (μgL^{-1})	I.R (%)	Mean ± SD (μgKg^{-1} dw)	I.R (%)
α- Endosulfan	ND	-	0.027 ± 0.015	27.8	0.38 ± 0.24	90.0
β-Endosulfan	ND	-	0.021 ± 0.010	13.9	0.18 ± 0.09	97.5
Endosulfan-sulphate	ND	-	0.022 ± 0.010	21.5	0.53 ± 0.24	98.3
Dieldrin	ND	-	ND	-	0.16 ± 0.04	35.0
p,p'-DDE	ND	-	ND	-	3.77 ± 1.90	25.0
p,p'-DDT	ND	-	ND	-	ND	-
Chlorpyrifos	ND	-	ND	-	1.23 ± 0.40	68.3

Table 3. Concentrations (Mean ± SD) and incidence ratios of pesticide residues in groundwater, stream water and stream-bed sediment samples analyzed. [n = number of samples analyzed; SD = standard deviation; ND = below detection limit (0.01 μgL^{-1} or μgKg^{-1}); I.R. = incidence ratio; dw = dry weight]

3.3 Pesticide residue levels in stream water

The mean concentrations and incidence of occurrence of pesticides detected in stream water are summarized in Table 3. Only 67 (35%) of the 192 stream water samples analyzed had pesticide residue detections. α-endosulfan, β-endosulfan and endosulfan sulphate were the only pesticide residues detected with mean concentrations of 0.027 ± 0.015, 0.021 ± 0.010, and 0.022 ± 0.010 μgL^{-1} (or ppb), respectively. The incidence of occurrence of these organochlorine pesticide residues were α-endosulfan (27.8%), β-endosulfan (13.9%) and endosulfan (21.5%). Technical endosulfan is a mixture of α- and β-endosulfan in a ratio of 7:3. Endosulfan sulfate is the principal metabolite of endosulfan and it is highly toxic. Endosulfan sulfate levels in stream water samples were nearly equal to those of the parent compounds (α- and β-endosulfan), suggesting current use of the pesticide. The occurrence of endosulfan residues in streams may be the result of direct overspray, spray drift, atmospheric transport of volatilized pesticides, agricultural runoff, pesticide misuse, and improper disposal of pesticide containers (Maule et al., 2007; Wan et al., 2005; Ntow et al., 2008). Inflows from shallow groundwater originating in the agricultural areas are however unlikely sources of pesticide contamination in the streams studied since pesticide residues were not detected in groundwater samples analyzed in the present study.

Pearson correlation analysis revealed an association ($r^2 > 0.6$) between endosulfan residue concentration and total suspended solids in stream water for most sites. Thus, increase in the level of suspended solids (sediment) resulted in a corresponding increase in concentration of endosulfan. This partitioning behavior of endosulfan in the streams studied may be influenced by physicochemical properties. Endosulfan has low water solubility (0.32 mgL at 22°C) and high affinity for sediment as indicated by the high soil adsorption coefficient of 2,400 mLg^{-1} which can be attributed to its high octanol-water partitioning coefficient (logKow = 3.6) (see Table 4). Therefore, with these properties, there is a high tendency for endosulfan to adsorb onto suspended sediments in the water column than to remain in solution as the study has shown.

Pesticide name	Water solubility at given temperature (mgL^{-1})	LogK_{ow}	Soil adsorption coefficient, K_{oc} (mLg^{-1})	Soil half-life
Endosulfan (α, β and sulfate)	0.32 (22°C)	3.6	2,400	50 d
Dieldrin	-	5.5	-	-
DDE	< 1 (20°C)	5.8	100,000	2-15 years
Chlorpyrifos	2 (25°C)	4.7	6,070	35-78 d

Table 4. Properties of pesticides detected in streams. Source: EXTOXNET (1996)

Endosulfan is banned or restricted in many countries because of its human health and environmental impacts. In the United States, for example, endosulfan is applied to grains, tea, fruits, vegetables, tobacco, and cotton (DeLorenzo *et al.* 2001). In Ghana, endosulfan has a restricted use that does not include vegetables (it has only been registered for use on cotton), yet it is used on vegetables. According to Ntow *et al.* (2006), endosulfan is one of the most commonly used pesticides in the study area. Different formulations of the active ingredient are sold in the study area under different trade names such as Thionex 35 EC/ULV, Thiodan 50 EC, Endosulfan, Endocoton, Caiman 350 EC, Phaser and Novasulfan 35 EC. Vegetable farmers in Ghana spray endosulfan on tomato, pepper, okra, egg-plant (garden eggs), cabbage and lettuce. Although there are numerous pests and diseases prominent on vegetables (for instance, there are 13 fungal pathogens on tomato alone), the use of endosulfan was not necessarily to control diseases. Application of endosulfan to control diseases was done on a trial-and-error basis because the local farmers were not able to identify the pests causing damage (Ntow *et al.*, 2006). The use of endosulfan on vegetables by Ghanaian farmers is of great concern due to the persistence and extreme toxicity of endosulfan to fish and aquatic invertebrates (Pérez-Ruzafa *et al.*, 2000). The presence of endosulfan in stream water also has implications for public health as rural communities depend on stream water for drinking. The levels of endosulfan residues obtained in the present study are comparable to those obtained in a previous study by Ntow (2001) (see Table 5).

Pesticide components	Stream water (n = 50)		Sediment (n = 42)	
	Mean ± SD (µgL^{-1})	I.R (%)	Mean ± SD (µgKg^{-1} dw)	I.R (%)
α- Endosulfan	0.062 ± 0.007	64	0.19 ± 0.02	90.0
β-Endosulfan	0.031 ± 0.011	60	0.13 ± 0.01	97.5
Endosulfan-sulphate	0.031 ± 0.012	78	0.23 ± 0.01	98.3
Dieldrin	-	-	-	35.0
p,p'-DDE	ND	-	0.46 ± 0.24	25.0
p,p'-DDT	-	-	-	-
Chlorpyrifos	-	-	-	68.3

Table 5. Concentrations (Mean ± SD) and incidence ratios of pesticide residues in stream water and stream-bed sediment. Source: Ntow (2001)

3.4 Pesticide residue levels in stream-bed sediment

The mean concentrations and incidence of occurrence of pesticides detected in stream-bed sediments are summarized in Table 3. Several pesticide residues were detected in the stream-bed sediment samples analyzed compared with stream water samples analyzed. α-endosulfan, β-endosulfan, endosulfan sulfate occurred in at least 90% of all the sediment samples analyzed while dieldrin, p,p'-DDE and chlorpyrifos occurred in 25%, 35% and 68% of all the sediment samples analyzed, respectively. Chlorpyrifos is an organophosphate pesticide while all the other pesticide residues detected belong to the organochlorine group of pesticides.

DDT is well-known to persist in the environment, even in tropical environments (Kidd *et al.* 2001). Although p,p'-DDT was not detected in stream water and sediment, its metabolite p,p'-DDE was detected in sediment at an average concentration of 3.77 ± 1.90 µgKg^{-1} dry wt. DDE is more persistent in the environment than DDT. Thus, when the use of DDT in a country ceases, its levels are expected to decrease more rapidly while the levels of DDE increases, thereby producing an increasing DDE/DDT ratio. The DDE/DDT ratio is often used as an indicator of recent DDT inputs into the environment; a ratio < 1 indicates recent input (Ballschmiter & Wittlinger, 1991). The absence of DDT and presence of DDE in sediment could imply the disuse of the parent compound, DDT in Ghana. The relatively high levels of p,p'-DDE detected in the present study is a justification of the ban of DDT from agricultural use in Ghana. The non-detection of DDT could also confirm the efficacy of the ban on the agricultural use of DDT in Ghana.

Dieldrin and chlorpyrifos were also detected in sediment with mean concentrations of 0.16 ± 0.04 and 1.23 ± 0.40 µgKg^{-1} dw, respectively, although they were not detected in stream water samples. Apart from its usage, dieldrin can occur in the environment as a result of the degradation of a related pesticide, aldrin. Aldrin and dieldrin are persistent in the environment and they have been banned from agricultural use in Ghana (Ntow & Botwe, 2011). The occurrence of dieldrin in sediment could therefore be due to previous use of dieldrin and/or aldrin. Chlorpyrifos recorded the highest incidence of occurrence (68%) in sediment samples. Chlorpyrifos is a broad-spectrum organophosphorus pesticide. Chlorpyrifos, under the trade name Dursban 4E, is a registered insecticide in Ghana for the control of scale borers in cereals, vegetables and ornamentals, and for public health purposes. The occurrence of chlorpyrifos in sediment could be as a result of their current use in vegetable plantations. Residues of chlorpyrifos have also been measured in vegetables from the Ashanti Region (Amoah *et al.*, 2006; Darko & Akoto, 2008).

Generally, the detected pesticides accumulated in sediment to several times their ambient water concentrations (Fig. 2). Thus, sediment is a better indicator of pesticide pollution than the overlying water. For example, endosulfan (α-endosulfan + β-endosulfan + endosulfan sulfate) accumulated to over 15 times its ambient water concentration. p,p'-DDE was also not detected in stream water although it occurred in relatively high concentrations in sediment (3.77 ± 1.90 µgKg^{-1}). There was also a significant correlation (r^2 > 0.6) between levels of pesticide residues and organic carbon content of sediment. This agrees well with the finding that sediment organic matter is the preferential site for the sorption of hydrophobic pollutants (Pignatello, 1998), which includes organochlorine pesticides.

The relatively higher levels of pesticides in sediment than the overlying water can be explained by the fact that pesticides are sequestered by sediments in aquatic systems

(Reinert *et al.*, 2002), which leads to the accumulation of pesticide residues in sediment over a period of time. The distribution of pesticide residues in water and sediment could be related to their physicochemical properties such as water solubility, soil adsorption coefficient and persistence as shown in Table 4. For example, endosulfan and DDE (organochlorine pesticides) have low water-solubility, high soil adsorption coefficients (*Koc*) and high persistence in soil, with half-lives between 50 days and 15 years (EXTOXNET, 1996). They are therefore expected to exhibit low degradation in sediment and so were frequently detected in sediments than water. These characteristics imply there could be a direct contribution to the streams from erosion of soil contaminated with these compounds (Munn & Gruber, 1997). The accumulation of chlorpyrifos in stream-bed sediment is in accordance with its high soil adsorption coefficient, K_{oc}, of 6,070 mLg^{-1} and its half-life of 35 to 78 d in the water-sediment system.
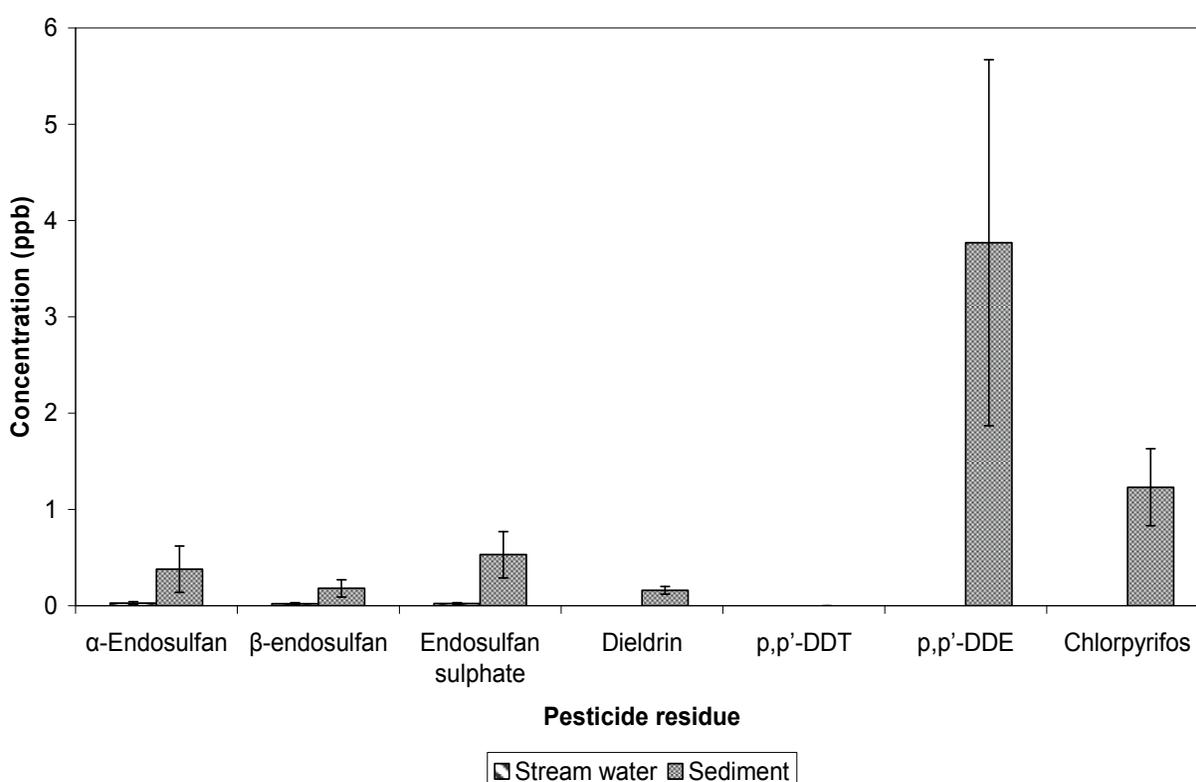
Fig. 2. Pesticide residue concentrations in stream water and underlying sediment

There were also differences in the distribution patterns of endosulfan, dieldrin, DDE and chlorpyrifos in sediment which could be related to the differences in their physicochemical properties. DDE, with the highest *K*oc (100,000 mLg^{-1}), recorded the highest levels in sediment, followed by chlorpyrifos (*K*oc = 6,070 mLg^{-1}) while endosulfan with the lowest *K*oc (2,400 mLg^{-1}) recorded the least concentration. The reverse trend was observed for stream water. The mean level of total endosulfan (α-endosulfan + β-endosulfan + endosulfan sulfate) in sediment from the present study (1.09 ± 0.57 µgKg^{-1} dw) was not significantly higher (*p* > 0.05) than that obtained from the previous study (0.54 ± 0.04 µgKg^{-1}

dw) by Ntow (2001). However, the mean sediment DDE level obtained from the present study (3.77 ± 1.90 µgKg $^{-1}$ dw) was significantly higher (p < 0.05) than that obtained from the previous study by Ntow (2001), possibly due to the accumulation of the residue in the environment over time.

3.5 Ecotoxicological significance of measured pesticides in stream water

To evaluate the ecotoxicological significance of pesticides contamination in streams, acute (ARR) and chronic (CRR) risk ratios were calculated for the water samples by comparing the pesticide concentrations in the samples with their toxicity values (Table 1).

The calculated risk ratios for acute toxicity are shown in Fig. 3. It was found that none of the detected pesticides had an acute risk ratio greater than 1. Using the quantification limit of 0.01 µgL^{-1}, chlorpyrifos had a value of 1 in the streams. This means that when chlorpyrifos is detected in water, its concentration is already equal to its acute risk criteria. Thus, any occurrence of chlorpyrifos in water could pose a risk of acute toxicity to fish and crustaceans, and especially, species such as cladocerans, which have been observed to be highly sensitive to chlorpyrifos (Brock *et al.*, 1992; van Wijngaarden *et al.*, 2005). According to the fringing communities, fish is scarce in the streams within the catchments although fingerlings and other aquatic organisms such as frogs and crabs are present. Considering that the maximum concentrations found in this study are not the highest possible concentrations that can occur, compounds with a factor > 0.1 could pose a moderate risk of acute toxicity. Also, for many compounds, there is not a large data set of toxicity values for aquatic organisms of different trophic levels. Furthermore, the great majority of compounds have not been tested with tropical organisms.
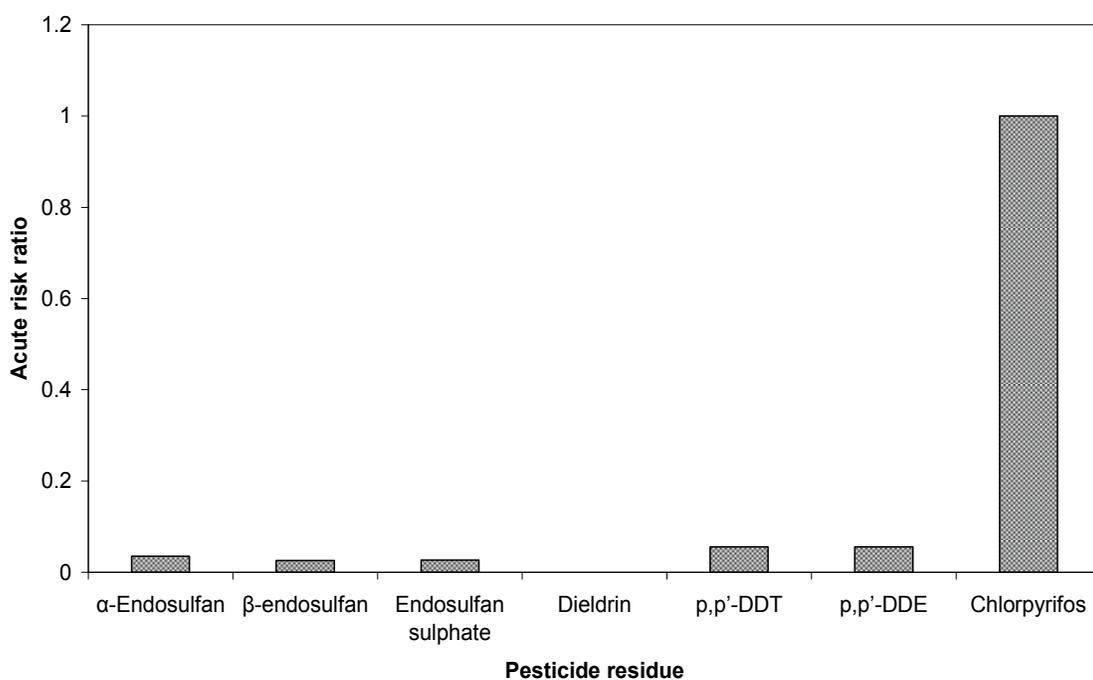

Fig. 3. Acute risk ratios for detected pesticides in stream water

The calculated risk ratios for chronic toxicity are shown in Fig. 4. It was found that DDT and DDE exceeded their chronic risk criteria in the streams. Although DDT and DDE were not

detected in water at the quantification limit of 0.01 µgL^{-1} in this study, the toxicity factor was considered relevant to estimate since the quantification limits for these pesticides were generally above their respective water quality criteria. For example, the water quality criterion for DDT and DDE is 0.001 µgL^{-1} (Table 5) and the quantification limit was 0.01 µgL^{-1}. This means that when DDT and DDE are detected, they have already exceeded their water quality criteria many times (see Figs. 3 & 4). The quantification limit was therefore used to calculate the toxicity factors. Thus, any occurrence of DDT and/or DDE in the streams is significant.

Endosulfan, dieldrin, DDE and chlorpyrifos are among the pesticides that are very toxic to fish and many aquatic invertebrate species. There were no records of fish or amphibian kills in the streams at the time of the study. However, simultaneous exposure to multiple contaminants is known to produce an additive, and sometimes even synergistic and complex effects in organisms which can affect the abundance and diversity of non-target species and alter trophic interactions (Rovedatti *et al.*, 2001). Sediment is an important reservoir of contaminants, acting as both an ultimate sink and potential source via a series of biogeochemical processes (Guo *et al.*, 2009). Pesticide contamination of sediments may thus lead to exposure of sediment-dwelling organisms to repeated pulses or fluctuating concentrations of pesticides (Reinert *et al.*, 2002). There is therefore the need to assess the impact of water and sediment contamination on species abundance and diversity in these aquatic systems.
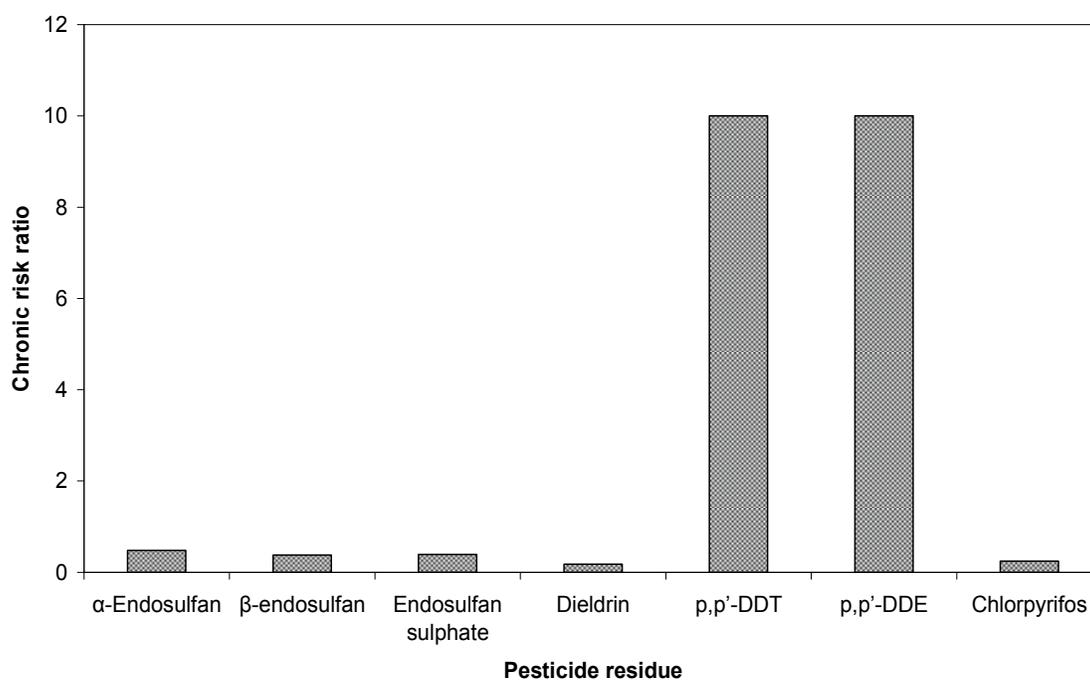

Fig. 4. Chronic risk ratios for detected pesticides in stream water

4. Conclusion

The results of this study have provided an insight into the levels of pesticide residue contamination in streams flowing in and around vegetable plantations in the Ofinso District of Ghana. Among the pesticides detected, endosulfan was the compound with the highest

incidence of occurrence in both water and sediment, which is also the most frequently used pesticide in the study area. Sediment samples exhibited greater number and higher concentrations of pesticides residues than stream water samples. Although acute and chronic risk ratios indicated that the concentrations of the detected pesticide residues in streams did not surpass aquatic quality criteria, the presence of endosulfan in stream water has implications for public health. The use of endosulfan in agriculture should continue to be carefully monitored given its persistence, bioaccumulation, and continued release into streams. An extension of both the study areas and range of pesticides residues analyzed should be considered in future work.

5. Acknowledgement

6. References

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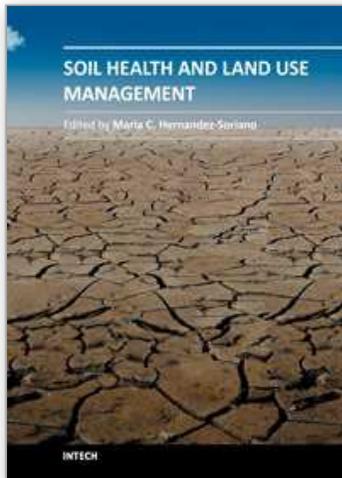
Soil Health and Land Use Management

Edited by Dr. Maria C. Hernandez Soriano

Soils play multiple roles in the quality of life throughout the world, not only as the resource for food production, but also as the support for our structures, the environment, the medium for waste disposal, water, and the storage of nutrients. A healthy soil can sustain biological productivity, maintain environmental quality, and promote plant and animal health. Understanding the impact of land management practices on soil properties and processes can provide useful indicators of economic and environmental sustainability. The sixteen chapters of this book orchestrate a multidisciplinary composition of current trends in soil health. Soil Health and Land Use Management provides a broad vision of the fundamental importance of soil health. In addition, the development of feasible management and remediation strategies to preserve and ameliorate the fitness of soils are discussed in this book. Strategies to improve land management and relevant case studies are covered, as well as the importance of characterizing soil properties to develop management and remediation strategies. Moreover, the current management of several environmental scenarios of high concern is presented, while the final chapters propose new methodologies for soil pollution assessment.

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