

**Environmental Study of Pesticide Residues in Soil and Water from Cotton Growing Areas
in Mali**

by

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Abstract:

A study was undertaken to obtain information on farmers' knowledge, attitudes and practices regarding pesticide usage and to determine the amount of pesticide in soil and water samples collected at four cotton producing areas of Mali. The results from a survey of 24 farmers identified various concerns regarding personal and environmental safety. Despite their training, sometimes growers did not use pesticides in an appropriate manner. Highly toxic pesticides are used by farmers with insufficient personal protective equipment. Sixty soil samples and eight water samples from four cotton growing areas in Mali were scanned for detectable levels of fifty pesticides in total. Pesticides were detected in 77% of the soil samples and the main pesticides were p,p-DDT and its breakdown products, endosulfan I endosulfan II, endosulfan sulfate and profenofos. Among the pesticides detected, p,p-DDT use in the study area had not been reported during the past ten years. The most common pesticide detected in the soil samples from cotton growing areas studied was endosulfan II constituting 65% of the detections with a maximum amount of 37 ng/g. Residues detected in soil samples were below the quantification limit for the newer cotton production region of Kita and for the intermediate region of San. Eight pesticides were detected in water samples: γ -BHC (lindane), endosulfan I, endosulfan II, endosulfan sulfate, dieldrin, p,p-DDD, p,p-DDE and atrazine. All detected pesticides in water had concentrations below the quantification limit except for atrazine. Even though pesticides were found at low concentrations in ground water samples, the fact that water from these wells is used for human and animal consumption is of concern. Also, soil pesticides may be taken up by plants and passed on to other organisms feeding on those plants. Further residues studies in the cotton growing areas of Mali are in order to monitor pesticides residues in Malian soils, water and living organisms.

Dedication:

This thesis is dedicated to my family. It is the product of two years of a work in which you all have contributed in different ways. I cannot fully express my gratitude to you all for having been concerned by the accomplishment of this study and by my well-being as an individual. My father, mother and step mother have been a wellspring of strong values for my brothers, sisters and me. You taught us how to love by love, how to be hard workers and most importantly how to forgive our peers and how to accept the difference from others would they be poor, rich or from another culture. Mother Komso, thanks to the courage you taught me during your shortened life with us I was able to brave fearless the confusion I have encountered alone far from family. You have been an example of kindness around you at such point that we were all amazed by the flow of more than a thousand of people that participated at your funeral. People were asking if you were a political figure? No Komso, you were just kind and just to others. Because of the kindness you have demonstrated in this world, God has guided me and let me achieve this work. Mohamed (Ladji), your love, patience, moral assistance, financial support and comprehension have been a source of consolation for all those days of turmoil during the time frame of this master. God bless you. Would I be irritated, you will have the right words to calm me down. You saved me from misinterpreting this turbulent world. I would always remember these sentences from you: “Be strong Atou, your moral strength will be your saver; we are only in transit in this world, and patience is mother of all virtues”. Your everyday phone calls have lessened difficulties during my stay away from you in Blacksburg. I cannot imagine a stronger and softer company for Soukhaina and me. I made the right choice by saying “yes” to you. You are the light which brightens the darkness of the world for me and help me sort out the

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Chapter 1

Introduction and Review of Literature

1.1. Introduction

Mali is a landlocked sub-Saharan country located in West Africa (17°00 North of the Equator, 4°00 West of Greenwich) (Greenwich 2000 Limited., 2004). It is also one of the poorest countries in the world with a per capita income of only \$240 per year (World Bank., 2001). The climate is subtropical to arid; hot and dry from February to June; rainy, humid and mild from June to November; cool and dry from November to February. Its economy is primarily based on agriculture and animal husbandry with agriculture employing 80% of the work force. The major food crops are millet, sorghum, maize and rice often grown in rotation with niébé (cowpeas), and peanuts. Cotton is an economically crucial crop in Mali. It constitutes the major exportable agronomic crop providing Mali with a means to obtain foreign currencies. Mali is currently the second largest producer of cotton in Africa with 517,400 tons produced in 1999 (Camara et al., 2000; The Economist Intelligence Unit Limited, 2004). Cotton fiber is the most important raw material used in textiles and cotton seed constitutes a source of vegetable oil and a high quality protein source for animal feed. Cotton production may suffer from pests' attacks and the most common cotton insect in Mali is the noctuid *Heliothis armigera* or bollworm. To ensure higher cotton yields farmers use pesticides. Cotton production is responsible for the largest amount (80%) of pesticide applied in Malian agriculture and most of the cotton pesticides are insecticides (Ajayi et al., 2002). Moreover, the expansion of cotton agricultural areas and the development of pest resistance have both contributed to the increase in pesticide use since 1995. In Mali, three major governmental companies, the Compagnie Malienne pour le Développement des Textiles (CMDT), the Direction Nationale de l'Appui au Monde Rural (DNAMR) and the Opération Haute Vallée du Niger (OHVN), jointly control the monopoly for input of chemical supplies in producing areas. Pesticide imports benefit from reduced tariffs and are exempt from sales tax. Total pesticide use in the Malian agricultural sector for the last decade is given in Table 1-1. Insecticides represent the main pesticides used in Malian agriculture and account for about 95% of the total pesticides used in cotton (Table 1-2).

Mangoes and green beans constitute the major exportable food crop in Mali. The European Union has set Maximum Residue Limits for imported food crops from outside the Union. In Mali, there are concerns that pesticide use on fruit and vegetable production is anarchic; growers having little or no knowledge about pest identification and the risks associated with pesticide application. Unlawful residues on fruits and vegetables may threaten the export market to the European Union. Alternatives to intensive pesticide use have been developed at a limited scale. For instance, the CMDT has adopted a scheme of reduced insecticide use, called in French “Lutte Etagée Ciblée”, on about 4% of its cotton growing area (Ajayi et al., 2002). Research for alternatives to intensive pesticide use has been initiated by the Institut d’Economie Rurale (IER) and the OHVN through financial support from the United States Agency for International Development. Extension and training on pesticide usage are carried out by DNAMR, CMDT, OHVN, and other agricultural organizations.

Chemical pesticides used for pest control have contributed to improvements of agricultural yields, and their use has helped the country to meet increasing economic needs due to population growth. In Mali, pesticide use is increasing, but little information is available regarding the environmental impacts (Camara et al., 2000). Intensive agricultural practices that use pesticides to improve yields, increase the risk of soil and water contamination. Pesticides can enter ground water resources and surface run-off during rainfall, therefore contributing to the risk of environmental contamination. Also, some carrier agents, (carbon tetrachloride, chloroform, etc.) used in pesticide formulations are classified as inert, but may be a concern for human health. For instance, dioxin contaminants in chlorophenoxy acid herbicides have been a concern because of their environmental persistence, potential to bio-accumulate, and chronic toxicity related to long term health effects (Garry, 2004; Water Sanitation and Health Unit, 2002).

Table 1-1. Quantities of pesticides (formulations) used in the Malian agricultural sector from 1990/1991 to 1998/1999¹

Pesticide type	Year								
	90/91	91/92	92/93	93/94	94/95	95/96	96/97	97/98	98/99
Fungicides (x1000Kg)	3	5	4	11	52	0	55	45	53
Insecticides (tons.eq.)	3168	2850	2982	1979	1812	1332	1440	3803	4070
Herbicides (x1000L)	160	196	175	269	212	206	246	669	683
Rodenticides (x1000Kg)	0.15	0.04	4.95	2	0.05	0	0	0	0
Total pesticides (tons.eq) ²	3350	3051	3166	2261	2075	1538	3120	4517	4806

¹Sources: Direction Nationale de l'Agriculture (DNA) (1992 to 1996); Direction Nationale de l'Appui au Monde Rural (DNAMR) (1999, 2000) reported by Ajayi et al., (2002).

²Metric tons equivalent: 1 ton = 1000kg or 1000L.

Table 1-2. Pesticide types used in cotton production in Mali from 1990 to 1999¹

Pesticide type	Growing season								
	90/91	91/92	92/93	93/94	94/95	95/96	96/97	97/98	98/99
Insecticides (x1000L)	2246	2244	2619	1738	1719	1256	2347	3046	3787
Herbicides (x1000L)	68.5	99.1	71.7	43.9	56.6	96.6	111	259	358
Fungicides (tons)	0.09	2.1	--	3.3	49.9	--	24.5	31	45.2
Total pesticides (tons.eq) ²	2314	2346	2690	1785	1826	1353	2482	3336	4190
% of total agricultural pesticide use	69	77	85	79	88	88	80	74	87

¹Sources: Direction Nationale de l'Agriculture (DNA) (1992 to 1996); Direction Nationale de l'Appui au Monde Rural (DNAMR) (1999, 2000); Compagnie Malienne pour le Développement des Textiles (CMDT) (2000a); Opération Haute Vallée du Niger (OHVN) (2000) reported by Ajayi et al., (2002).

²Metric tons equivalent: 1 ton = 1000kg or 1000L.

In Mali, where pollution from pesticides is of increasing concern, there is a need to improve the legal framework of pesticide management. As a result, the Malian government is developing legislation which will regulate the import, distribution and use of pesticides. In 1985,

Mali adopted the Food and Agriculture Organization's (FAO) Code of Conduct for the Distribution and Use of Pesticides. The objectives of this Code are to set responsibilities for all public and private entities engaged in the distribution and use of pesticides, particularly in countries where there are no national laws to regulate pesticides. Pesticide distribution and use in Mali are controlled by the Direction Générale de la Réglementation et du Contrôle (DGRC). The Direction Nationale de l'Assainissement et du Contrôle des Pollutions et des Nuisances (DNACPN) is responsible for the control of pesticide production and formulation (Ajayi et al., 2002). Mali also adopted the Stockholm convention in 2001 which is a global treaty to protect human health and the environment from persistent organic pollutants. The country is also a signatory of the legislation of pesticides common to member states of "Comité Inter-états de Lutte contre la Sécheresse dans le Sahel" (CILSS). However, Mali and other countries in West Africa are behind in the implementation of the Code of Conduct for the Distribution and Use of Pesticides (Diarra, 1999). Greater access to pesticide markets has led to increased pesticide sales (legal and illegal) and their use. Pesticide retail sales are uncontrolled and pesticides may enter Mali fraudulently from several neighboring countries (Diarra, 2003a).

It is well-established that the misuse and mishandling of pesticides can cause significant harmful impacts on human health and on the environment. In Mali, farmers and pesticide salesmen are neither aware of, nor have sufficient knowledge of, the potential risks of pesticide application/use. Most farmers don't use appropriate personal protective equipment for pesticide applications nor do they always use the appropriate pesticide application equipment. Exposure to pesticide substances can occur by multiple routes: air, food, unsafe discarded containers, contaminated soils and water. A survey of Malian pesticide vendors in Bamako, Mali was conducted by Moore et al. (2001). The purpose of the survey was to obtain information about the pesticide marketing chain, pesticide repackaging, safe use and handling practices and the transfer of pesticide use practices and other safety related issues. This study reported that pesticide salesmen repackage pesticides in smaller quantities into plastic containers. These repackaged products are poorly labeled which can lead to the use of an inappropriate pesticide on the wrong crops or to errors in applying pesticides in appropriate dosages (Moore et al., 2001). Disposal of empty pesticide containers is also a problem. Diarra (2003a) reported that "The proper procedure for disposing of empty containers is almost never followed. Empty pesticide containers of all kinds are on public sale everywhere. These empty containers may be reused as

drinking water containers or for storage of food products” (Diarra, 2003a). Pesticide container disposal also may present other problems. In many cases they are discarded without regard for where they may end up and may be retrieved and reused for other purposes, such as storage of other liquid products or they may even be fashioned into other items such as toys. Reused containers may represent an exposure hazard to persons, especially children who will come in contact with the poison residues when using these items, making children vulnerable to pesticide poisoning. Adverse pesticide effects are more likely to occur in children who are at special developmental and behavioral risk (Garry, 2004).

Outdated pesticides constitute a problem in Mali. The total quantity of out of date/expired pesticides stored in Mali is estimated to be about 110,420 liters (Diarra, 2003a). There is a potential risk of expired products being marketed fraudulently and used inappropriately by farmers. Also, these obsolete pesticides need to be disposed of correctly to avoid the contamination of environment and risks to human health.

According to Beylneh (2002) the source of growing obsolete pesticide stocks in developing countries are:

- 1) Over donations/importations, especially under emergency conditions
- 2) Importation/Exportation of expired/near expiring products
- 3) Untimely delivery, poor transportation facilities, etc.
- 4) Inappropriate formulations, not compatible with the existing spray equipment
- 5) Lack of knowledge, skills and experience in obsoletes pesticides management
- 6) Sub-standard infrastructure, improper storage facilities, (75-85% of all storage facilities can be described as such).

Few pesticide residue studies have been done in Mali and information available about pesticide contamination of soils and water in Mali is limited. Pesticides have polluted water and soils in northern villages in Mali where obsolete pesticides are stored. A water quality improvement program is being conducted and includes construction of new wells, cleaning up storage depots of expired pesticides and sealing of contaminated wells. Also, a study conducted by the Compagnie Malienne pour le Developpement des Textiles (CMDT) and the Direction Nationale de l’Hydraulique et de l’Energie (DNHE) from 1992 to 1994 has shown the pollution of the Niger river tributary named Banifing by dimethoate, cypermethrin, chlorpyrifos ethyl, profenofos, omethoate, deltamethrin and cyfluthrin (Coulibaly and Derlon, 1994). In this study,

thirty three sites were sampled three times each year (June, September and December). Water samples were analyzed for pesticide residues (wells and surface waters) at laboratories located in France. Water pollution by pesticides was frequent in areas where cotton was grown significantly.

The Environmental Toxicology Laboratory (ETL) of the Central Veterinary Laboratory (CVL) in Mali has a comprehensive mandate that reflects the needs of Mali and the West African region. The expectation for the ETL is to provide information on pesticide and other toxic chemicals, which may occur on crops or find their way into the environment.

According to the United Nations' Food and Agriculture Organization (FAO), pesticide use in African developing countries increases by more than 10% each year. Even though the use of pesticides has contributed to the augmentation of production and avoidance of starvation in some areas, it has also resulted in environmental and health problems. A higher proportion of pesticide poisoning and deaths occurs in developing countries where there are inadequate occupational and other safety standards, insufficient enforcement, poor labeling of pesticides, high illiteracy, inadequate clothing and washing facilities, and lack of knowledge of pesticide hazards (Pimentel et al., 1993). The inappropriate use of pesticides can lead to soil pollution which may cause damage to crops planted in rotation. The main concerns related to pesticides in soil are leaching and run-off into surface or underground water sources. Pesticide run-off from agricultural activities can lead to pollution of water supplies and exposure of the general public, since many pesticides are not used in accordance with registration requirements or are used without suitable precautions associated with their application. The risk is even greater in Mali because health is already compromised by poor sanitation, malnutrition, and poverty.

Both the acute and chronic health effects of pesticides constitute a concern. Toxic outbreaks or collective acute pesticide poisonings have been reported from misuse of almost every type of pesticide. They may occur from oral or cutaneous exposure or they may be occupational in nature, involving workers in manufacturing or formulators, mixers, or applicators in agriculture and public health. Chronic effects of pesticides include carcinogenesis, neurotoxicity, and reproductive and development effects (Hodgson and Levi, 1996; Safi, 2002). Hayes et al. (2002) studied the effect of atrazine on sexual development in African clawed frogs. Larvae were exposed to concentrations of atrazine ranging from 0.01 to 200 ppb. Atrazine at levels ≥ 0.1 ppb induced hermaphroditism and demasculinized the larynges of exposed males. The

authors hypothesize that atrazine induced the conversion of testosterone to estrogen. This result suggests that other amphibian species exposed to atrazine in the wild could be at risk of impaired sexual development (Hayes et al., 2002). This widely used pesticide and other endocrine disruptors may be a factor in global amphibian decline. The banned nematicide, dibromochloropropane (DBCP) has been associated with reduced sperm counts in human studies (Garry, 2004; Water Sanitation and Health Unit, 2002). Also, there is evidence from animal studies that pesticides can cause immune dysfunction over time. Based on animal studies, there is evidence that some pesticides can cause cancers due to long-term exposure (Pimentel et al., 1993). Pesticides have a negative impact on soil microorganisms and invertebrates, which play a vital role in the soil ecosystem. Soil microbial diversity may be markedly changed following pesticide use despite unaltered nitrogen and carbon metabolism, and such changes may affect soil fertility (Johnsen et al., 2001). Moreover, a number of pesticides seem to affect the growth of organisms such as earthworms, marine organisms, mussels, fish, birds, pigeons and deer (Edwards, 1993). The damage to bees caused the loss of many crops in California because of the lack of pollination (Pimentel et al., 1993).

Very little is known about pesticide residues in cotton producing areas of Mali. However, the intense use of pesticides in these areas suggests that contamination problems might exist. The purpose of this research was to assess the conditions under which pesticides are used by farmers in Mali and to obtain information on the status of pesticide residues in soils and water in cotton growing regions of Mali. Knowledge of farmers' practices will help reduce the potential for "acute toxic accidents", chronic exposure, and environmental contamination. Information on pesticide residue levels in soil and water will be useful in assessing the need for improving pest control technology to minimize environmental effects.

1.2. Significance of pesticide residues in soil and water

Agricultural pesticide use may result in undesirable residues in soil and water which can persist in the environment and have adverse effects on living organisms. Historically, a persistent pesticide was considered to be one whose residues remained in the soil in significant quantities after application until the next growing season or until the sowing or planting of a following crop. The concept of the time taken for degradation (in the laboratory) or dissipation (in the field) of 50% of the active substance originally applied has supplanted the former concept of persistence. Therefore, the DT_{50} value (the time required for 50% dissipation of the initial concentration) is similar to the more traditional term “half-life” (Craven, 2000). DT_{50} values provide a numerical indicator of pesticide persistence in soil (Beulke and Brown-Colin, 2001). Predictions of pesticide concentrations in soil, surface water and groundwater are a significant part of the data package submitted for pesticide registration. Pesticide degradation in soil is one of the most important processes influencing the environmental behavior of a pesticide. Some major factors which influence pesticide persistence in soil are: 1) soil properties (pH, organic matter content, microbial activity, etc.); 2) prevailing temperature and seasonal fluctuations; 3) soil moisture content and availability; 4) aerobic or anaerobic conditions (Craven, 2000).

Translocation of soil residues into crops may constitute a potential hazard to the consumer eating crops that are grown in these soils (Lichtenstein, 1971). Soil pesticide residues may be directly toxic to animal and/or plant life in the soil. The effects of pesticides on nontarget organisms may include: 1) reduction of species numbers, 2) alteration of habitat with species reduction, 3) changes in behavior, 4) growth changes/altering reproduction, 5) changes in food quality and quantity, 6) increased resistance, 7) increased disease susceptibility, and 8) biological magnification (Ware, 1980). Selection pressures due to continued use of pesticides may result in resistant populations. Pesticides may also accumulate in soil flora and or fauna and can be passed on to other organisms which may affect soil arthropod populations. In general, root crops tend to take up greater residues, and residues are higher in the peel than in the pulp. In other crops, residues are higher in the roots and lower portions than in the aerial part of the plants (McEwen and Stephenson, 1979). Soil and sediments contaminated with persistent organohalogenated pesticides may be attributed to point sources (industrial discharges and waste plant effluents), but more frequently it is attributed to diffuse or non-point sources (precipitation, agriculture runoff, particle transport, etc.) (Falandysz et al., 2001).

The persistence of pesticides in water depends on several factors of which pesticide solubility in water is one of the most important. Insoluble pesticides such as DDT, dieldrin, and endrin have the potential to persist in surface water for long periods and are primarily associated with sediments. The nature of the water (chemical composition, pH, temperature, aquatic life) and amount of suspended organic and inorganic material are also important. Pesticide contaminated ground water and surface water pose a risk due to their possible use as drinking water and their effects on aquatic ecosystems (Barbash and Resek, 1996).

1.3. Environmental fate of pesticides in soil and water

1.3.1. Sources of pesticides found in soil and water

High concentrations of pesticides may reach the soil through direct application to the soil surface, incorporation in the top few inches (metric) of soil, or during application to crops (Jury et al., 1987; McEwen and Stephenson, 1979; Seiber and Woodrow, 1983). When pesticides are applied to crops, it is estimated that up to one-third of the total amount sprayed can contaminate the soil. The amount deposited onto soil is variable and depends on the crop canopy (Barber and Parkin, 2003). Also large amounts of pesticide may reach the soil through drift during pesticide application, and through atmospheric fallout and can be carried by the wind to nontarget areas (Suntio et al., 1988). Toxic chemicals with a sufficient atmospheric lifetime (on the order of a few days or longer), including those of low volatility, can be distributed throughout the global troposphere (Jury et al., 1987; Koziol and Pudykiewicz, 2001). When pesticides are applied in granular form and/or injected into the soil, the impact of drift approaches zero compared to 50% or more which may be lost when spraying techniques are employed. The extent of drift to nontarget areas is determined by variables such as droplet size in the spray stream, boom height, temperature, relative humidity and the size of the area being treated. Pesticide movement and deposition is affected by the form in which the pesticide enters the air, and the dimensions of the pesticide-containing droplets. Transport or drift over distances of several miles may be responsible for adverse effects on nontarget species (Woods et al., 2001). Pesticide deposits have been measured at various distances downwind from the point of application (Siebers et al., 2003). There is a relatively heavy deposit immediately adjacent to the treatment swath declining rapidly as the distance from treatment increases. This is to be expected, since large droplets drift

a shorter distance compared to smaller droplets and also the amount of pesticide carried per droplet increases with large droplets. McEwen and Stephenson (1979) reported on studies done in Arizona showing that although total DDT residue levels in soil were 6.7 ppm within a few meters of a cotton field, residues declined sharply as the distance from the cotton field increased. They were in the 0.1 ppm range at 100 meters and in the 0.01 ppm range at 10,000 meters from the treatment area. In the early 1960s, a number of studies demonstrated the presence of pesticides in rain water and/or snow. High levels of residues in soils observed in March 1966 could not be explained on the basis of field usage of the pesticides at the time of year, it was suggested that low rainfall during the period might explain the high levels detected (McEwen and Stephenson, 1979). However, the pesticide levels that may be present in rainfall are not sufficiently high to serve as a major source of soil contamination. A variety of chemically polar pesticides have been found in precipitation throughout the world (Grynkiewicz et al., 2001; Huskes and Levsen, 1997; Majewski and Capel, 1995). Pesticides may also reach soil by direct deposition of atmospheric dust (McEwen and Stephenson, 1979). Direct applications of pesticides to control weeds and algal blooms, insects such as mosquitoes, black flies and biting midge that breed in water and prior to restocking may contribute to the contamination of surface waters. Also drift during application and atmospheric fallout on rain and dust can contaminate water. Pesticides soluble in water that are applied to soil may be carried to nearby waters by surface runoff. Industrial effluents, sewage and spills are other possible sources of contamination (Gerecke et al., 2002; Larson et al., 1997). Pesticide may be leached away from target organisms in the upper layers of soil to deeper layers (Nicholls, 1988).

1.3.2. Fate of pesticides in soil and water

Prediction of pesticide environmental fate in pre-market tests is important to ensure with a high degree of confidence, that a chemical will not pose adverse environmental effects (Seiber, 1987). The movement of pesticides in the environment is very complex with movement occurring continually among different environmental compartments. Sometimes, these exchanges occur not only between areas that are close together, but also may involve transport of pesticides over long distances. No single factor can be used to predict the environmental fate of pesticides. Only knowledge of the interaction of several factors will provide this information. Many factors influence the behavior and fate of pesticides after they come into contact with soil.

These factors include volatilization to the atmosphere, leaching with the downward percolation of water, adsorption to clay and organic matter, uptake by soil organisms or plants, movement with runoff water or eroded soil, microbial degradation, chemical degradation, and photolysis (Lichtenstein, 1980; White and Cruz, 1971).

The fate of pesticides in tropical regions is not as well understood as in temperate regions. Field investigations of tropical pesticide fate indicate that dissipation often occurs more rapidly than for pesticides under temperate conditions. Mechanisms involved in this accelerated dissipation are related to the effect of tropical climates and include: 1) increased volatility; 2) enhanced chemical and microbial degradation (Racke, 2003).

Figure 1-1 illustrates the processes influencing the behavior and fate of pesticides in the soil environment.

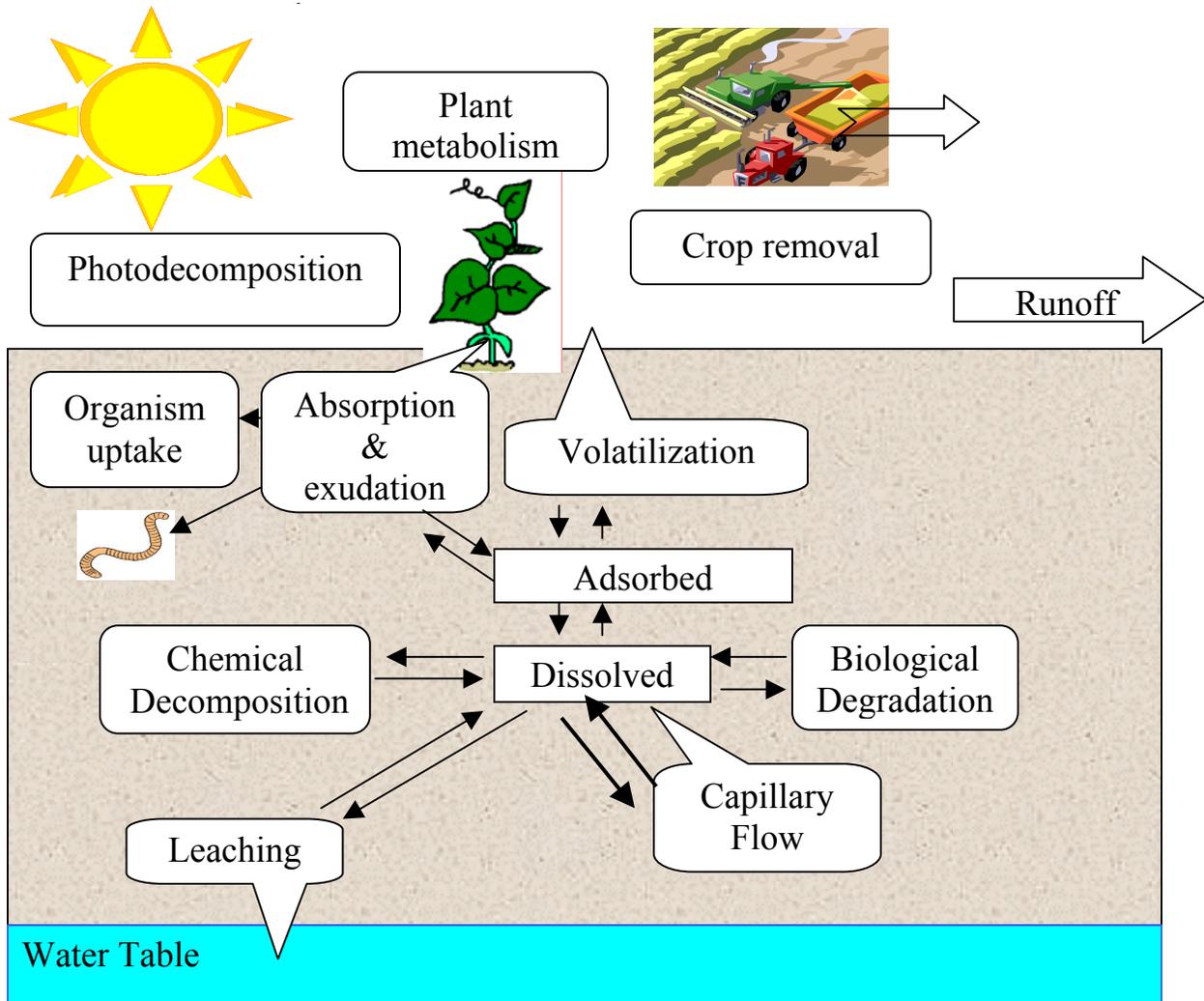


Figure 1-1. Processes influencing the behavior and fate of pesticides in the soil environment modified and redrawn from McEwen and Stephenson, 1979.

Physical environmental partitioning processes can be described in terms of equilibrium expressions between compartments which are summarized in Table 1-3.

Table 1-3. Key physical and environmental properties in fate assessment (adapted after Swann et al., 1983).

Property	Definition
Soil sorption coefficient (K_d)	$\frac{\mu\text{g chemical soil/g of soil}}{\mu\text{g chemical water/g of water}}$
Soil sorption constant (K_{oc})	$\frac{K_d}{\% \text{ organic carbon}} \times 100$
Bioconcentration factor (BCF)	$\frac{\mu\text{g chemical/g of organic matter}}{\mu\text{g chemical/g of water}}$

Three measurements are commonly used to describe the sorption potential of pesticides. The partitioning coefficient (K_d) depends on properties of the compound and the solid phase of the soil. The organic phase is the main sorption site for many nonpolar, nonionic compounds. Larger K_d values reflect higher organic matter percentage in the soil. Therefore, a more useful parameter K_{oc} is introduced to reflect the fraction of organic carbon in the soil ($K_{oc} = K_d/f_{oc}$), where f_{oc} is the fraction of organic carbon in the soil (Cheng and Koskinen, 1985). Four major factors influence the fate of pesticides in soils. They are: properties of the pesticide, properties of the soils, site conditions and management practices (Lichtenstein, 1971; White and Cruz, 1971).

1.3.2.1. Physico-chemical pesticide properties that may influence their environmental fate

1.3.2.1.1. Volatility

Volatilization is a major pathway for loss of applied pesticides (Jury et al., 1987; Lichtenstein, 1971; Rudel, 1997; Spencer et al., 1973). Pesticide volatilization from soil has been widely studied (Suntio et al., 1988). The tendency of pesticides to volatilize and leave soil as a vapor is influenced by several factors including the vapor pressure of the chemical (Koskinen and Clay, 1997; Spencer and Cliath, 1983), its solubility in the soil water phase and its tendency to be adsorbed. The vapor pressure of many pesticides increases three to four fold for each 10 °C increase in temperature (Spencer and Cliath, 1983). The upward transport of pesticide through the soil to the soil-atmosphere interface occurs either by gaseous diffusion through the air-filled volume of the soil, or by the upward flow of soil solution induced by water evaporation. Partitioning according to Henry's Law is a major determinant of the rate of pesticide volatilization from soil. Cool, dry conditions in soils with high organic matter or clay content normally result in very little loss of even the most volatile pesticide from the soil, since pesticides may be adsorbed tightly. Conversely, warm, moist conditions cause greater desorption and greater volatilization losses (McEwen and Stephenson, 1979). The more volatile a pesticide, the greater is its potential to enter the atmosphere and to move long distances. Pesticides may volatilize appreciably from water bodies such as ponds, rivers, or lakes during or after application. Volatilization rates from water can be calculated as a flux (moles of pesticide per square meter of water surface area per hour) or as a first order rate constant or half-life (Smith et al., 1983).

1.3.2.1.2. Solubility

Water solubility is a critically important determinant of pesticide environmental behavior and fate (Lichtenstein, 1971). The fundamental equilibrium thermodynamics that control solubility also play a key role in determining environmental partitioning behavior in soils, water and the environment at large. Three fundamental parameters, including solubility, octanol-water partition coefficient K_{ow} and vapor pressure, control partitioning into different phases. Octanol-

water partitioning and aqueous solubility are closely related, and one can be predicted from the other (Finizio et al., 1997; Larson and Weber, 1994). However, solubility and K_{ow} are inversely related, thus the partitioning behavior is essentially controlled by vapor pressure (which can be viewed as "solubility" in air or in a vacuum) and solubility in water. Partitioning between organic phases such as lipid and water is primarily controlled by the water solubility. Many organic chemicals differ greatly in their hydrophobicity or solubility in water, compared to their lipophilicity or solubility in organic phases which is similar. The octanol-water partition coefficient is used in evaluative models for the prediction of distribution among environmental compartments, in equations for estimating bioaccumulation in animals and plants and in predicting the toxic effect of a substance in Quantity Structure Activity Relationships (QSAR) studies (Finizio et al., 1997).

Henry's Law constant describes partitioning between air and water as essentially a balance between air and water solubilities (Suntio et al., 1988). Pesticides possessing low water solubilities may appreciably partition into air even when they have low vapor pressure, as is the case of DDT. The strong partitioning tendency from water into organic phases such as lipids or humic acids causes appreciable fractions of these chemicals present in water to become associated with particulate matter and thus not available for evaporation or bioconcentration (Shiu et al., 1990).

Not only does water solubility affect equilibrium partitioning, it also affects the rates of processes such as evaporation from water or soil to air, or uptake from water by fish. Solubility is also an important consideration when devising pesticide application processes and influences the tendency for them to be leached from soil by irrigation or by rain water, and thus influencing the potential for groundwater contamination (McEwen and Stephenson, 1979). Water solubility also plays a role in controlling uptake and translocation in plants. For instance, many herbicides are selected on the basis of relatively high water solubility. Notable examples are the phenoxy acids such as 2,4-D (Shiu et al., 1990).

Pesticide partitioning effects from aqueous solutions are controlled by their activity or fugacity. Fugacity of a pesticide is based on its activity coefficient γ . Therefore, solubility is only an indirect determinant of partitioning because it is related to γ . Because solid solubility is significantly influenced by melting point, it is expected that solubility alone will be a poor correlating quantity for environmental partitioning quantities such as bioconcentration factors or

organic carbon-water partition coefficients. Indeed, the correlation should be with γ not with solubility, but this necessitates some thermodynamic calculations involving fugacity ratios. This can be avoided by using K_{ow} which is directly related to γ (Shiu et al., 1990). Solubility- K_{ow} relationships are interesting because K_{ow} can often be estimated from merely a knowledge of chemical structure using for example, fragment constant methods (Schwarzenbach et al., 2003). This enables solubility to be deduced. K_{ow} is the ratio of a chemical in octanol and in water. K_{ow} can be expressed in logarithmic form in general with fitted parameters A and B: $\log K_{ow} = A - B \log C^s$.

Several correlations of this type can be found in the literature:

- $\log K_{ow} = 0.323 - 0.833 \log S$ for insecticide chemicals (Bowman and Sans, 1983)
- $\log K_{ow} = 0.710 - 0.862 \log S$ for DDT, aromatic hydrocarbons and chlorinated benzenes (Shiu et al., 1990).

Therefore, a physico-chemical basis exists for correlating solubility and octanol-water partition coefficient. Partition coefficients of environmental importance such as organic carbon-water partition (K_{oc}) or bioconcentration factors are most easily correlated with K_{ow} . Several other factors influence solubility or apparent solubility. For instance, electrolytes present in solution generally act to “salt out” chemicals (Shiu et al., 1990). Dissolved organic material and surfactants generally increase the apparent solubility, and in natural waters present in lakes, rivers, and soils, the prevailing solubility may thus differ from the values reported in the literature.

Water solubility is also important; a very soluble pesticide can easily be carried with rain water as runoff or through the soil as a potential groundwater contaminant (leaching). Pesticides highly or moderately soluble in water are leached from soils more quickly than those which are less water soluble. Thus the highly insoluble organochlorine insecticides such as DDT and dieldrin tend to persist, do not readily leach and are found predominantly in the upper few inches of agricultural soils (McEwen and Stephenson, 1979).

1.3.2.1.3. Adsorption, desorption and bound residues

Many pesticides do not leach because they are adsorbed by soil particles. Adsorption depends on the chemical properties of the pesticide and also on the soil type and amount of soil organic matter present. Mechanisms involved in adsorption range from van der Waals-London forces, hydrogen bonding, ligand and ion exchange, charge transfer, ion-dipole and dipole-dipole forces, hydrophobic bonding, to chemical adsorption (Bailey and White, 1970; Cheng and Koskinen, 1985). Pesticide molecules vary in their tendency to be adsorbed, attracted to clay or organic matter particles or dissolved in the aqueous phase. Soil clay mineral fractions with organic matter may play a significant role in the retention of certain pesticides (Cheng and Koskinen, 1985; Edwards, 1966; Li et al., 2003; Ma and Selim, 1996). In both the mineral and organic fractions of the soil colloid, the surfaces of reactive sites consist primarily of oxygen and/or hydroxyl, carboxyl, amino, phenolic hydroxyl and alcoholic hydroxyl groups. The fraction representative of the soil organic matter is the humic acid fraction which is the insoluble precipitate resulting from neutralization of the alkaline soil extract; the soluble portion is the fulvic acid. The inorganic fraction of soil colloids consists of crystalline and amorphous oxides and hydroxides of silica, iron and aluminum. Minerals such as montmorillonite and vermiculite which have high surface area and cation exchange capacity are more reactive than illite and kaolinite (White and Cruz, 1971). The adsorption sites on clay or organic matter are negatively charged and constitute the “cation exchange capacity” (CEC) of a particular soil. A different equilibrium for each pesticide, for each soil type, and for each set of soil conditions can be established between the amount of pesticide adsorbed and the amount dissolved in the soil solution (McEwen and Stephenson, 1979). Cation exchange capacity is the amount of exchangeable cations per unit of soil (dry basis). Soils with a high CEC can retain higher amounts of cations which may reduce leaching of pesticides. The CEC of a soil increases with content of clay and soil organic matter. Ranges of CEC within soil textural classes are: sands: 1-5, sandy loams: 5-10, loam and silt loam: 5-15, clay loam: 15-30 and clay: more than 30 milliequivalents per 100 g. The effects of soil organic matter on CEC are most important in sandy soils which have intrinsically low CEC values (MeisterPro, 1998). As organic carbon content increases, sorption of many pesticides increases (Koskinen and Clay, 1997). The cation

exchange capacity of humic acid is 200 to 400 meq/100 g. Metolachlor adsorption in soils has been positively correlated with high clay/or organic matter content (Peter and Weber, 1985; Wood et al., 1987). Conversely, the mobility of metolachlor has been shown to be inversely correlated to the clay and/or organic matter contents of the soil (Novak et al., 2001; Ogrigawitch et al., 1981). Also, ash particulates remaining after burning of crop residues are potentially effective adsorbents for pesticides in agricultural soils. Therefore, as crop residues are frequently burned in the field, pesticides in agricultural soils may be highly immobilized due to the presence of ashes (Yang and Sheng, 2003a). Ashes remaining from the burning of crop residues may be an important determinant of pesticide immobilization and environmental fate in soils (Yang and Sheng, 2003b). Aging (herbicide-soil contact time) has been shown to significantly influence the sorption-desorption characteristics of many herbicides, which in turn, can affect the availability of the herbicide for transport, plant uptake, and microbial degradation (Koskinen et al., 2003).

Pesticide adsorption at equilibrium is usually expressed as adsorption isotherms. The two commonly used isotherms are the Freundlich and the Langmuir. The Freundlich isotherm equation may be expressed as $S = K_f C^N$, and the Langmuir isotherm can be written as: $S = (S_T C)/(K_L + C)$, where S is the amount sorbed at equilibrium ($\mu\text{g/g}$), C is the equilibrium concentration of the pesticide in the liquid phase ($\mu\text{g/mL}$), K_f is the Freundlich coefficient (mL/g), and N is the Freundlich exponent (dimensionless). The term S_T is the pesticide adsorption capacity ($\mu\text{g/g}$), and K_L is a pesticide affinity parameter ($\mu\text{g/mL}$). The Freundlich equation is the most commonly used isotherm in pesticide studies. When $N = 1$, the Freundlich equation is reduced to the linear isotherm equation $S = K_d C$, where K_d is the distribution coefficient (mL/g) which is dependent on both pesticide characteristics and soil properties (Bailey and White, 1970; Ma and Selim, 1996).

Pesticides can be released from soil adsorption sites when their concentration in the solution phase decreases due to dilution, volatilization, or translocation. This process is called desorption hysteresis and can be initiated by diluting or replacing the soil solution with pesticide-free solutions (Ma and Selim, 1996).

A significant proportion (20 to 70%) of degradation products from certain agricultural pesticides may remain in soils as bound residues, soil organic matter being largely responsible for their formation by chemical binding and by a process that probably involves adsorption on

external surfaces (Calderbank, 1989; Ma and Selim, 1996). The use of radiolabeled pesticides in laboratory has made it possible to detect unextractable soil residues. Bound ^{14}C -residues can be released from soils by combustion or strong hydrolysis (Khan, 1991; Kovacs, 1986; Lichtenstein, 1980). The plant uptake ratio of pesticides and their degradation products from freshly-treated soils compared to soils containing bound residues is approx. 5:1 (Khan, 1991). With longer residence time in soil, bound pesticide residues "age", i.e., as time progresses residues tend to become more firmly bound, more resistant to decomposition and show little evidence of any biological activity. This may be the result of residue movement into the humic soil fraction. Also, although bound residues persist in soil they are slowly decomposed by microorganisms (Calderbank, 1989). Dankwardt and Hock (2001) have reviewed the application of immunochemical methods for the investigation of non-extractable (bound) residues. Non-extractable residues may be presented to antibodies as antigenic determinants, which are exposed for instance in plant tissue and humic substances. Fluorescent probes as well as enzyme markers have been applied for the detection of bound residues. The use of antibodies with different recognition patterns provides information on the ligation of non-extractable residues to a matrix (Dankwardt and Hock, 2001).

1.3.2.1.4. Degradation

Pesticidal substances entering the soil or water environments may be subjected to various conversion processes characteristic of the system encountered. Soil and water systems provide an environment which is moist and aerated and, therefore, favorable to oxidation and hydrolysis. Anaerobic parts of these environments can undergo reduction reactions. Other chemical transformations may take place according to the reactants available, microbial and enzymatic processes. Enzymatic reactions include ether cleavage, hydrolysis of esters and amides, dealkylation, epoxidation, reductive dehalogenation and N-dealkylation (Coats, 1990; Hartley and Graham-Bryce, 1980). Pesticides can be degraded by the action of sunlight, chemicals, or microorganisms following release into the environment (Koskinen and Clay, 1997). Sometimes, the breakdown products can be biologically active substances (Lichtenstein, 1971; Coats, 1990) and more toxic than the parent compound.

1.3.2.1.4.1. Abiotic degradation (photochemical decomposition, chemical decomposition)

Photochemical reactions of pesticides in the environment have been recognized as an important factor influencing their fate (Floesser-Mueller and Schwack, 2001). Photodegradation is probably not the major means of pesticide inactivation or disappearance in soil. Dinitroaniline herbicides such as trifluralin may be broken down in sunlight, but their application as soil incorporated treatments prevents excessive exposure to light (McEwen and Stephenson, 1979). Mansour et al. (1999) have investigated the photolysis of selected pesticides in aqueous solutions. The photolysis produced intermediate substances which were also found to be soil and microbial degradation products. The results from this study indicate that degradation products of isoproturon are more toxic to *Daphnia magna* than the parent compound. The photolysis rates of environmental chemicals can be altered by the suspended and dissolved matter in water, and temperature has been considered a major factor modifying the rate of pesticide hydrolysis in water and soil. The acceleration of hydrolytic reactions is well described by the Arrhenius Equation and may be used to predict pesticide behavior in soil (Mansour et al., 1999). Temperature effects on first-order rate constant, k , for degradation are expressed as:

$k = k_0 e^{-\Delta E/RT}$, where k_0 is a frequency factor depending on the compound and specific conditions, ΔE is the activation energy, R the gas constant, and T is temperature in °K (Kelvin).

Chemical reactions in soils can inactivate some pesticides and activate others. Also adsorption may enhance the chemical degradation of some compounds. Hydrolysis data are important in assessing the fate of organic chemicals that have hydrolysable functional groups, e.g. esters, epoxides and halogenated compounds. Besides substitutions, halogenated substances can undergo elimination reactions in water to produce dechlorinated products. The hydrolysis rates of organophosphorus pesticides are dependent on their chemical structure. At 30°C and pH 6.0 buffered solutions, the hydrolysis rates range from half lives of 10 hours to 8 days and longer still for phosphorimides. At 20°C, the rates are several hundreds times slower. Oxidation of pesticides usually results in decreased stability (Mansour et al., 1999). The relative pH may also influence the rate of chemical degradation. However, the influence of pH varies for different pesticides. In soils, hydrolysis of atrazine has been found to be favored by low soil pH (Koskinen and Clay, 1997; Ma and Selim, 1996). Whereas the chemical degradation of atrazine

and diazinon occurs faster at low pH, the reverse is true for malathion. Carbofuran persisted much longer than expected in acid soil under actual field conditions, a situation that resulted in poisoning of ducks in British Columbia. Carbofuran had been applied in granular form at the beginning of the season, but ducks picked up toxic granules as late as November (McEwen and Stephenson, 1979).

1.3.2.1.4.2. Biotic degradation (microbial decomposition)

Pesticides may be degraded by microbes such as algae, fungi, actinomycetes, and bacteria which are dependent on organic compounds for energy and growth. When organic pesticides are incorporated into soil and reach an equilibrium between the soil colloids and the soil solution, those molecules remaining in the soil solution are subject to attack by microbes as potential sources of energy (Jury et al., 1987; Ma and Selim, 1996; McEwen and Stephenson, 1979).

1.3.2.2. Properties of soil

Soil physico-chemical properties may have a significant effect on the chemical and biological processes associated with pesticide degradation, and thus play an important role in soil pesticide persistence and on identification of the degradation products. The physico-chemical properties include: texture, permeability, organic matter content, temperature and pH.

1.3.2.2.1. Soil texture

Soil texture is determined by the relative proportion of various particle sizes making up the matrix. These particles are often referred to as soil separates and include sand, silt and clay, all of which vary in size through a particular range. Soil nomenclature used to classify soils is based on the relative proportions of each of these three soil separates (Edwards, 1966; MeisterPro, 1998). Soil texture affects movement of dissolved pesticides through soil. The coarser the soil, the faster the movement of the percolating water, and the less opportunity for soil adsorption of dissolved chemicals. Soils with more clay and organic matter tend to retain water and dissolved chemicals longer. These soils also have more surface area onto which pesticides can be adsorbed (Ma and Selim, 1996). The coarser the texture of the soil, the greater is the probability that the pesticides may contaminate groundwater (Bailey and White, 1970;

Nicholls, 1988). However, Sadeghi et al. (2000) studied the influence of soil texture and tillage on herbicide transport and found higher leaching of atrazine to groundwater in a silt loam soil than in a sandy loam soil. A predominance of macropore flow in the silt loam soil, possibly due to greater aggregate stability, may account for the observed leaching patterns for both field and laboratory studies they undertook. To quantify and prove the impact of macroporosity on chemical leaching, intact versus repacked soil columns of each soil were examined for their potential leaching. Their results showed that the highest leaching was in intact columns for each respective soil texture compared to the repacked columns. Conclusions obtained in this study corroborate the findings under the field conditions regarding higher leaching of atrazine in silt loam textured soil than the sandy loam textured soil despite the tillage systems which were in use (Sadeghi et al., 2000).

1.3.2.2.2. Soil permeability

Soil permeability can be defined as the characteristic of a soil horizon that enables water or air to move through it. The permeability of a soil is controlled by the least permeable horizon even though the other horizons are permeable (MeisterPro, 1998). Soil permeability and organic carbon content (f_{oc}) control the degree to which pesticide residues pass through the rhizosphere to groundwater (Barbash and Resek, 1996). The organic carbon content of soils tends to increase with increasing clay contents (Nicholls, 1988), due to the strong tendency for natural organic solutes to form surface complexes with clays. Low permeability soils usually exhibit higher f_{oc} values than highly permeable soils (Barbash and Resek, 1996). Lower permeability also restricts pesticide movement by slowing the downward migration of the bulk soil solution (Barbash and Resek, 1996; Helling and Gish, 1986). The presence of larger amounts of organic matter reduces the quantity of pesticide reaching deeper depths through the combined effects of enhanced microbial activity (Goetz et al., 1990) and sorption. Since highly permeable soils may lose dissolved pesticides with the percolating water, timing and methods of pesticide application are critical in highly permeable soil to minimize leaching losses.

1.3.2.2.3. Organic matter content

Many pesticides bind quite readily to organic material (Ma and Selim, 1996; McEwen and Stephenson, 1979). The organic matter is an important soil component composed of carbonaceous material of plant or animal origin containing essential plant nutrients. Many organic materials from different sources may combine with pesticides occurring in soil. The most important are solid or liquid organic amendments, such as manure, city refuse compost, peat, sewage sludge, liquid “humic” acids, and surfactants, which are used as adjuvants in pesticide formulations and also are present in irrigation water (Iglesias-Jimenez et al., 1997). Organic matter provides adhesives for soil particles and it is characterized by a high cation exchange capacity and absorptive capacity for water. Soil organic matter influences the quantity of water a soil can hold and to a large extent, the adsorption of pesticides. Practices such as application of manure or plowing under of cover crops increase the soil’s organic matter and its ability to hold water and pesticides in the root zone where they will be available to plants and to degradation.

1.3.2.2.4. Soil temperature, moisture content and pH

Temperature has been considered a major factor modifying the rate of pesticide hydrolysis in water and soil (Mansour et al., 1999). Optimum temperature and soil water for biodegradation range from 30 to 40°C and from 50 to 90% of available soil water capacity (Truman et al., 1998). The adsorption of pesticide in soils is an exothermic process. Heat is given off when hydrogen bonds or ionic bonds are formed. Therefore, when the temperature increases, the heat can break down some of these bonds and causes the desorption of some pesticide molecules with more pesticide being available in the soil solution (McEwen and Stephenson, 1979). Many studies indicate that increased temperature accelerates the disappearance of insecticides from soil by causing desorption and increasing the rate of chemical and microbial degradation.

There is considerable evidence that soil moisture exerts a great indirect influence on the adsorption of insecticides by soil (Edwards, 1966). Decreases in soil moisture are expected to

shift sorption equilibria toward greater adsorption. This assertion is true in moderately light (sandy) to very light soils but not in heavy soils (clay). The impact of fluctuations in soil moisture on the amount of atrazine dissolved in the soil solution has been demonstrated to be inversely related to the adsorption capacity of soil. The addition of moisture may cause the release of pesticides adsorbed on mineral soils but not on muck soils (McEwen and Stephenson, 1979).

Soil pH may influence pesticide persistence. The effects of pH on chemical degradation (hydrolysis, etc.) have already been discussed. It is also known that pH affects sorption phenomena. Soil pH also influences chemical degradation. Within a group of similar soils differing mainly in their pH, pesticide adsorption is usually enhanced in the more acidic soils. Soil colloids represent a negatively charged cation-exchanging environment. Slight increases in soil acidity may convert pesticides from negatively charged anions to uncharged molecules or even to cations and thus increase their adsorption (McEwen and Stephenson, 1979).

1.3.2.3. Conditions of the study sites

The movement of pesticides within a system is affected by the general environment where they may be applied. In previous sections, the physico-chemical properties of soil and abiotic and biotic factors were discussed. However, it is the collective impact of leaching, water runoff, depth to groundwater, geological conditions, climate and agricultural practices that influence the movement of pesticides in the environment.

1.3.2.3.1. Pesticide leaching and runoff

It is difficult to predict the environmental fate of a pesticide based on “exact” integration of transport and transformation processes. Leaching is strongly affected by soil variability (van Alphen and Stoorvogel, 2002). Meteorological and geographic factors also affect each process. Many types of computer simulations based on mathematical models have been developed (Katagi, 2002). Several field-oriented transport models of pesticides have been documented including the Pesticide Root Zone Model (PRZM), Groundwater Loading Effects of Agricultural Management Systems (GLEAMS), Root Zone Water Quality model (RZWQM). A review conducted by Ritter (1990) showed that in the United States, over 70 pesticides have been

detected in ground water. The most frequent pesticides detected in ground water were aldicarb and atrazine along with soil fumigants like ethylene dibromide (EDB) and dibromochloropropane (DBCP). “Downward movement of atrazine may occur from percolating water carrying it to lower soil depths. Well-structured soils have been reported to have more chemical movement to deeper depths when compared to non-structured soil as the result of water flow through macropores in structured soils. Increased permeability, percolation, and solute movement can result from increased porosity, especially in no-tillage systems” (Ritter, 1990). Earthworm burrows can function as preferential flow conduits (Koskinen and Clay, 1997). Some other triazine herbicides (simazine and cyanazine) have also been detected in ground water. Several factors are important in determining ground-water contamination potential by pesticides (annual amount of recharge, soil type, depth of aquifer from the surface, nitrate contamination and soil pH are important field parameters). Pesticide leaching can be reduced by proper choice of crop rotation, increasing pesticide application efficiency, and integrated pest management (Ritter, 1990).

Many studies have shown pesticide movement from the point of application in runoff water (Gerecke et al., 2002; Koskinen and Clay, 1997). Environmental conditions such as rainfall pattern and tillage practices affect pesticide runoff (Ma and Selim, 1996). Kennedy et al., (2001) studied the fate and transport of endosulfan applied to cotton fields throughout three consecutive years on two selected locations in New South Wales (Australia). Rates of dissipation from foliage and soil, volatilization from the field, and transport of residues in irrigation and/or storm runoff waters were measured in order to estimate a total field balance. Concentrations of endosulfan residues in runoff water varied from 45 to 2.5 $\mu\text{g/L}$ depending on the residue levels present on field soil at the time of the irrigation or storm events. These in turn are related to the total amounts applied, the cotton canopy cover at application, and the time since the last application. Most of the endosulfan in runoff was found in the water phase (80%), suggesting it was bound to colloidal matter. Total endosulfan residues in runoff for a whole season accounted for no more than 2% of the pesticide applied on-field (Kennedy et al., 2001).

The greater the depth of an aquifer below the land surface, the less likely it is to be contaminated by surface-derived pesticides. If the groundwater depth is shallower, there will be less pesticide degradation and adsorption. Therefore, in areas where groundwater is relatively shallow extra precautions need to be taken to reduce impact on groundwater. The presence of

low permeability materials at or below the land surface may provide protection to shallow aquifers from contamination by surface applied pesticides (Barbash and Resek, 1996). In arid areas, groundwater may be several hundred feet below the soil surface and leaching of pesticide to ground water may be a slow process, thus reducing the relative effects on groundwater contamination.

1.3.2.3.2. Geological and climatic conditions

The permeability of the geological layers between the soil and the groundwater also play a role in the movement of pesticide. Highly permeable materials such as gravel deposits or karst topography allow water and dissolved pesticides to freely percolate to groundwater. Layers of clay, which are less permeable, inhibit the movement of water. Therefore, groundwater quality is vulnerable in areas where geological layers are highly permeable. Frequencies of pesticide detection are higher in unconsolidated formations (sand and gravel aquifers) than in bedrock (Barbash and Resek, 1996)

The breakdown of pesticides in soil has been found to be related to climate (Racke, 2003). There is a greater risk for pesticide leaching in areas with high rates of rainfall or irrigation (Bailey and White, 1970), especially if the soils are highly permeable.

1.3.2.4. Management practices

Specific management practices influence pesticide movement. The breakdown of pesticides in soil has also been found to be related to agronomic practices (Koskinen and Clay, 1997). Application methods such as injection or incorporation into the soil, as in the case of nematicides, make the pesticide most likely to leach. Also, application to foliage may contribute to pollution due to overspray, then incorporation of crop debris into soil after harvest. The larger the amount of pesticide used and the closer the time of application to a time of heavy rainfall or irrigation (Willis and McDowell, 1987), the more likely that some pesticides will leach to groundwater. For instance, previous studies have shown that metolachlor transfer is influenced by climatic factors such as timing of rainfall events after herbicide application (Novak et al., 2001) and the total volume and rate of water application (Sanchez-Martin et al., 1995). Paradoxically, the previous study demonstrated that periods of high evapo-transpiration and soils

with low permeability may favor the downward translocation of pesticides into drainwater to a greater extent than periods of low evapo-transpiration and large precipitation and soils with high permeability. Pesticide persistence is influenced by different cultural practices. Pesticides persist longer when thoroughly mixed in the soil than when not. This could reflect loss of pesticides by surface erosion and volatilization. When soils containing DDT and aldrin were mixed daily for three months, both pesticides disappeared more rapidly than when comparable soils were mixed only once (McEwen and Stephenson, 1979).

Chapter 2

Research Project Overview

2.1. Institutional collaboration

Because this research was one of the first of its kind in Mali, it was very important to communicate with officials from several institutions which are involved in the agricultural sector. These include the Environmental Toxicology Laboratory (ETL) at the Central Veterinary Laboratory (CVL) and the United States Agency for International Development (USAID). Also, because soil samples had to be brought back to the United States, it was necessary to obtain a soil permit from the USDA (United States Department of Agriculture). A copy of this permit is included in Appendix I-i. I traveled from the United States to Mali in May 2003 to carry out the farmers' survey and to collect soil and water samples. At the onset of my travel, I delivered letters of support to the entities listed in Table 2-1.

I met with Mr. Boubacar Sékou Soumaré (Liaison-Recherche-Développement office at the CMDT) and Mr. Issa Sidibé (OHVN) to discuss the proposed research and decide which CMDT regions to select for the survey and sampling. Four regions were chosen, namely Koutiala, Sikasso, San, and Kita. The rationale was to compare older cotton production areas like Koutiala versus intermediate production areas like Sikasso, San and newer production areas like Kita. Mr. Soumaré left the selection of the specific villages for study on the recommendation of the local CMDT agents. He also offered to write a letter of support for this project in CMDT areas. An official letter of support was written on June 3rd, 2003 by Mr. Mamadou Guissé, Director of Human Resources at the CMDT and copies were sent to the four regional offices of CMDT which would be included in our study. The letter of support to the project from the CMDT facilitated the introduction of the survey and sampling team to the local farmers. A copy of this letter of support may be found in Appendix I-ii. The CMDT also provided personnel, logistics and facilities for refrigeration of samples at the local sites to assist

the project. Documentation and maps of the study areas were also obtained from the CMDT. The CVL provided four personnel (Dr. Traoré Halimatou Koné, Mr. Fousséni Diallo, Mr. Sanogo Oumar and Mr. Yoroté Oumar) to assist the project and provided the logistics for the field trips at lower cost than otherwise possible. Some of the CVL facilities and equipment were also used and these included the cold room for sample storage, sampling equipment, room for air-drying of soil samples.

Table 2-1. Entities to which letters of support for this project were sent.

Contact persons	Agencies
Dr. Dennis McCarthy	United States Agency for International Development (USAID)
Dr. Cheick F. Simbé	Central Veterinary Laboratory (CVL)
Mr. Mahamar Maïga	Compagnie Malienne pour le Développement des Textiles (CMDT)
Mr. Issa Djiré	Opération Haute Vallée du Niger (OHVN)
Mr. Issa Sidibé	Opération Haute Vallée du Niger (OHVN)
Dr. Halimatou Traoré Koné	Central Veterinary Laboratory (CVL)
Dr. Kadiatou Gamby Touré	Institut d'Economie Rurale (IER)
Dr Héry Coulibaly	Direction Générale de la Réglementation et du Contrôle (DGRC)
Mr. Ibrahima Doumbia	Direction Nationale de l'Assainissement et du Contrôle des Pollutions (DNACPN)

Several Virginia Tech laboratory facilities were used for this research. The majority of the laboratory work was conducted at the Pesticide Residue Laboratory (PRL) which provided facilities and equipment for sample storage, extraction and analysis. The Virginia Tech Soil Testing Laboratory and Soil Physics Laboratory analyzed the soil samples for percent organic matter, pH, textural class, percent clay, percent silt and percent sand. The Civil and Environmental Engineering laboratory facility was also used for further confirmation of pesticide residues in soil using Gas Chromatography-Mass Spectroscopy (GC-MS).

2.2. General methods

Twenty four farmers from 12 villages were surveyed on knowledge, attitudes and practices regarding pesticide usage. Results from this survey were later used to develop a strategy on which pesticides were analyzed in the soil and water samples. Information obtained

from the survey was coded and analyzed using SPSS 12.0 for Windows. Sixty soils samples were collected from the upper soil layer (0-15cm) to be analyzed for pesticide residues in the same villages as the ones surveyed. Eight water samples (6 from ground water and 2 from surface water) were collected from the older cotton production area (Koutiala). Soil and water samples were refrigerated (4°C) shortly after their collection until their shipment to the United States. Two groundwater samples were lost (broken containers) during the shipment to the USA. Samples and the soil permit were checked at the port of entry in the US (Atlanta) by the US customs officers.

Multi-residue extraction methods for both soil and water samples were conducted. Soil samples were analyzed on a gas chromatograph (GC) Agilent 6890 equipped with a microelectron capture detector (μ ECD ^{63}Ni) and an RTX-5 capillary column (30m length x 250 μm internal diameter x 0.25 μm film thickness) from Restek. Positive results were confirmed on the same GC using a different column (RTX-35). Water samples were analyzed on a GC Agilent 6890 equipped with an electron capture detector and a RTX-35 capillary column. Confirmation runs for water samples were conducted on the same GC using a RTX-5 column. Soil samples with positive pesticide identifications were further confirmed on a Agilent GC-MS 6890.

Table 2-2. Pesticides of interest in the residue study.

Pesticide chemical classes	Specific pesticides
Organohalogenated pesticides	aldrin, α -BHC, β -BHC, δ -BHC, lindane, α -chlordane, γ -chlordane, p,p-DDD, p,p-DDE, p,p-DDT, dieldrin, endosulfan I, endosulfan II, endosulfan sulfate, endrin, endrin aldehyde, endrin ketone, heptachlor, heptachlor epoxyde and methoxychlor
Organophosphate pesticides	dichlorvos, mevinphos, demeton-o, ethoprop, naled, phorate, demeton-s, diazinon, disulfoton, parathion methyl, ronnel, fenthion, chlorpyrifos, trichloronate, merphos, stirafos, tokuthion, fensulfothion, sulprofos, azinphos methyl, coumaphos, tetraethyl pyrophosphate (TEPP), sulfotepp, monocrotophos, dimethoate, malathion, parathion, epn, and profenofos
Pyrethroids	cypermethrin

Chapter 3

Assessment of Pesticide Use in Four Cotton Growing Areas in Mali

3.1. Introduction

Agricultural production in the southern part of Mali is mainly based on a cereal-cotton rotation with cereals including millet, sorghum and corn. Other cultivated crops are peanuts, fonio and niébé. All crops are rain-fed and grown in one cropping season (rainy season). Cotton has been cultivated in the southern part of Mali since the 11th Century. However, modern cotton production began in 1930 when a program on rain-fed cotton was initiated in the irrigated area of the Office du Niger (Ségou region of Mali). In 1974, the Compagnie Malienne pour le Développement des Textiles (CMDT) was created through an agreement between the Republic of Mali and the Compagnie Française pour le Développement des Textiles (CFDT) in the form of a public, limited company with mixed economy. Today, thousands are involved in diverse aspects of cotton processing, transport, input supply and the cotton by-product industry (animal feed, oil and soap). The cotton-producing area is among the richest in the country, with an estimated household income approximately five times the national average (Bingen, 1998). The cotton growing season starts at the end of May and continues through the end of September-October. The duration of the crop depends on the length of the rainy season.

To improve productivity and reduce the damage caused by insects, cotton growers rely on the use of pesticides. They are intensively used in cotton growing areas in Mali to control pests such as *Heliothis armigera* (cotton bollworm) which is the most common cotton insect pest. Other insects pests include true bugs, aphids and white flies (Silvie et al., 2001). Three types of spraying programs are used in the cotton growing areas in Mali. The first and most common spray regimen is the calendar based spraying. In this program, farmers apply pesticides 35 days after planting. Later, pesticides are applied biweekly. The calendar based spraying program has improved cotton production and was originally based on pyrethroid-organophosphate mixtures

applied fortnightly from the appearance of the first flower to the first boll opening. Following significant damage caused by *H. armigera*, endosulfan, a cyclodiene compound, was recommended in 1999-2000 for the early months of the cotton-growing season to reduce the selection pressure exerted by pyrethroid pesticides on *H. armigera* populations (Ajayi et al., 2002; Diarra, 2003b; Silvie et al., 2001). The second spray regimen is called Lutte Etagée Ciblée (LEC) in which half doses of regular application rates are recommended. Later, pest densities observed in the field determine the choice of the active ingredient and the quantity to be applied. In Mali, where cotton is grown on an area of about 500,000 ha, the LEC program which started in 1994, covered more than 18,000 ha in 1999 (Silvie et al., 2001). The third treatment is purely a threshold-based intervention. Booklets written in the local dialect (Bambara) are provided by the CMDT to farmers to improve their knowledge on pests and pest damage. Pegboards are also used by growers to tabulate and facilitate field observations.

As a result of rigid pesticide application regimens, pesticide use has risen substantially in Mali. The increase in pesticide use means increased potential exposure hazards for pesticide mixer/loaders, applicators, and field workers involved with hand cultivation and harvesting. Although pesticides are indispensable in modern agriculture, their use and misuse can lead to serious problems such as acute and chronic toxicity in people exposed to pesticides, groundwater contamination, and effects on nontargets organisms. These problems are usually a result of misapplication, improper storage and careless disposal of pesticides and containers (Laprade, 1992). Various cases of illness associated with pesticide use have been reported worldwide. The majority of the toxicity problems encountered are due to pesticides that are used by many small-scale farmers, without adequate knowledge of the risks involved and when farmers fail to wear appropriate protective clothing (Matthews et al., 2003). Global estimates of acute pesticide poisoning, derived from mathematical models and projections, have risen from 500,000 in 1972 to 25,000,000 in 1990 (Levine and Doull, 1992). Studies on knowledge, attitudes, and practices have shown that pesticides are unsafely used in many developing countries (Matthews et al., 2003; Salameh et al., 2004). Integrated Pest Management (IPM) or other management practices that use insect scouting to evaluate the need for and type of pesticide application are not often utilized in developing countries. Strategies to minimize pesticide use such as IPM are not widely used in Mali.

Information on farmers' knowledge, attitudes and practices regarding pesticides usage is limited in Mali. A study on pesticide application practices was conducted to obtain information directly from growers, which could be linked to pesticide residues which may result from these practices (Chapter 4). It was designed to assess pesticide usage in agricultural areas in Mali and to get an overview of the conditions under which pesticides are used in southern Mali. It was thought that obtaining information on farmer knowledge and practices associated with pesticide usage could be useful in providing a baseline from which education and regulation of pesticide use could be improved.

The specific objectives of the survey were to:

- 1) identify acreage, crops and farm management practices
- 2) assess farmers' general education and training regarding pesticide usage
- 3) determine pesticide usage (name and formulation, rate of application, equipment used)
- 4) evaluate pesticide storage and disposal options used in the study areas.

3.2. Material and methods

3.2.1. Survey areas

Farmer surveys were conducted in four cotton growing areas of Mali. Preliminary contact was made with extension agents from the areas selected before the actual survey took place. Letters were sent to different entities to inform them about the nature of this study and to solicit their assistance. These entities included the United States Agency for International Development (USAID), the Central Veterinary Laboratory (CVL), the Compagnie Malienne pour le Développement des Textiles (CMDT), the Opération Haute Vallée du Niger (OHVN), the Institut d'Economie Rurale (IER), the Direction Nationale de l'Assainissement et du Contrôle des Pollutions et des Nuisances (DNACPN) and the Direction Générale de la Réglementation et du Contrôle (DGRC). After meeting with the agents at the Liaison-Recherche-Développement Office of the CMDT in Bamako, the four survey areas were chosen: Kita, Sikasso, Koutiala and San. One of the criteria for selection of the sites was old versus new production areas. Kita is a newer cotton growing area compared to Koutiala which is the oldest and most well-established site. Sikasso and San are considered to be intermediate producing

areas based on the time they have been involved in cotton production. A letter of support to this project was obtained from the Human Resources Office of the CMDT to facilitate the introduction of the survey team to the farmers. Copies of this letter of support were also sent to the regional offices of the CMDT in each of the survey areas.

The specific choice of the villages to survey was made upon the recommendation of the local CMDT agents. Twelve villages were chosen in total. They were:

- Kita region: Baliani, Batimakana, and Massala
- Sikasso region: Tiola, Lofigué, and Loutana
- Koutiala region: Finkoloni, Farakoro, and Nankorola
- San region: Tiediana Poguon, Fono, and Nitia.

The first criterion for the village selection was based on practical logistics. Since the survey was conducted during the rainy season, a time when roads are most often inaccessible, villages were chosen based on ease of accessibility. Furthermore, villages closer to higher population densities, which we assumed to have higher pesticide usage, were chosen for the survey. Two farmers per village were surveyed by direct interview. A total of 24 farmers were interviewed using a standardized questionnaire. Interviews were conducted from July to August 2003. Logistical support for the survey consisted of two vehicles and two drivers provided by the CVL and the CMDT. At each of the survey sites, assistance was obtained from two to three extension agents from CMDT, one extension agent from OHVN and one CVL personnel.

3.2.2. Survey questionnaire

A questionnaire was developed and designed with the assistance of a Virginia Tech sociologist (Dr. Keith Moore) and an entomologist (Dr. Carlyle Brewster), who are both experienced in the area of socioeconomic studies. The questionnaire consisted of different parts including: site description, farmer's education level, field description, present and past management histories of the land, pesticide use, pesticide storage and disposal, and farmer training. A sample of the questionnaire is provided in the Appendix II. Some of the questions were asked in two different ways to test uniformity in the responses. The questionnaire was written in English and was verbally translated into Bambara (the local dialect spoken in the study areas) when used to interview farmers. A total of twelve days were required to conduct the survey interviews; with two interviews completed per day. The average interview required about

one and one-half hours to complete. Once we arrived at a survey site, introductions were made to the Village Chief and to the Village Association Secretary. The two farmers selected to be interviewed were chosen based on their willingness to participate. The meeting with each of the farmers to be interviewed usually began with formal introductions, followed by an explanation of the purpose of the survey. During all of the interviews, the extension agents from CMDT facilitated the process of information gathering. A qualitative evaluation of the interviewees' response was done based on the consistency of their answers to similar questions. It was determined that 12.5% of the interviews could be qualified as very reliable, 75% as reliable, and 12.5% as perhaps reliable. In the last case, the interviewed farmers may have exchanged "visual cues" with people assisting the interview and consequentially they may have modified/changed some of their answers. A total of 24 surveys were conducted. The majority of the farmers (79.2%) interviewed, provided access to their fields to collect samples as part of the residue and soil structure studies (Chapter 4).

3.2.3. Data analyses

Upon returning to Virginia Tech, the data were coded and analyzed using SPSS 12.0 for Windows (SPSS, 2004). Parametric statistic (percentage) was used to collate and summarize the responses to the survey questions.

3.3. Results

3.3.1. Farmers' education level and pesticide training

It was believed that an assessment of farmers' general education and pesticide training would be helpful in understanding some of our findings regarding their practices. The educational level of the farmers interviewed is presented in Table 3-1.

The results indicate that 33.3% of the farmers surveyed had received elementary school level training, and 29.2% had functional literacy education (local dialect, for explanation see footnote 4 in Table 3-1). None of the farmers surveyed had high school or university education and 37.5% of farmers indicated they had not received any formal education. Overall, the educational levels of survey respondents were low. Most of the farmers (87.5%) had received

training in pesticide application techniques, primarily from extension agents from the CMDT (70.8%). Others had received training from the Village Association Secretary (8.3%), were self-trained (8.3%), or trained by a relative (8.3%). A small proportion of the respondents (4.2%) had received no training in pesticide use. It should be noted that the Village Associations are responsible for cotton grading and weighing, equipment and supply orders and credit management (Bingen, 1998). A majority of the farmers (91.7%) had received training on pesticide disposal, primarily by extension agents from the CMDT (79.2%). The remaining farmers had received training from their Village Association Secretary (8.3%), rural radio program or a relative (8.3%). No answer was obtained from one interviewee.

Table 3-1. Education level of the farmers interviewed from the cotton growing regions in Mali.

Education level ¹	Percent of farmers interviewed ^{2,3}
University	0
High School	0
Functional literacy ⁴	29.2
Elementary school	33.3
No education	37.5

¹The different categories of education received by farmers.

²Percentage of farmers having reached a specific level of education.

³n = 24 total number of farmers interviewed.

⁴The functional literacy program in the Bambara language enables farmers to have the literacy, numerical and computational skills needed to fulfill credit and marketing tasks and to prepare account books (Bingen, 1998).

3.3.2. Field description

The farmers' fields were distributed among three size groups: those falling between 2 and 5 hectares (45.8%), those less than 2 hectares (45.8%) and a small group with fields greater than 5 hectares (8.4%). It was of interest for us to assess the slope of the fields, since fields with a high slope would have greater surface water runoff, and as a result, present potentially increased hazards for contamination at non target areas. A majority of the fields were flat (95.8%) and only a few (4.2%) had slopes ranging from 1 to 5%.

The distance of the nearest water supply to field was evaluated. The results presented in Table 3-2 indicate that about 33.3% of the farmers had a well within 10 meters of their field, 12.5% between 10 and 50 meters, 4.2% between 50 and 100 meters, 20.8% between 100 and 500 meters, and 29.2% had wells located more than 500 meters from their field. Farmers indicated that water from their wells was used as a drinking water source for both human and animal consumption. The proximity of wells to fields where pesticides are sprayed/stored may increase the risk of groundwater contamination resulting from both leaching and runoff of pesticide-contaminated water. Six field wells, which were all uncovered, were sampled for pesticide residue testing (Chapter 4).

Table 3-2. Distance of nearest water supplies to fields in Mali cotton growing areas.

Distance well to field	Percent of fields ¹
0-10 meters	33.3
10-50 meters	12.5
50-100 meters	4.2
100-500 meters	20.8
More than 500 meters	29.2

¹n = 24 farmers interviewed.

Figure 3-1 illustrates an open well in close proximity to a cotton field and a small chicken consuming runoff water from the cotton field.



Figure 3-1. Uncovered well within 5 meters of a cotton field in the Koutiala region (Village of Farakoro).

3.3.3. Current field use and history of crop rotation

Traditionally, Malian farmers have relied on long fallow periods to replenish the soil fertility depleted through cropping. However, due to the increases in human and animal populations and land-use pressure, fallow periods have been reduced both in length and area or even abandoned in many farming systems. This is particularly true for the Koutiala region (Diarra, 2003b; Kaya et al., 2000). Information provided in Chapter 4 will evaluate increased higher land-use pressure and the occurrence of pesticide residues in these cultivated fields.

All crops in the survey area were rain-fed and none of the farmers interviewed irrigated their crops. Since cotton is the crop on which farmers use the most pesticides (mainly insecticides), the proportion of cotton fields compared to the other crops was assessed. The percentages of the different crops grown in 2003 are presented in Table 3-3. Cotton constituted more than half of the areas cultivated (58.3%), followed by corn (12.5%), sorghum (12.5%), millet (4.2%) and peanuts (4.2%). Some of the farmers (8.3%) reported growing other commodities (watermelon) or not planting (fallow) in 2003.

Table 3-3. Types of crop grown by Malian farmers in the survey areas in 2003.

Crop grown in 2003	Percent of fields ¹
Cotton	58.3
Corn	12.5
Sorghum	12.5
Millet	4.2
Peanuts	4.2
Other ²	8.3

¹n = 24 farmers surveyed.

²This category included crops such as watermelon and fallow fields.

The practice of crop rotation allows growers to diversify crop production and reduce the likelihood of pest build-up associated with continuous cropping. Crop rotations may help mitigate certain pest problems by directly or indirectly affecting pest and beneficial arthropods, by changing the habitat or by directly influencing survival (Hummel et al., 2002). This could in turn reduce pesticide use. All of the survey respondents indicated that they do rotate crops in their fields. However, although all of the growers indicated that they routinely rotate crops, it is somewhat puzzling to note that in 2003, 12.5% of them indicated that they had grown cotton consecutively after cotton?

3.3.4. Pesticide use

Studies on knowledge, attitudes, and practices indicate that unsafe use of pesticides is common in developing countries (Salameh et al., 2004). Proper pesticide application is important for crop protection as well as environmental safety. Precise delivery of pesticides to the intended targets is essential to achieve the desired biological effect and to minimize adverse impacts on the immediate and adjacent land areas and the environment (Bohmont, 2003; Smith and Thomson, 2003). Personal communication with inhabitants of Lofigué in the Sikasso region of Mali revealed cases of endosulfan misuse as a mosquito control pesticide in households, i.e. several farmers had used it to spray their bedrooms (Traoré, 2003b).

Since pesticide retail sales in Mali are uncontrolled (Diarra, 2003a), we examined the sources of pesticides used by the farmers we interviewed. All of these farmers indicated that their sole supplier for pesticides was the CMDT. Their answers excluded the possibilities that the farmers acquired pesticides from a local market place and/or from other pesticide dealers.

Farmers were also asked where they obtained information regarding the proper pesticide usage on their cotton crops. Survey choices provided in the interview included: extension agents from the CMDT, pesticide dealers and other sources. Most farmers (66.7%) indicated that they received information on pesticide usage from their supplier (CMDT), but some (33.3%) indicated that they received this information from their Village Association Secretary or relied upon their own knowledge of pests. As a cross-checking (confirmatory) question to the previous question on pesticide usage, farmers were asked from whom they sought advice when they observed a major pest outbreak in their field. The results summarized in Table 3-4 indicated that according to half of the farmers surveyed (54.2%), the extension specialists from the CMDT

advised them on what actions should be taken when they had an outbreak of pests in the field. Other farmers (37.5%) applied pesticides themselves according to their own knowledge of chemicals and pests. Finally, a small proportion of growers (8.3%) obtained advice from their Village Association Secretary. These results indicate that none of the farmers interviewed had obtained advice on pesticide products from dealers.

Table 3-4. Cotton growers' advisor used in case of major crop pest infestation.

Advisor for pesticide use	Percent of farmers ¹
Extension specialists from CMDT	54.2
Don't get advice from anyone	37.5
Village Association Secretary ²	8.3
Pesticide dealer	0

¹n=24 farmers interviewed.

²The Village Association Secretary is generally an educated farmer who has received training from the CMDT and whose role is to teach other farmers in the village and to communicate the village activities to the CMDT.

An attempt was made to obtain a ten year history of pesticide use in the survey areas to assist us in the process of screening the soil and water samples that were to be a part of the residue study (Chapter 4). The results summarized in Tables 3-5 and 3-6 indicate that a total number of 20 pesticides (single active ingredients or combination of two to three active ingredients) were applied during the last 10 years in the survey areas. Overall, a majority of the interviewees were not certain about the names of the pesticides they had used. The only exception was endosulfan which they all recognized and acknowledged using. None of the farmers were able to give the specific information regarding the formulations of pesticides they had used. Most of these materials were insecticides, indicating that herbicides didn't appear to be extensively used in these areas. Previous data from the Koutiala office of CMDT has indicated that herbicides were only used on six per cent of cotton fields and nine per cent of maize fields in that region in 1996 (Benjaminsen, 2001). Information on the most recent (within one year) pesticide application was obtained. The results summarized in Table 3-6 indicate that endosulfan was the most frequent pesticide applied to fields and represented 20.8% of the total pesticides used, followed by cypermethrin-acetamiprid (16.7%), cypermethrin-chlorpyrifos ethyl (12.5%), profenofos (8.3%) and atrazine (8.3%).

The growers were also asked who had been in charge of their pesticide applications. The responses indicate that basically, the person in charge of pesticide applications in all farming operations was either a member of the farm household or a farm employee. Further, the farmers indicated that all of the pesticides were diluted with water before application. Growers are taught two ways of diluting pesticides. They are: 1) pesticide formulations containing acetamiprid should be diluted at the ratio of 0.5 L of pesticide to 9.5 L of water; and 2) pesticide formulations not containing acetamiprid should be diluted at the ratio of 1 L of pesticide for 9 L of water. These dilution rates are designed for application to one hectare. Many of the farmers surveyed (62.5%) knew the pesticide/water ratio for formulations with acetamiprid, and 87.5% of the respondents knew the pesticide/water ratio for formulations not containing acetamiprid. It is not clear why there is only one way of diluting pesticides, whereas there is a variety of pesticide formulations used in the study area.

Table 3-5. Pesticides which farmers in the survey areas indicated that they had used during the last ten years in Malian cotton growing areas.

Pesticide used by growers during the last ten years	Percent of farmers ¹		
	Yes ²	No ³	Didn't know ⁴
Profenofos	37.5	4.2	58.3
Cypermethrin	25	25	50
Cypermethrin-profenofos	33.3	12.5	54.2
Cypermethrin-acetamiprid	12.5	70.8	16.7
Cypermethrin-chlorpyrifos ethyl	29.2	8.3	62.5
Cypermethrin-metamidophos	0	29.2	70.8
Cypermethrin-monocrotophos	33.3	16.7	50
Cypermethrin-dimethoate-triazophos	20.8	16.7	62.5
Endosulfan	100	0	0
Indoxacarb	25	16.7	58.3
Spinosyn	25	8.3	66.7
Haloxifop-methyl	16.7	25	58.3
Atrazine	8.3	29.2	62.5
Fluometuron-promethrin	16.7	29.2	54.2
Paraquat	0	29.2	70.8
Thiram-lindane	0	29.2	70.8
Endosulfan-chlorothalonil	4.2	29.2	66.7
Cypermethrin-dimethoate	12.5	16.7	70.8
Dimethoate-triazophos	0	29.2	70.8
Deltamethrin-triazophos	12.5	16.7	70.8

¹n = 24 farmers interviewed.

²Farmers in this category were absolutely certain that they had used a particular pesticide.

³Farmers in this category were certain that they had not used a particular pesticide.

⁴Farmers in this category were not certain if they had used a particular pesticide.

Table 3-6. Most recent pesticide¹ applied reported by farmers interviewed from the cotton growing regions of Mali.

Pesticide compounds	Percent of farmers ²
Profenofos	8.3
Cypermethrin-acetamiprid	16.7
Cypermethrin-chlorpyrifos ethyl	12.5
Cypermethrin-dimethoate-triazophos	4.2
Endosulfan	20.8
Indoxacarb	4.2
Haloxypop-methyl	4.2
Atrazine	8.3
Fluometuron-promethrin	4.2
Endosulfan-chlorothalonil	4.2
Information not available	12.5

¹Most recent pesticide applied within the time frame of one year (July 2002-July 2003).

²n = 24 farmers interviewed.

The annual undiluted pesticide volume used per hectare as shown in Table 3-7 indicates that total volumes ranged from 3 to 8 L, with the majority of farmers (29.2%) spraying 5 L per hectare.

Table 3-7. Annual undiluted total volume of pesticide used per hectare by Malian cotton growers (based on 2002-2003).

Annual pesticide volume used per hectare ¹	Percent of farmers ²
3 liters	12.5
4 liters	25
5 liters	29.2
6 liters	4.2
7 liters	16.7
8 liters	8.3
Information not available	4.2

¹Farmers were not able to give the actual active ingredients of the pesticide materials applied. Information obtained from CMDT for the

2000/2001 cotton growing season permitted us to obtain the amount of active ingredient in g per L for some insecticides (Table 3-8).
²n =24 farmers interviewed.

An assessment of the amount of active ingredient applied per hectare in the survey areas was made for the pesticides used during the past ten years. This assessment was based on information obtained from the CMDT and Comité Inter-états de Lutte contre la Sécheresse dans le Sahel (CILSS). The results are summarized in Table 3-8.

Farmers were also asked how frequently they applied pesticides on their cotton per season. Most of the farmers (45.8%) applied pesticides 5 times in one cotton growing season, followed by 25% applying 6 times, 16.7% applying 4 times and 12.5% applying 7 times. These results are in agreement with the annual total volume sprayed for which 5 liters was the most frequent application rate. Most of the survey respondents (58.3%) used the hand-held sprayer Berthoud™ compared to 33.3% who used the hand-held sprayer Ulva plus™. Information on type of spraying equipment was not available from the remaining survey respondents. Farmers were also asked who was responsible for pesticide mixing. Pesticide mixing was done in all cases (100%) by the household member or an employee of the household.

Table 3-8. Application rate in grams active ingredient per hectare of pesticides used in the past ten years in the cotton growing areas of Mali.

Active ingredients	Concentration (g/L) active ingredient	Application rate (g active ingredient / hectare)
Profenofos	150	150
Cypermethrin	50	50
Cypermethrin/profenofos	36/150	36/150
Cypermethrin/acetamiprid	36/8	18/4
Cypermethrin/chlorpyrifos ethyl	36/150	36/150
Cypermethrin/metamidophos	36/300	36/300
Cypermethrin/monocrotophos	36/250	36/250
Cypermethrin /dimethoate-triazophos	36/240/150	36/240/150
Endosulfan	500	500
Indoxacarb	150	150
Spinosyn	480	480
Haloxyp-methyl ¹	104	104
Atrazine	500	500
Fluometuron/promethrin ²	250/250	250/250
Paraquat ²	200	200
Thiram/lindane ²	250/200	Seed protectant
Endosulfan/chlorothalonil ³	NA	Seed protectant
Dimethoate-triazophos ³	NA	NA
Cypermethrin-dimethoate ⁴	36/400	36/400
Deltamethrin-triazophos ⁴	9/150	9/150

¹Composition obtained from the Comité Inter-états de Lutte contre la Sécheresse dans le Sahel (CILSS) and from an empty container found in one field.

²Composition obtained from CILSS.

³Information on composition was not available.

⁴Pesticide used in 1999/2000 cotton growing season.

3.3.5. Farmers' safety issues

Most of the farmers (62.5%) did not use separate clothing for pesticide application, but about one third of the farmers (33.3%) indicated that they used special clothing for pesticide applications. A small proportion of growers (4.2%) indicated that to protect themselves, they used two layers of clothing, a mask and closed shoes. Table 3-9 summarizes the types of personal protective equipment used by the growers.

Table 3-9. Types of personal protective equipment used by the cotton growers interviewed.

Protection types	Percent of farmers ^{1,2}
Long sleeve clothing	75
Goggles or face shields	8.3
Rubber boots	8.3
Rubber gloves	4.2
Other ³	70.8

¹Percent of farmers using some form of protection listed under protection types.

²n = 24 farmers interviewed.

³Other types of personal protection included the use of glasses, plastic bags covering their extremities, a hat, and a mask.

The results indicated that a very low proportion of farmers (8.3%) used goggles or face shields. The hands are known to generally receive considerable exposure to pesticides including full strength pesticides when performing pesticide applications (Branson and Sweeney, 1991). Nevertheless, only 4.2% of the farmers reported using rubber gloves and only 8.3% of them reported using rubber boots. However, 75% of the farmers indicated they wore long sleeve clothing as a regular precaution. Other precautions used by the survey respondents included: the use of glasses, plastic bags (which were not chemical resistant) to cover their head, hands, and feet, and a hat. Previous research has established that the principal means of pesticide exposure

is dermal (Branson and Sweeney, 1991; Cloud et al., 1987; Laughling, 1993) and that clothing can serve as a barrier to dermal exposure (Davies et al., 1982; Lillie et al., 1981). Studies on pesticide contamination of clothing indicate three activities in which exposure may occur. They are: 1) Mixing/loading may allow direct contact (spills) of undiluted pesticide on applicator (Easley et al., 1982), 2) Applicators may be exposed to the pesticide in spray form as it is applied (Cloud et al., 1987) and 3) Harvesters and other fields workers may encounter pesticide residues as they work in treated fields (Cloud et al., 1987). It is clear that these farmers failing to wear adequate personal protective equipment had exposed themselves and their family members to the chemicals they had applied.

Farmers were aware of the negative impacts of coming into contact with spray drift. All of the growers surveyed assessed the wind direction before they applied pesticides. They indicated they would spray downwind from sensitive sites and only on calm days. Techniques for wind measurement that they employed included the use of dust (16.7%), plastic bag tied to rope or tree branch (29.2%), or hanging clothes (29.2%).



Figure 3-2. Farmer applying pesticide with bare-hands and wearing a short-sleeve shirt.

3.3.6. Pesticide storage

Proper storage of pesticides reduces the risk of exposure to humans and animals and may extend the chemical's shelf life (Bohmont, 2003). Pesticide storage practices used in the survey areas are summarized in Table 3-10. The results indicate that only 37.5% of the farmers locked their pesticides in a storage room. Some of the farmers indicated that they stored pesticides in

the open either under cotton plants or inside a termite mound. Many farmers (37.5%) stored chemicals in an unlocked storage room. An example of this type of storage is shown in Figure 3-3.

Table 3-10. Pesticide storage practices in the Malian cotton growing areas.

Pesticide storage location	Percent of farmers ¹
Locked storage room ²	37.5
Unlocked storage room ³	37.5
Storage in the open ⁴	8.3
Granary ⁵	12.5
Other storage locations	4.2

¹n = 24 farmers interviewed.

²Pesticides were stored locked in a secure room and were inaccessible to unauthorized personnel.

³Pesticides were stored in an unlocked storage room accessible to anyone.

⁴Pesticides were stored in the open, i.e. either under cotton plants, inside termite mounds, etc.

⁵Pesticides were stored in the upper level of a granary in which cereals were stored, with an adobe layer between chemicals and grains.

Some of the interviewees (12.5%) reported that they stored pesticides in granaries (Figure 3-4) which pose a serious health risk to people eating cereals that are stored in those granaries. In the Koutiala region, one poisoning episode was reported after an entire household had consumed contaminated cereals from a granary which had been sprayed with indoxacarb (Diarra, 2003b). Although not a case of poisoning due to pesticide storage in a granary, the risk of a similar poisoning is high if pesticides are stored in the same area as food.



Figure 3-3. Storage of pesticides in an unsecure room.



Figure 3-4. Storage of pesticides in a granary.

Farmers were also asked how long they stored unused pesticides at the farm. All of the respondents indicated that they did not store pesticides for more than a year. Most of them

(54.2%) confirmed that they were not storing any pesticide at the time of the survey, compared to the 29.2% of farmers who were storing pesticides.

3.3.7. Pesticide disposal

Inappropriate pesticide waste and container disposal has resulted in human and animal poisonings and environmental contamination worldwide. All growers recognized that empty pesticide containers should be disposed of according to approved procedures provided by the CMDT. Many farmers (70.8%) had obtained information about container disposal from the CMDT. Other growers (16.7%) had been informed by the Village Association.

Container disposal practices were assessed and the results summarized in Table 3-11 indicate that farmers disposed of empty containers in various ways. Empty plastic pesticide containers were burned by 41.7% of the farmers. A majority of growers (79.2%) buried empty metallic containers after destroying them, rendering them unusable. A quarter of the respondents admitted that they sometimes leave empty containers in the field which pose environmental contamination risk (Figure 3-5). Some farmers (16.7%) also admitted they sometimes allow other people to obtain their pesticide containers for reuse (Figure 3-6). Under these circumstances, empty containers are hand washed after being soaked for several days in soap, ash and lemon juice mixture or infusion of the leaves and bark of the Samanère tree. Farmers believe that empty containers are completely free of pesticides after this type of cleaning procedure. They consider that containers cleansed in this fashion may then be used for various purposes (storage containers for milk, water, gasoline, etc.) which undoubtedly pose a serious threat to human health. Acute and chronic pesticide poisoning has posed serious concerns in many countries. It is estimated that less developed countries suffer about one-half of the poisoning cases and nearly 75% of the poisoning deaths even though they use only 15 to 20% of the world's total pesticide (Bull, 1982). Workers occupationally exposed to pesticides and children accidentally poisoned comprise the most frequently reported acute pesticide poisoning cases. Chronic pesticide exposure has purportedly been implicated in cancer cases dating since the 1960's. Some pesticides may cause cancer in laboratory animals, but whether this is true in humans has not been conclusively determined (Branson and Sweeney, 1991).

Table 3-11. Disposal of empty pesticide containers.

Containers disposal practices ¹	Percent of farmers ²
Burying ³	79.2
Burning ⁴	41.7
Abandoning in field	25
Retrieved for reuse purpose ⁵	16.7
Retrieved by extension agents ⁶	0
Other	0

¹Farmers interviewed disposed of empty containers in more than one way.

²n = 24 farmers interviewed.

³Farmers indicated sometimes burying metallic pesticide containers.

⁴Farmers indicated sometimes burning plastic pesticide containers.

⁵Empty containers were sometimes retrieved for reuse purpose (drinking water, milk, gasoline, etc.).

⁶Extension agents or pesticide supplier, e.g. CMDT.

For developing countries, disposal of unused, unwanted, or obsolete pesticide stocks has been a major problem (Felsot et al., 2003). Farmers were asked how they disposed of pesticide application equipment rinsing solutions. A majority of farmers (75%) disposed of their pesticide rinsates in the field by pouring them on the ground and 20.8% of the respondents dug a hole before pouring out their rinsates. The remainder of the growers indicated that they washed their equipment in a pond and also claimed that they washed themselves in the same pond after cleaning their equipment. Information from personal communication with Mr. Djibril Traoré and with others inhabitants of Loutana (Sikasso) revealed that livestock poisoning incidents were not unusual in their region (Traoré, 2003a). However, overall, no comprehensive statistics exist in Mali on pesticide poisonings (Ajayi et al., 2002).



Figure 3-5. Empty pesticide container abandoned in a field.



Figure 3-6. Reuse of empty pesticide containers for drinking water storage.

3.4 Discussion

Pesticides are intensively used in cotton growing areas in Mali. Crop rotation is frequently practiced in the southern part of Mali and cotton is the major crop grown. Many of the farms are small scale (family) operations. Most of the farmers included in the survey had a low educational level. The majority of farmers were trained in pesticide application techniques and pesticide disposal. However, the survey results have shown that despite their training, sometimes growers did not use pesticides in an appropriate manner. The pesticide supplier for all the growers in the study area was the CMDT. A total of 20 pesticides were used in the cotton growing areas during the last ten years. A majority of the farmers were not certain about the names of the pesticides nor were they able to provide specific information regarding the formulations of pesticides they had used. Endosulfan was the most frequently used pesticide followed by profenofos, cypermethrin, monocrotophos, and chlorpyrifos. Most of the pesticide compounds were insecticides, indicating that herbicides didn't appear to be used extensively in these areas. Farmers applied pesticides with either a backpack Berthoud™ sprayer or an Ulva plus™ sprayer. It is not advisable to use the same sprayer for insecticide/fungicides and herbicides. However, the types of herbicides used by the Malian cotton growers interviewed should not result in cross contamination problems, if sprayers are rinsed one time. Most of the survey respondents knew the dilution ratio of pesticides commonly used. Although, farmers use many pesticides/formulations, they only have two mixing protocols: 1) formulations with acetamiprid are diluted at the rate of 0.5L pesticide for 9.5L water; 2) formulations without acetamiprid are diluted at the rate of 1L pesticide for 9L water (Diarra, 2003b). These mixing dilutions are oversimplified for convenience but may not be accurate according to label specifications. The practice of using lower application rate may reduce pesticide efficacy, resulting in the need for more frequent pesticide applications. Conversely, higher pesticide application rates may damage plants, increase the probability of insect resistance problems and may result in higher accumulation levels of residues in soil. According to Sheets and Harris (1965) herbicide residues in soils may: 1) injure sensitive plants grown in rotations with sprayed

crops; 2) cause accumulation of residues from pesticide application rates exceeding dissipation rates; 3) cause unlawful residues in crops grown in rotations with treated crops and 4) inhibit beneficial soil microorganisms. Herbicides used in the study area are not persistent and should not cause carryover problems since all crops are grown during the rainy season which lasts 4 months. Therefore, they are likely to be degraded during the following 8 months of dry season before the next growing season. Carryover of insecticides may be a problem if they are persistent and mobile enough to be absorbed by food crop (i.e. corn after cotton) and consumed. Some farmers grew water melons consecutively to cereal crops, during the same growing season in fields that were sprayed with herbicides. Such practices may result in water melon contamination and cause human exposure to pesticides through consumption.

Overall the farmer survey results identified various concerns:

1) Personal safety-

Highly toxic pesticides are used by growers with insufficient personal protective equipment. Current labeling of pesticides calls for the prudent use of protective clothing by handlers who mix, load, transfer, apply, and/or dispose of pesticides (Laughling, 1993; Pedigo, 2002). Most of the farmers did not have specific clothing set aside for pesticide application and used their regular working clothes during these operations. Very few of the farmers interviewed used personal protective equipment thereby exposing themselves to the hazards of exposure to the pesticides they applied. In many of the areas of study, a minimal storage requirement is not met, providing opportunities for anyone to have free access to stored pesticide. Highly toxic pesticides were stored in the open. Only 37.5% of the farmers locked their pesticides in a storage building. Practices such as storage of pesticides in granaries in close proximity to stored cereals intended for human consumption should be curtailed. The reuse of empty pesticide containers is frequent. After cleaning they are often reused as drinking bottles or for the storage of milk, gasoline and other liquids. This common practice should also be discouraged.

2) Environmental safety-

There is a poor disposal of empty pesticides containers and rinsing solutions. Such practices should be curtailed as they may cause the contamination of the environment and lead to undesirable exposure of human, animals, soils and ecosystems. About half of the interviewees had a well within their field or at less than 50 meters. Some of the wells were used as a drinking water source and were uncovered, directly exposed to runoff contamination or potential leaching.

3) Lack of pesticide applications recordkeeping-

None of the interviewees were able to specify the exact formulations of pesticides they had used. Also, there was no written record at the farm level of pesticides and the formulations applied.

Similar findings to our study have been previously reported in other developing countries. A study conducted in Cameroon has shown that small-scale farmers were using pesticides, even if they had not received training on pesticide selection or application techniques. Few farmers had appropriate storage facilities (Matthews et al., 2003). Further they found that over 85% of the farmers did not use protective clothing, because it was either not available or was too expensive. A quarter of the interviewees washed their sprayer equipment in the river. They suggested that the empty containers are washed, possibly at the river, and used for other purposes, such as the storage of grain, kerosene or palm oil. Salameh et al. (2004) have studied farmers' knowledge, attitudes, and practices in Lebanon. They reported a majority of farmers who ignored protective measures or knew little about them. Almost half of the farmers did not know any names of the pesticides they were using. The proportion of those who practiced appropriate container disposal was low (41.2%), i.e. digging special holes, incinerating, etc. The majority of interviewees (40%) would discard pesticide container wastes directly into the environment (soil or water) or with other trash (27%). Some farmers used containers for storing water or food (Salameh et al., 2004). Another study in Zimbabwe has shown that acute pesticide poisoning symptoms were determined in large part by pesticide use practices, notably the lack of protective clothing. Many small scale farmers did not understand the health risks associated with pesticide application and did not protect themselves (Maumbe and Swinton, 2003). In the Kolda region of Senegal in November 2002, thirty inhabitants of some villages were sickened by ethyl chlorpyrifos after consumption of mayonnaise. The cooking oil used to prepare the mayonnaise was contaminated subsequent to its storage in reused empty pesticide containers (Diouf et al., 2003).

Pesticide management practices may result in three categories of human exposure which are: acute, chronic high or occupational, and chronic low or incidental. The hazards associated with pesticides may be substantially reduced by effectively using appropriate risk reduction techniques and practices. The use of appropriate personal protective equipment can reduce or eliminate pesticide exposure by minimizing dermal deposition of pesticides and reducing

pulmonary exposure from airborne volatiles and particulates (Hock, 1987). As a minimum, the following protective items should be available to Malian cotton growers when handling pesticides: 1) long-sleeved shirt and long trousers; 2) chemical resistant gloves; 3) chemical resistant boots; 4) goggles or face-shield; 5) waterproof hat; 6) respirator with a clean cartridge or canister (which types will depend on the specific pesticides being applied). However, because Malian farmers are poor, buying such personal protective equipment may not be feasible for them. Because cotton growers are organized into Village Associations, a solution to this problem could be to have each Association provide a few complete sets of protective equipment which could be shared by the farmers. In the CMDT areas, agricultural inputs such as pesticides, equipments and sprayers can be obtained by credit from the Banque Nationale de Développement Agricole (BNDA) (Ajayi et al., 2002). In conclusion, because failure to use appropriate protective clothing or to adopt adequate mixing application, storage, and disposal of pesticides may result in high hazards exposure there is a need for farmers' pesticide safety education in Mali. Highly toxic pesticides are being applied by farmers who have little education (pesticide safety). Pesticide safety training will ensure that farmers better understand the risks implicated in pesticide use and that they will adopt the better attitudes regarding proper pesticide application, storage and disposal. Improper handling of pesticide wastes and containers often results in unacceptable levels of environmental contamination and excessive exposure to the applicators themselves (Hock, 1987). New recommendations by the Food and Agricultural Organization (FAO) stipulate that pesticide distributors should take back used containers for recycling (Ajayi et al., 2002). Some type of a container collection program should be initiated in Mali, either by state agencies or CMDT in order to collect and destroy empty containers. Future studies are in order to assess pesticides in well water during peak periods of application, evaluate adoption of additional personal protective equipment and safe application practices, and to continue environmental monitoring in the cotton growing areas of Mali where pesticides are heavily used. Also, pesticide residue studies of drinking water collected from reused pesticide containers should be initiated. Cholinesterase testing in Malian farmers exposed to organophosphorus pesticides may be carried out to prevent and detect poisoning. For erythrocyte cholinesterase, 70% activity has been recommended as an action level by the World Health Organization (WHO) (Vandekar, 1975).

Chapter 4

Determination of Pesticides Residues in Soil and Water from Four Cotton

Growing Areas

4.1. Introduction

Pesticides are chemicals used to kill or control pests. For a grower or farmer, the term pests includes insects and mites that damage crops; weeds that compete with crops for nutrients; fungal, bacterial and viral diseases of plants; nematodes, snails and slugs; rodents that feed on grain, young plants, and the bark of fruit trees; and birds that eat young plants seedlings and grain from fields, feedlots and storage (Ware, 2000). The use of pesticides has enabled farmers to improve their yields worldwide. It is well known that intensive agricultural practices that enhance yields constitute a risk of agrichemical contamination of water and soil. The improvement in yield is sometimes concomitant with the occurrence and persistence of pesticide residues in soils and water. Pesticides may reach the soil through direct application to the soil surface, incorporation in the top few inches of soil, or during application to crops (McEwen and Stephenson, 1979). Pesticides can enter ground water resources and surface run-off during rainfall, thereby contributing to the risk of environmental contamination. The fate of a pesticide in the soil and water environments is influenced by the physico-chemical properties of the pesticide, the properties of the soil and water systems (presence of clay materials, organic matter, pH etc.), climate, biology, and other factors (Singh, 2001). The increased use of pesticides has caused pollution of soils and water worldwide. Substantial concentrations of organochlorine pesticide residues, particularly the oxidized form of heptachlor, remain in soils from South Korea, even though their use has been discontinued since 1980 (Kim and Smith, 2001). Residues of toxaphene, DDT, trifluralin, and hexachlorocyclohexane have been detected in cotton field soils collected from South Carolina (Kannan et al., 2003). Carvalho et al. (2002)

identified chlorinated hydrocarbons and organophosphorus pesticides in coastal lagoons of Nicaragua (Carvalho et al., 2002). The DDTs were the main contaminants detected in soils and water from Banjul and Dakar (West Africa) (Manirakiza et al., 2003). A study on surface water quality in Ivory Coast has demonstrated the occurrence of organochlorine pesticides at low concentrations (Wandan and Zabik, 1996).

In Mali, pesticide use is increasing, but little information is available regarding the environmental impacts resulting from their use (Camara et al., 2000). Few data are available on pesticide residues in soils and water in Mali. In 1998, newspapers and other media reported on the occurrence of DDT in the tap water of the capital city of Mali. In a study conducted from 1992 to 1994 on pesticide residues in water from some CMDT (Compagnie Malienne pour le Developpement des Textiles) areas, pollution of the Niger River tributary Banifing was reported. Pesticide substances identified were dimethoate, cypermethrin, chlorpyrifos ethyl, profenofos, omethoate, deltamethrin and cyfluthrin (Coulibaly and Derlon, 1994). In their study, thirty-three sites were sampled three times each year (June, September and December). Water samples were analyzed for pesticide residues (wells and surface waters). Water pollution by pesticides was frequent in areas where cotton was intensively grown.

The Malian cotton grower survey report (Chapter 3) indicated that highly toxic pesticides are used by farmers with low education levels. Despite the fact that the majority of farmers have been trained in pesticide application techniques and pesticide disposal, sometimes growers do not use pesticides in an appropriate manner. Such practices may result in the contamination of the environment by pesticides. A total number of 20 pesticides have been used in the study areas during the last ten years. Endosulfan was the most frequently used pesticide followed by profenofos, cypermethrin, monocrotophos, and chlorpyrifos (Chapter 3).

A study of pesticide residues in soil and water was conducted to obtain information on the status of residues in four cotton growing areas in Mali. It is reasonable to assume that pesticide residues levels in soil and water should be linked to farmers' practices (Chapter 3) and to the time of cotton establishment as a major cultivated crop in these areas. For this reason, the study was designed to compare the occurrence of pesticide residues in an older cotton producing area (Koutiala) versus intermediate producing areas (Sikasso, San) and a newer cotton growing area (Kita).

4.2. Materials and methods

4.2.1. Sampling

4.2.1.1. Soil sampling

Top soil samples were obtained from four intensive cotton growing areas of Mali in June-July 2003. Maps of the sampling areas are provided in Appendices III-i and III-ii that show the sampling areas. Sampling sites were selected in part based on geographic proximity to villages with higher population densities (assumed to have higher pesticide usage), and interviews with farmers were conducted at the same sites (Chapter 3). These sites included Koutiala (an older cotton producing area), Sikasso and San (relatively intermediate cotton producing areas) and Kita (a more recent cotton producing area). Three villages within each of these four areas were selected from which 5 samples were collected per village. A total of 60 samples were collected (4 areas x 3 villages x 5 samples per village = 60).

Each soil sample was a composite of 20 subsamples collected at each site using random sampling within a grid. To accomplish this, the approximate center of a field was determined and a grid system was established consisting of 5 rows, 10 paces apart, with 4 core samples taken per row for a total of 20 cores (Mullins et al., 1971). Soils were collected from the 0-15 cm layer using a 19" Oakfield soil auger. The subsamples were placed into a 16-liter bucket, thoroughly mixed, and sifted through a No.5 (4mm/0.1575") brass soil sieve (W.S. Tyler™) at the collection site. After each collection, the soil auger, bucket, sieve and mixing tool were rinsed with tap water and dried before next use. Separate sampling equipment (bucket, soil auger) was used for control samples. One of the 5 samples collected at each village was obtained from an uncultivated field and used as a control.

A coding system for sample identification was developed at Virginia Tech before the actual sampling took place. A field identification number was given to each sample using the following coding: first 2 letters of the region, first two letters of the village and adjunction of a number from one to five. Samples from uncultivated areas were always given the number one.

If two villages had the same first two letters we chose the first letter and the last letter. Example: KIBI01 would be a sample from an uncultivated area in the village of Baliani (region of Kita). KIMA02 would be the second sample from the village of Massala (region of Kita) and so forth. Sample field numbers were penned on pre-printed labels at the time of collection. In addition, a chain of custody form was initiated to provide documentation of the date/time of sample transfer. The collected samples were stored in a refrigerator at the sampling sites and shipped to the Central Veterinary Laboratory (CVL) under ice. Upon return to the CVL, soil samples were air dried and sieved through a No.20 (850 μm /0.0335") brass soil sieve (W.S. Tyler™). Samples were refrigerated at about 4°C until shipment by airline to the United States. Samples were then transported to the Pesticide Residue Laboratory (PRL) at Virginia Tech in August 2003. Upon arrival at the PRL, soil samples were assigned a unique laboratory number, and then stored in a freezer at about -18°C. Freezer temperatures were monitored daily to ensure sample integrity. In addition, the freezer was locked at all times, as required by the United States Department of Agriculture (USDA) permit, except when soil samples were accessed. This permit was required for importation of foreign soil to the United States. A copy of the permit is included in Appendix I-i.

4.2.1.2. Water sampling

Water samples were collected at the CMDT regions of Koutiala and San in June-July 2003. Eight samples in total were collected, six from field wells and two from tributaries (surface waters) of Niger River at the Barrage Kouoro and Bani Bridge. Water sampling bags constructed of rubber were used to collect water samples. The sampling bags were lowered and raised by hand from the wells and from the surface waters. After collection, the water temperature and pH were measured directly from the sampling bags using a pH meter (Hanna Instruments HI 991301) and Panpeha™ pH paper (Sigma Aldrich). Then, samples were poured into a 1/2-gallon glass jar. Sample field numbers were penned on pre-printed labels at the time of collection. The collected samples were stored at the CMDT refrigerator and transferred under ice to the CVL cold room in Bamako. The collected water samples were shipped by airline to the United States in August 2003. Upon receipt by the PRL, chain of custody documents were signed, water samples were assigned a unique laboratory number and stored at about 4°C.

4.2.2. Analytical methods

4.2.2.1. Reagents and pesticide standards

4.2.2.1.1. Reagents

High purity pesticide grade solvents (hexane, methylene chloride) were purchased from Fisher Scientific. Reagent grade (ACS) hexane was purchased from Ashland Chemicals and acetone of the same grade was purchased from Fisher Scientific. Each solvent was distilled and checked for purity according to the PRL SOP 4.18 version (Appendix IV-iii). Anhydrous granular sodium sulfate (certified ACS, 10-60 Mesh) was obtained from Fisher Scientific. Folded filters (240 mm diameter) manufactured by Schleicher and Schuell Microscience were purchased from Fisher Scientific. Bulk sand was obtained from a local hardware store and rinsed with solvents prior to soil extraction. The cleaning method for the sand is included in Appendix IV-iv. Control soil was obtained locally (Blacksburg, VA) and was pre-tested to ascertain if any co-extractives would interfere with chromatographic identification and quantification of pesticides.

4.2.2.1.2. Pesticide standards

Survey results were used to develop a strategy on which pesticides would be screened. Each of the 60 soil samples and 8 water samples were analyzed for 50 pesticides. Pesticides standards were purchased from commercial vendors and are summarized in Table 4-1.

Table 4-1. List of pesticide standards which were used to identify pesticides in Mali soil samples from cotton growing regions.

Standards	Source	Pesticide(s)
Organochlorine pesticide mix AB#1 (20 components)	Restek ¹ # 32291 200 µg/mL each in hexane:toluene (1:1)	aldrin, α-BHC, β-BHC, δ-BHC), γ-BHC (lindane), α-chlordane, γ- chlordane, p,p-DDD, p,p-DDE, p,p-DDT, dieldrin, endosulfan I, endosulfan II, endosulfan sulfate, endrin, endrin aldehyde, endrin ketone, heptachlor, heptachlor epoxyde, methoxychlor (purity 97-99%)
Organophosphorus pesticide mix A (20 components)	Restek # 32277 200 µg/mL each in hexane:acetone (95:5)	Azinphos methyl, sulprofos, chlorpyrifos, coumaphos, demeton O and S, diazinon, dichlorvos, disulfoton, ethoprop, fensulfothion, fenthion, merphos, methyl parathion, mevinphos, naled, phorate, ronnel, stirofos, tokuthion, trichloronate (purity 93-99%)
Organophosphorus pesticide mix B (7 components)	Restek # 32278 200 µg/mL each in hexane:acetone (95:5)	dimethoate, EPN, malathion, monocrotophos, parathion, TEPP, sulfotepp (purity 98-99%)
Organophosphorus individual standard	Chemservice ²	profenofos (purity 93.4%)
Pyrethroids	Chemservice	cypermethrin (purity 98%)
Triazines	Chemservice	atrazine (purity 98%)

¹Restek: 110 Benner Circle, Bellefonte, PA 16823-8812.

²Chemservice: 660 Tower Lane, P.O. Box 599, West Chester, PA 19381-0599.

Retention time

The retention time of each component in the pesticide mixtures purchased from Restek (OC mix AB#1, OP mix A, OP mix B) was determined by injection of individual pesticide standards. However individual standards were not available for TEPP, sulfotepp, tokuthion, sulprofos and previous chromatography at the PRL was used as a reference for elution order using an RTX-5 column. Retention times of pesticides screened are included in Appendix V.

Working (calibration) standards

Organochlorinated pesticides

Pesticide stock standard solution of 4 µg/mL was prepared by transferring 1 mL of 200 µg/mL to a 50 mL volumetric flask and diluting to the mark with pesticide grade hexane. A set of calibration working standards of 0.04, 0.08, 0.16 and 0.32 µg/mL was prepared by serial dilution of the stock solution with pesticide grade hexane.

Organophosphate pesticides

Pesticide mixture stock standard solution of 4 µg/mL was prepared by transferring 1 mL of 200 µg/mL to a 50 mL volumetric flask and diluting to the mark with pesticide grade hexane. A set of calibration working standards of 0.64, 1.28, 2.56 µg/mL was prepared by serial dilution of the stock solution with pesticide grade hexane. The profenofos standard was prepared differently, because the standard was not part of the mixture of organophosphates. After a calculation adjustment for purity, 26.76 mg (instead of 25 mg) of profenofos (purity 93.4%) was weighed and diluted to mark with pesticide grade acetone in a 25 mL volumetric flask to make a 1000 µg/mL stock solution; 1 mL of the 1000 µg/mL was diluted with hexane in a 100mL volumetric flask to make a 10 µg/mL stock solutions. A set of calibration working standards of 1.0, 2.0 and 4.0 µg/mL was prepared by dilutions of the 10 µg/mL stock solution using hexane.

Triazines (Atrazine)

Previous stock solutions and working standards of 0.2, 0.5, 1.0, 2.0 µg/mL already prepared at the PRL were used.

Pyrethroids (Cypermethrin)

100 mg of cypermethrin (purity 98%) were weighed and diluted to mark with pesticide grade acetone in a 100 mL volumetric flask to make a 1000 µg/mL stock solution; 1 mL of the 1000 µg/mL was diluted with pesticide grade hexane in a 100mL volumetric flask to make a 10 µg/mL stock solutions. A set of calibration working standards of 0.05, 0.1, 0.25, 0.5 and 1.0 µg/mL was prepared by dilutions of the 10 µg/mL stock solution with hexane.

Storage of standards

All stock and working standards were transferred to Qorpak™ glass jars. After preparation, standards were stored at 4°C, and only removed from storage for use.

Quality Control

Control and fortified (spiked) samples were extracted every 6 samples using soil known not to contain detectable levels of pesticides. Soil used in the recovery assay was collected from the local area, pre-tested and stored at room temperature until fortification. For fortified samples, known amounts of pesticide were added to control soil for the purposes of recovery determination. The recovery studies were usually performed in triplicate on soil and water fortified. Data on recoveries may be found in Appendix V. Control and fortified samples were included in the analytical set each day to monitor the extraction procedure.

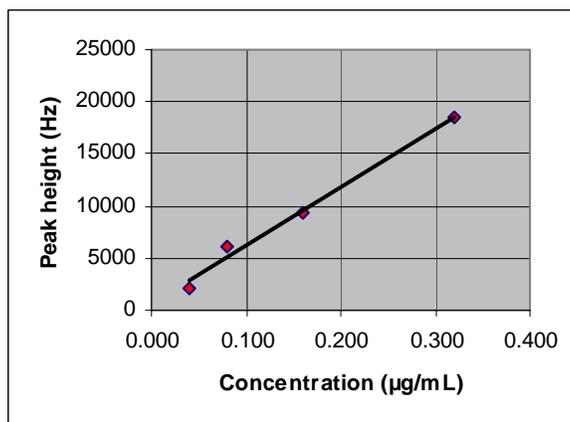


Figure 4-1. Calibration curve for endosulfan II.

Calibration curves of working standards were used to evaluate the linearity of the gas chromatograph response each day of analysis. Figure 4-1 shows an example of calibration of a calibration curve for endosulfan II. If the calibration curve gave a correlation (R) greater than 0.99, then the Y intercept and slope were used to calculate the amount of pesticide in the original sample as follows. The equation of the calibration curve can be written as $Y = mX + b$. After fortification, the amount of pesticide extracted may be calculated from the above equation as:

$$X = \text{extract concentration} = (Y - b) / m$$

The residue concentration can be calculated as:

$$\text{Residue concentration} = (\text{extract concentration} \times \text{final volume}) / \text{sample amount}$$

$$\text{Percent recovery} = 100 \times (\text{residue concentration} / \text{fortification concentration}).$$

Method detection limit

An acceptable method detection limit was considered to be that level with a consistent and /or reliable (>70% recovery) of the pesticide from fortified samples. If this was not possible, the most consistent pesticide recovery was used to establish the method detection limit.

4.2.2.2. Analytical methods for soil samples

4.2.2.2.1. Soil characteristics

Because the laboratories at the Virginia Tech Soil Testing Laboratory and Soil Physics Laboratory were not authorized to process unsterilized samples of foreign origin, the samples were sterilized (autoclaving at 120°C for 20 minutes). A subset of each sterilized soil sample was sent to these laboratories where they were analyzed for pH, percent organic matter, percent clay and textural class.

4.2.2.2.2. Multi-residue extraction method for soil samples

An analytical weighing balance (Mettler PC 2000) was checked against Fisher™ weights prior to weighing of each soil sample using weights that bracketed the amount to be weighed. Soil samples were removed from the freezer and allowed to thaw to room temperature. Then, a 25 g subsample was weighed and placed in a 4 oz. glass jar. If appropriate, the soil was fortified

at this step. Pre-cleaned sand (25 g) and granular sodium sulfate (50 g) were added to the sample. The sample mixture was then manually shaken for 30 seconds and placed on a roller for 30 seconds (US Stoneware™). Afterwards, the sample was allowed to stand for 20 minutes to allow the sodium sulfate to adsorb moisture from the soil. The sample mixture was carefully transferred to a 250 mL bulb column plugged with a small piece of glass wool. Sample flask was triple rinsed with small amounts (3 to 5 mL) of hexane each time. Each rinsing was transferred to the top of the soil in the bulb column. The column soil contents were rinsed with 250 mL of 1:1 (v/v) acetone:hexane. The eluate was collected in a 500 mL Erlenmeyer flask and concentrated to approximately 100 mL using a rotary evaporator (Büchi R 110, Brinkmann™). The concentrated eluate was “washed” by liquid-liquid partitioning with 25 mL saturated sodium sulfate and 300 mL distilled water in a 500 mL separatory funnel. After shaking the sample for two minutes, the aqueous and organic solvent layers were allowed to separate for 10 minutes. Then, the aqueous layer (bottom layer) was drained into a beaker and the hexane (top layer) was transferred to a 250 mL separatory funnel. The aqueous layer was returned to the 500 mL separatory funnel and re-extracted with 40 mL of 15% methylene chloride in hexane. The sample extract was shaken again for 2 minutes and the aqueous and organic layers were allowed to separate for 10 minutes. The aqueous (bottom) layer was discarded and the organic layer (top) was transferred to the 250 mL separatory funnel. Next, 100 mL of distilled water was added to the combined organic layers and the extract was gently washed for 30 seconds. The aqueous layer (bottom) was discarded. The organic layer was drained through a sodium sulfate column into a 250 mL Erlenmeyer flask. The sample extract was evaporated to near dryness on a rotary evaporator. The sides of the flask were rinsed down with 20 mL of hexane. The flask was returned to the rotary evaporator and the sample was evaporated to approximately 1 mL. Small amounts of hexane were quantitatively transferred (1 to 2 mL each transfer with a minimum of 10 mL) into a 15 mL centrifuge tube. Then, the sample was concentrated on nitrogen evaporator (Organomation, model No. 111) to 0.5 mL and rediluted to exactly 2 mL with hexane and vortex (Genie2, 12-812 Fisherbrand™). At this step the extract was ready to be analyzed on gas chromatograph (GC).

4.2.2.2.3. Instrument analysis

4.2.2.2.3.1. Identification of pesticides in soil samples

Analysis of soil for pesticide residues was carried out using an Agilent gas chromatograph 6890 equipped with a microelectron capture detector (^{63}Ni). Separation of the pesticides was achieved using a Restek 30 m length x 250 μm internal diameter x 0.25 μm film thickness capillary column (RTX-5, 5%-phenyl methylpolysiloxane). The temperature program was as follows: 90°C for zero minute 30°C/min to 190°C held for 20 min, 20°C/min to 275°C held for 10 minutes. Helium was used as the carrier gas at a constant column flow rate of 1.1mL/min. The make up gas was nitrogen at a flow rate of 60 mL/min. Injections were in splitless mode on an Electronic Pressure Control (EPC) split-splitless inlet with a purge flow to split vent at 35.2 mL/min @ 1 min and pressure at 14.7 psi with a total flow of 39.2 mL/min, injector temperature was 250°C and the detector temperature was 350°C. Hewlett Packard Chemstation software (GC 2071, Rev.A.06.01) was used to acquire and process data.

Chromatographic peaks were identified based on the retention times of analytes measured from the time of sample injection to the time of peak maximum. The peak height was used to measure the amount of a component in the sample mixture. Figure 4-2 shows an overlay of the chromatogram of one component (endosulfan) in a chlorinated pesticides mixture (OC mix AB#1) with that of a soil sample (Kiba02). There is a perfect overlay of the two chromatograms at 26.6 minutes which corresponds to the retention time of endosulfan II, indicative of endosulfan II detection in the sample (yet to be confirmed on GC using another column).

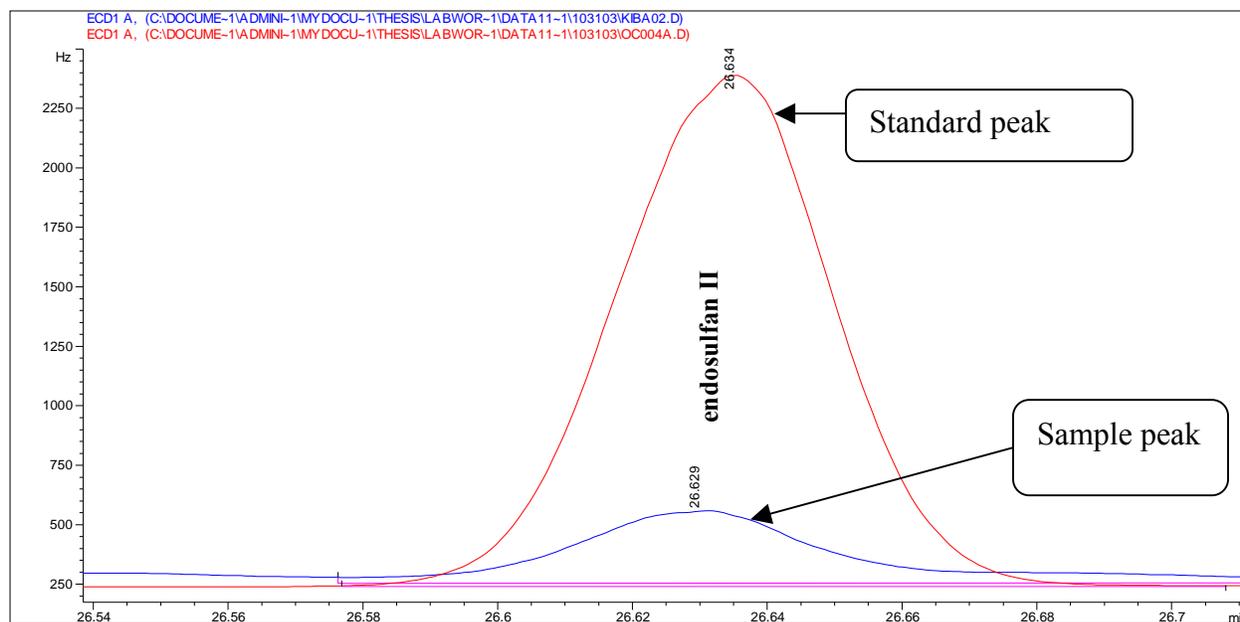


Figure 4-2. Overlay of chromatogram of organochlorinated pesticide mixture (OC mix AB#1) with chromatogram of the soil sample (Kiba02).

Pesticides were quantified using the Y-intercept and slope of the calibration curve equation of standards for each analyte detected in samples. In some cases where the peak height of sample was lower (or higher) than the peak height of working standards in calibration curves, the samples were concentrated (or diluted).

4.2.2.2.3.2. Confirmations of results

4.2.2.2.3.2.1. Gas chromatography

Confirmation runs for positive samples were carried out using a 6890 Agilent GC fitted with a microelectron capture detector (^{63}Ni) and an RTX-35, instead of an RTX-5 capillary column that was used for initial screening. Separation of the pesticides was completed using a Restek 30 m length x 250 μm internal diameter x 0.25 μm film thickness capillary column (RTX-35, 35%-phenyl methylpolysiloxane). The temperature program was as follows: 100°C held for two minutes, 15°C/min to 160°C, 5°C/min to 270°C held for 5 min. Helium was used as the carrier gas at a constant flow rate of 1.1 mL/min. The make up gas was nitrogen at a flow rate of

60 mL/min. Injections were in splitless mode on an Electronic Pressure Control (EPC) split-splitless inlet with a purge flow to split vent at 35.2 mL/min @ 1 min and pressure at 15.9 psi with a total flow of 39.3 mL/min, injector temperature was 225°C and the detector temperature was 300°C. Hewlett Packard Chemstation software (GC 2071, Rev.A.06.01) was used to acquire and process data.

4.2.2.2.3.2.2 Gas chromatography-Mass spectroscopy

Confirmation analyses were conducted on four of the positive soil samples (containing the highest residues levels). These samples were Silo05, Kofi02, Kofa05 and Sila04. Gas chromatography-mass spectroscopy (GC-MS) was done using a gas chromatograph Agilent 6890 and mass spectroscopy detector. Separation of the pesticides was completed using a J & W, 30 m length x 250 µm internal diameter x 0.30 µm film thickness capillary column (DB-5, 5%-phenyl methylpolysiloxane). The temperature program was as follows: 100°C held for two minutes, 15°C/min to 160°C, 5°C/min to 270°C held for 5 min. Helium was used as the carrier gas at a constant flow rate. Injections were done in splitless mode. Injector temperature was 225°C. Chemstation software package was used to acquire and process data.

4.2.2.3. Analytical methods for water samples

4.2.2.3.1. Temperatures and pH

At the time of collection, temperature and pH were measured in each water sample using a pH meter Hanna instruments (HI 991301) and Panpeha™ pH paper from Sigma Aldrich.

4.2.2.3.2. Multi-residue extraction method for water samples

Water samples were filtered through a folded filter of 240 mm diameter from Schleicher and Schuell Microscience™ into a 1000 mL graduated cylinder to a volume of 900mL. The sample was transferred to a 1000 mL separatory funnel. Sodium sulfate (10g) was added and dissolved in the water by shaking. Methylene chloride (100mL) was added and the mixture was manually shaken for 2 min with release of pressure at the beginning. The aqueous and organic layers were allowed to separate for 10 min. The bottom layer (methylene chloride) was drained

through anhydrous sodium sulfate in a 500 mL Erlenmeyer flask. The extraction was repeated twice with 100 mL methylene chloride. The combined methylene chloride layers were evaporated on a rotary evaporator (Büchi R 110, Brinkmann™) to about 5 mL. Hexane (15-20 mL) was added to the sample flask and the evaporation was continued to about 2 mL. The concentrated extract was removed from the rotary evaporator and the sides of the flask were rinsed down with hexane. The sample extract was quantitatively transferred with hexane (5 times with approximately 2 mL solvent each time) to a calibrated centrifuge tube (15 mL). Sample was evaporated to 0.5 mL on a nitrogen evaporator (Organomation, model No. 111) and diluted to exactly 2 mL with hexane and vortexed (Genie2, 12-812 Fisherbrand™).

4.2.2.3.3. Instrument analysis

4.2.2.3.3.1. Identification of pesticides in water

Analysis of water for pesticide residues was carried out using a 6890 Agilent GC fitted with an electron capture detector (^{63}Ni). Separation of the pesticides was achieved using a Restek 30 m length x 250 μm internal diameter x 0.25 μm film thickness capillary column (RTX-35, 35%-phenyl methylpolysiloxane). The temperature program was as follows: 50°C for zero minute, 10°C/min to 230°C held for 5 minutes, 20°C/min to 280°C held for 12 min. Helium was used as the carrier gas at a constant flow rate of 1.3 mL/min. The make up gas was nitrogen at a flow rate of 60 mL/min. Injections were done on splitless mode on an Electronic Pressure Control (EPC) split-splitless inlet with a purge flow to split vent at 15.0 mL/min @ 1.00 min and pressure at 14.8 psi with a total flow of 19.3 mL/min. Injector temperature was 250°C and the detector temperature was 350°C. Hewlett Packard Chemstation software (GC 2071, Rev.A06.01) was used to acquire and process data.

4.2.2.3.3.2. Confirmations of results

Confirmation runs for positive identifications in water samples were carried out using a 6890 Agilent GC fitted with an electron capture detector (^{63}Ni). Separation of the pesticides was achieved using a Restek 30 m length x 250 μm internal diameter x 0.25 μm film thickness capillary column (RTX-5, 5%-phenyl methylpolysiloxane). The temperature program was the

same as above for the identification of pesticides (see section 4.2.2.3.3.1). Hewlett Packard Chemstation software (GC 2071, Rev.A.06.01) was used to acquire and process data.

4.3. Results

4.3.1. Soil samples

4.3.1.1. Soil characteristics and sampling locations

Soil physico-chemical characteristics and sampling geographic coordinates are compiled in Appendix VI. Texture distribution of soils in the study area is: sandy-loam (58%), loam-sandy (30%), loam (10%) and silt (2%). Soils from the regions of Kita, Sikasso and San were mostly sandy-loam while soils from Koutiala were mostly loam-sandy (Figure 4-3). Soil pH ranged from 5.0 to 7.2 and percent organic matter ranged from 0.2% to 1.7%.

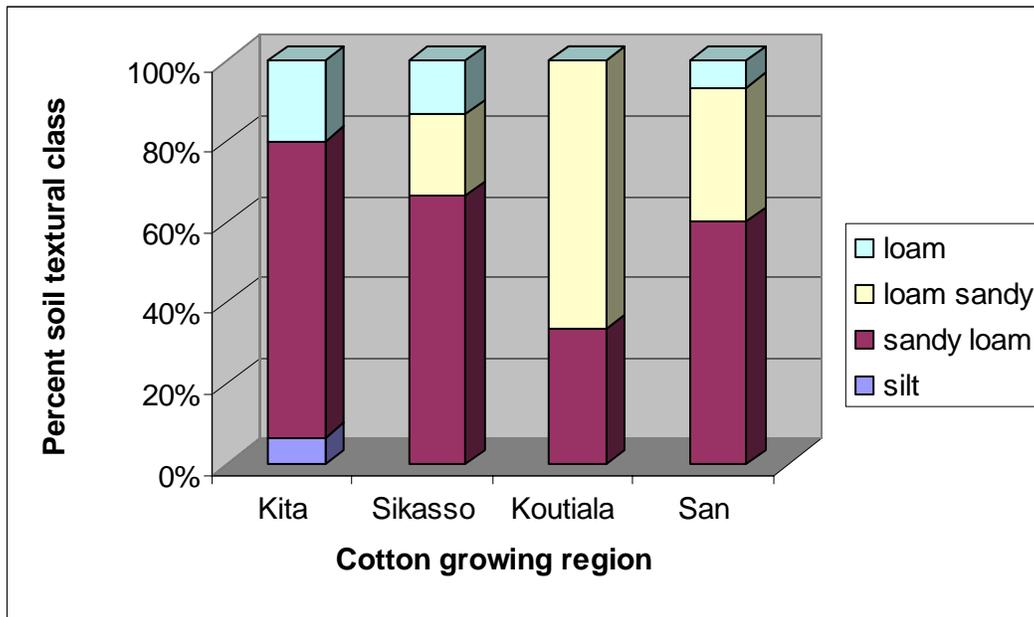


Figure 4-3. Distribution of soil textural classes.

4.3.1.2. Residues detected

Tables of pesticide residues (identity, concentration) of the 60 soil samples from Mali which were analyzed can be found in Appendix VII. All pesticides detected in the soil samples were confirmed using a different capillary column. No adjustment for recovery was done when calculating residue levels. In addition, four of the positive samples yielding the highest pesticide level were analyzed on GC-MS. Overall 46 of the 60 soil samples (77%) analyzed were positive for one or more pesticides. Seven pesticides or pesticide metabolites were detected: endosulfan I, endosulfan II, endosulfan sulfate, p,p-DDD, p,p-DDE, p,p-DDT and profenofos. Figure 4-4 summarizes the occurrence of the pesticides detected in study area soils.

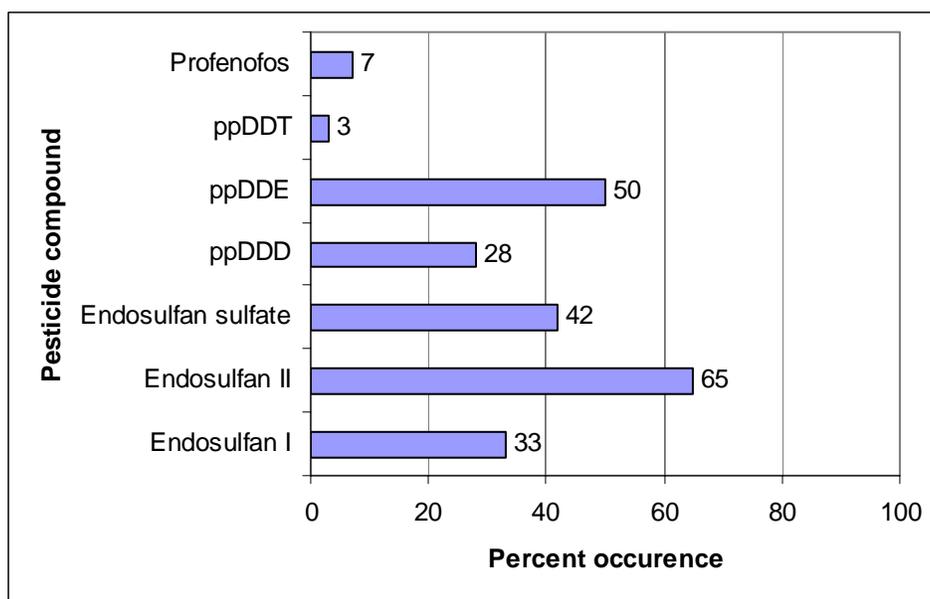


Figure 4-4. Percentage occurrence of pesticides found in soil samples from all four cotton growing areas.

The most common pesticide soil residue detected in the cotton growing study area was endosulfan II, constituting 65% of the detections with a maximum of 37 ng/g. The other pesticide materials include: [p,p-DDE (50%-121 ng/g); endosulfan sulfate (42%-49 ng/g); endosulfan I (33%-10 ng/g); p,p-DDD (28%-below the method quantification limit); profenofos (7%-below the method quantification limit) and p,p-DDT (3%-11 ng/g); % occurrence-highest level detected respectively].

4.3.1.2.1. Residues detected in samples from Kita

Endosulfan (I and II) was the sole pesticide detected in soil samples from Kita (Table 4-2). The endosulfan I isomer was detected in one out of fifteen samples constituting 7% of the samples. Endosulfan II was detected in 6 samples constituting 40% of those samples examined. All detected pesticides were below the quantification limit (6.4 ng/g).

4.3.1.2.2. Residues detected in samples from Sikasso

Results from the pesticide residue analysis for samples from Sikasso are summarized in Table 4-3. Six pesticides were detected in samples from Sikasso. Endosulfan (I and II) and the metabolite endosulfan sulfate, p,p-DDT and its breakdown products (p,p-DDE and p,p-DDD) are the pesticides detected in samples from Sikasso. Endosulfan II was detected in fourteen (93%) out of fifteen samples among which 4 samples (27%) were above the quantification limit with a maximum concentration of 26.4 ng/g. Endosulfan sulfate was detected in 11 samples (73%) among which 7 samples (47%) were above the quantification limit with a maximum concentration of 49 ng/g. Endosulfan I was detected below the quantification limit in six (40%) out of fifteen samples. p,p-DDE was detected in 9 samples (60%) among which one sample (7%) was above the quantification limit at a concentration of 20 ng/g. p,p-DDD was detected below the quantification limit in 5 samples (33%). One sample (7%) contained p,p-DDT below the quantification limit of 6.4 ng/g.

Table 4-2. Occurrence and range of pesticide soil residues detected in the Kita region¹.

Pesticide reporting status	Pesticides detected	Samples below the quantification limit ²		Samples above the quantification limit		Range concentrations (ng/g)
		Number	% ³	Number	%	
Reported as used in past ten years						
Endosulfan	endosulfan I	1	7	0	0	ND ⁴ -(<MQL ⁵)
	endosulfan II	6	40	0	0	ND-(<MQL)
Dimethoate	ND	ND	ND	ND	ND	ND
Cypermethrin	ND	ND	ND	ND	ND	ND
Profenofos	ND	ND	ND	ND	ND	ND
Atrazine	ND	ND	ND	ND	ND	ND
Not reported as used in past ten years, but detected	ND	ND	ND	ND	ND	ND

¹n = 15 samples analyzed.

²Sample residues were detected above the method detection limit (0.1 ng/g), but residues were not quantified.

³Percent of samples.

⁴ND = Not Detected.

⁵Method Quantification Limit (MQL) = 6.4 ng/g dry weight.

Table 4-3. Occurrence and range of pesticide soil residues detected in the Sikasso region¹.

Pesticide reporting status	Pesticides detected	Samples below the quantification limit ²		Samples above the quantification limit		Range concentrations (ng/g)
		Number	% ³	Number	%	
Reported as been used in past ten years						
Endosulfan	endosulfan I	6	40	0	0	ND ⁴ -(<MQL ⁵)
	endosulfan II	10	67	4	27	ND-26.4
	endosulfan sulfate	4	27	7	47	ND-49
Cypermethrin	ND	ND	ND	ND	ND	ND
Profenofos	ND	ND	ND	ND	ND	ND
Atrazine	ND	ND	ND	ND	ND	ND
Monocrotophos	ND	ND	ND	ND	ND	ND
Not reported as used in past ten years, but detected						
	p,p-DDD	5	33	0	0	ND-(<MQL)
	p,p-DDE	8	53	1	7	ND-20
	p,p-DDT	1	7	0	0	ND-(<MQL)

¹n = 15 samples analyzed.

²Sample residues were detected above the method detection limit (0.1 ng/g), but residues were not quantified.

³Percent of samples.

⁴ND = Not Detected.

⁵Method Quantification Limit (MQL) = 6.4 ng/g dry weight.

4.3.1.2.3. Residues detected in samples from Koutiala

Table 4-4 summarizes pesticide residues detected in soil samples from Koutiala. A total of six pesticides were detected. They were: endosulfan (I and II) and the metabolite endosulfan sulfate, p,p-DDT and the breakdown products p,p-DDE and p,p-DDD. Endosulfan II was detected in thirteen (87%) out of fifteen samples among which 3 samples (20%) were above the quantification limit with a maximum concentration of 37 ng/g. Endosulfan I was detected in 10 samples (67%) one of which was above the quantification limit (10 ng/g). Endosulfan sulfate was detected in 8 samples (53%) and 5 samples (33%) were above the quantification limit with a maximum concentration of 49 ng/g. p,p-DDE was detected in 14 samples (93%) and 2 samples (14%) were above the quantification limit with a maximum concentration of 121 ng/g. p,p-DDD was detected below the quantification limit in 12 samples (80%). One sample (7%) contained p,p-DDT above the quantification limit (11 ng/g).

4.3.1.2.4. Residues detected in samples from San

Five pesticides were detected in soil samples from San (Table 4-5). They were: endosulfan (I and II), endosulfan sulfate, profenofos and p,p-DDE. Endosulfan II and endosulfan sulfate were each detected below the quantification limit in 6 samples (40%). Endosulfan I was detected in 3 samples (20%) below the quantification limit. Profenofos was detected in 4 samples (27%) below the quantification limit. p,p-DDE was detected in 7 samples (47%) below the quantification limit.

4.3.1.2.5. Residues detected using Gas Chromatography-Mass Spectroscopy (GC-MS)

DDTs and endosulfan residues detected in the soil samples Silo05, Kofi02, Kofa05 and Sila04 were confirmed on GC-MS on both SCAN and Selected Ion Mode (SIM).

Table 4-4. Occurrence and range of pesticide soil residues detected in the Koutiala region¹.

Pesticide reporting status	Pesticides detected	Samples below the quantification limit ²		Samples above the quantification limit		Range concentrations (ng/g)
		Number	% ³	Number	%	
Reported as been used in past ten years						
Endosulfan	endosulfan I	9	60	1	7	ND ⁴ -10
	endosulfan II	10	67	3	20	ND-37
	endosulfan sulfate	3	20	5	33	ND-49
Cypermethrin	ND	ND	ND	ND	ND	ND
Profenofos	ND	ND	ND	ND	ND	ND
Atrazine	ND	ND	ND	ND	ND	ND
Monocrotophos	ND	ND	ND	ND	ND	ND
Chlorpyrifos	ND	ND	ND	ND	ND	ND
Dimethoate	ND	ND	ND	ND	ND	ND
Not reported as used in past ten years						
	p,p-DDD	12	80	0	0	ND-(<MQL ⁵)
	p,p-DDE	12	80	2	14	ND-121
	p,p-DDT	0	0	1	7	ND-11

¹n = 15 samples analyzed.

²Sample residues were detected above the method detection limit (0.1 ng/g), but residues were not quantified.

³Percent of samples.

⁴ND = Not Detected.

⁵Method Quantification Limit (MQL) = 6.4 ng/g dry weight.

Table 4-5. Occurrence and range of pesticide soil residues detected in the San region¹.

Pesticide reporting status	Pesticides detected	Samples below the quantification limit ²		Samples above the quantification limit		Range concentrations (ng/g)
		Number	% ³	Number	%	
Reported as used in past ten years						
Endosulfan	endosulfan I	3	20	0	0	ND ⁴ -(<MQL ⁵)
	endosulfan II	6	40	0	0	ND-(<MQL)
	endosulfan sulfate	6	40	0	0	ND-(<MQL)
Cypermethrin	ND	ND	ND	ND	ND	ND
Profenofos	profenofos	4	27	0	0	ND-(<MQL)
Atrazine	ND	ND	ND	ND	ND	ND
Monocrotophos	ND	ND	ND	ND	ND	ND
Chlorpyrifos	ND	ND	ND	ND	ND	ND
Dimethoate	ND	ND	ND	ND	ND	ND
Not reported as used in past ten years						
	p,p-DDE	7	47	0	0	ND-(<MQL)

¹n = 15 samples analyzed.

²Sample residues were detected above the method detection limit (0.1 ng/g), but residues were not quantified.

³Percent of samples.

⁴ND = Not Detected.

⁵Method Quantification Limit (MQL) = 6.4 ng/g dry weight for all pesticides detected except for profenofos which quantification limit is 8 ng/g.

4.3.1.3. Recovery data

The recoveries of the pesticides detected in soil range from 40% for p,p-DDE to 99% for p,p-DDT and are summarized in Table 4-6. The wide range of recoveries suggests that there is inherent variability in the multi-residues extraction method used. Also, the soil medium can be considered as a complex matrix which may contain components of diverse origins. Co-extractives that are present in the soil sample extract, in spite of cleanup during extraction may interfere with the analysis and result in variability of recoveries.

Table 4-6. Recoveries of pesticides detected in soil samples.

Compound	Retention time (minutes)	Method quantification limit ¹	% Recovery ² ± SD
Endosulfan I	23.72	6.4	52 ± 10
Endosulfan II	26.62	6.4	46 ± 10
Endosulfan sulfate	27.78	6.4	72 ± 29
p,p-DDD	26.94	6.4	71 ± 21
p,p-DDE	25.43	6.4	40 ± 9
p,p-DDT	27.87	6.4	99 ± 5
Profenofos	21.53	8	87 ± 25

¹Results in ng/g dry weight.

²Mean percent recovery based on n = 3 replicates ± Standard Deviation of the mean.

4.3.2. Water samples

4.3.2.1. Sampling locations, water temperature and pH

Appendix VI-5 summarizes water sampling geographic coordinates, water temperature and pH. Water pH ranged from 4.89 to 7.18 and water temperatures at the time of sampling ranged from 29°C to 32.5°C.

4.3.2.2. Residues detected

Occurrence and range of pesticide water residues are summarized in Table 4-7. Eight pesticides were detected in these water samples: γ -BHC (lindane), endosulfan I, endosulfan II,

endosulfan sulfate, dieldrin, p,p-DDD, p,p-DDE, and atrazine. All pesticides detected in these samples were below the quantification limit except for atrazine (one sample, 1.4 ppb). Endosulfan I and pDDE were each detected in 75% of the samples; followed by endosulfan II (62%), endosulfan sulfate (50%), p,p-DDD (37%), atrazine (25%), γ -BHC (12%), dieldrin (12%).

Table 4-7. Occurrence and range of pesticide water residues¹.

Pesticides detected	Samples below the quantification limit ²		Samples above the quantification limit		Range concentrations in part per billion (ppb)
	Number	% ³	Number	%	
γ -BHC (lindane)	1	12	0	0	ND ⁴ -(<MQL ⁵)
Endosulfan I	6	75	0	0	ND-(<MQL)
Endosulfan II	5	62	0	0	ND-(<MQL)
Endosulfan sulfate	4	50	0	0	ND-(<MQL)
Dieldrin	1	12	0	0	ND-(<MQL)
p,p-DDD	3	37	0	0	ND-(<MQL)
p,p-DDE	6	75	0	0	ND-(<MQL)
Atrazine	1	12.5	1	12.5	ND-1.4

¹n = 8 water samples analyzed.

²Samples residues were detected above the method detection limit (0.01ppb), but residues were not quantified.

³Percent of samples.

⁴ND = Not Detected.

⁵MQL = Method Quantification Limit is 0.1 ppb for all pesticides detected except atrazine (1.1 ppb).

4.3.2.3. Recovery data

The recovery for pesticides detected in water range from 80% for p,p-DDD to 141% for atrazine. These recovery data summarized in Table 4-8, appeared to be uniformly distributed.

Table 4-8. Method quantification limit, mean recovery and standard deviation for pesticides detected in water.

Compound	Retention time	Method Quantification Limit ¹	% Recovery ² ± SD
Gamma-BHC	19.12	0.1	98 ± 8
Dieldrin	25.36	0.1	87 ± 9
Endosulfan I	24.61	0.1	82 ± 9
Endosulfan II	26.59	0.1	79 ± 11
Endosulfan sulfate	27.79	0.1	101 ± 10
p,p-DDD	26.36	0.1	80 ± 11
p,p-DDE	25.09	0.1	102 ± 8
p,p-DDT	27.14	0.1	139 ± 16
Atrazine	18.69	1	141 ± 23

¹Results in part per billion (ppb).

²Mean percent recovery based on n = 3 replicates ± Standard Deviation of the mean.

4.4. Discussion

The results from this study demonstrate the occurrence of several persistent and moderately persistent pesticides at low concentrations in soil and water from Malian cotton growing areas. It was not possible to compare the soil residue levels with soil type, organic matter and clay content because of insufficient data on cropping systems and pesticide application history. However, the soil types among the four geographical areas were similar and none of the samples had high residue levels. Even though pesticides were found at low levels in groundwater samples, the fact that water from these wells is used for human and animal consumption is a concern. Also, soil pesticides may be taken up by plants and passed on to other organisms feeding on those plants, which could be hazardous to humans and animals.

The farmer survey revealed that endosulfan was the most frequent pesticide used. Results from the residue analyses corroborate the findings of the farmer survey for endosulfan II which was detected in 65% of the soil samples. Forty percent of the soil samples had a history of endosulfan use (Appendix VII). Usually, endosulfan is applied as an insecticide for the first two pesticide applications during the cotton growing season. Technical endosulfan is a mixture of two stereoisomers endosulfan I (64-67%) and endosulfan II (29-32%) (British Crop Protection Council, 2003). After release onto soil, endosulfan isomers are vulnerable to photo and chemical degradation. The high soil-sorption coefficients of the isomers reduce the potential for volatilization and leaching. Once released into water, endosulfan isomers rapidly hydrolyze under alkaline conditions and more slowly at neutral and acidic pH levels. The half-lives of endosulfan I are 35 and 150 days for pH 7 and 5.5 respectively; the half-lives of endosulfan II are 37 and 187 days for pH 7 and 5.5, respectively (Howard, 1991). Given the half-lives for endosulfans and the pH of the soil samples, the residues detected in the soil samples were probably from the current year pesticide applications. The fact that endosulfan sulfate was not detected in soil samples from the Kita region support the idea that the detected residues came from more recent applications. However, it should be noted that in some cases endosulfans have been reported several months or years after application. In 1964, when 0.38 ppm endosulfan was applied to Colorado soil, 0.04 ppm remained three years later (Mullins et al., 1971). The concentration of endosulfan residues detected in soils in this study can be considered to be low.

McEwen and Stephenson (1979) reported on the occurrence of endosulfan residue levels of 4600 ng/g and 400 ng/g in orchard and vegetable soils, respectively (McEwen and Stephenson, 1979). In general, the range of the endosulfan concentrations detected in soils from Kita and San were below the quantification limit and below those observed in soils from Sikasso and Koutiala (ND - 49 ng/g dry weight). In all regions, endosulfan II was the most prevalent pesticide identified compared to endosulfan I and endosulfan sulfate (Figure 4-5).

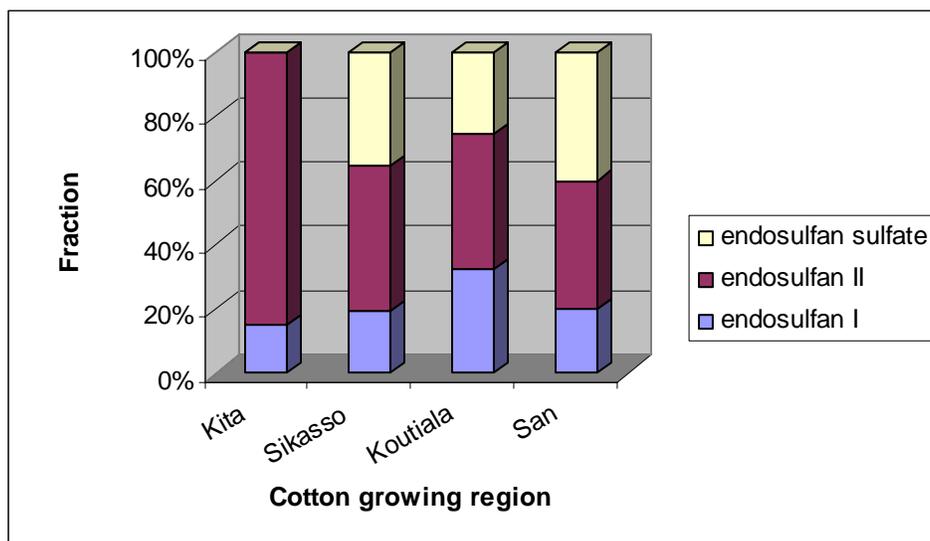


Figure 4-5. Endosulfans distribution in soil samples.

Of the various pesticides detected, p,p-DDE, a metabolite of p,p-DDT representing 50% of the detections, was the second most frequent compound found in soils. Only 5% of the sixty soil samples had DDE residues above the detection limit. Technical DDT is a mixture primarily comprised of mainly p,p-DDT (70%) and o,p-DDT (<30%) which, being of insecticidal value, is not usually removed (British Crop Protection Council, 2003). DDT may undergo dehydrochlorination under alkaline condition to non-insecticidal DDE. In soil, DDT is biologically degraded to the stable and toxic metabolites DDE and DDD (Harner et al., 1999). The half-life of DDT is estimated to be 15 years in soil, 350 days in surface waters and 31 years in ground water (Howard et al., 1991). Figure 4-6 compares the distribution of DDT and its metabolites in Malian soils. There was no previous history of DDT use reported in the four Malian agricultural regions (Chapter 3). It is interesting to note the occurrence of DDT or its

degradation products in the Sikasso, Koutiala and San regions, although it has reportedly not been used in those areas. Conversely, neither DDT nor its degradation products were detected in the Kita soil samples which suggests that it has probably never been used in this region. In Sikasso and Koutiala, p,p-DDT, p,p-DDE and p,p-DDD were all detected although the presence of a small proportion of p,p-DDT suggests that this pesticide has probably not been used for many years in these areas. In San, only p,p-DDE was detected at levels below the quantification limit, suggesting that the use of DDT in this region is probably older than that of Koutiala and Sikasso. DDT residues detected in soils in this study are similar to other reports. Cotton field soils from South Carolina and Georgia contained DDT residues ranging from 0.11 ng/g to 45 ng/g dry weight (Kannan et al., 2003). Conversely other studies have reported DDT residues as high as 3000 ng/g and 5000 ng/g in alfalfa and desert soils (Ware et al., 1971). In our study, p,p-DDE accounts for an average of 96% of the total DDT concentrations and p,p-DDT accounts for 7% of the total DDT concentrations. The ratio of DDT/DDE may be used as an indicator of the approximate time of DDT application if the half-life of DDT for the specific environment is known. No such half life information is available for Malian soils. The time elapsed since DDT application to date of measurement can be calculated from the expression: $t = T_{1/2} \times \ln(C_f/C_i)/\ln 1/2$ where $T_{1/2}$ is the half life of the substance in that environment (time for 50% of degradation from initial concentration), C_i is the initial concentration and C_f is the final concentration of a substance which has not degraded. Calculation of the DDT/DDE ratio in the Koutiala region was 0.08 suggesting that this lower DDT/DDE ratio is indicative of an older DDT application (Tavares et al., 1999). Assuming that half life values for DDT in soils under tropical conditions is 672 days as reported in a study in Brazil (Racke, 2003), DDT may have been applied in the study area of Koutiala around 1997.

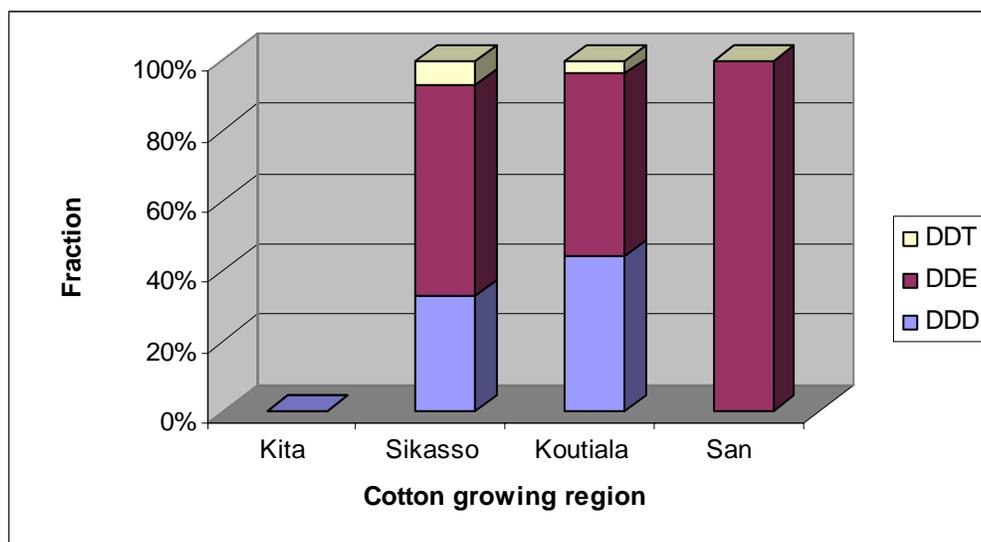


Figure 4-6. Distribution of DDT and its breakdown products in soil samples.

Soil samples taken from fallow fields in Koutiala (Kofi01, Kona01, Kofa01) and Sikasso (Silo01, Sila01) were positive for one or more pesticides. This finding supports the high land-use pressure reported for these two regions. Due to the increases in human and animal populations, fallow periods have been reduced both in length and area, or even abandoned in many farming systems (Diarra, 2003b; Kaya et al., 2000).

Profenofos was detected only in samples from San which is understandable since this pesticide is used in the first two yearly treatments of cotton plants in this region. Conversely, profenofos was not detected in the other regions probably because it is not applied in these areas. Even if it had been used the previous years, given its reduced half-life in soil of one week, it would have been degraded by the time of sampling (British Crop Protection Council, 2003).

Other pesticides that have been used by farmers in the study area during the past ten years (Chapter 3) were not detected in the soil samples. They included: [cypermethrin (13 weeks) chlorpyrifos (7-15 days), monocrotophos (1-5 days), dimethoate (7-16 days), atrazine and γ -BHC (lindane) (240 days)/ pesticide (half-lives)] (British Crop Protection Council, 2003; Howard et al., 1991). Their non-detection status is probably related to their low soil persistence.

Eight pesticides were detected in water samples (γ -BHC or lindane, endosulfan I, endosulfan II, endosulfan sulfate, dieldrin, p,p-DDD, p,p-DDE and atrazine). Among those detected dieldrin and DDT were not reported in the farmer survey as being applied in the study

areas. Therefore, they may have originated from old applications given their reported high persistence in soil and water. All pesticides detected in the water samples had concentrations below the quantification limit except for atrazine (1.4 ppb) which was detected in one sample (surface water sample). Atrazine may be released into the environment at application points where it is used as an herbicide. The half life of atrazine in natural water is 10-105 days (British Crop Protection Council, 2003). Therefore, atrazine residues detected in surface water in this study may originate from recent use and from water runoff.

Endosulfan detected in surface and ground waters most likely came from runoff water from treated cotton fields. Endosulfan has a very low leaching tendency (British Crop Protection Council, 2003). Atmospheric fallout or drift during pesticide application and practices such as washing spraying equipment in surface waters could be the source of the contamination of soil and water. The farmer survey (Chapter 3) indicated that none of the wells were sealed in the survey areas and therefore they could be easily contaminated with runoff water. No Malian drinking water norms exist for pesticides. Therefore, we compared the results of this research with the United States Environmental Protection Agency (US EPA) norms. The Maximum Contaminant Level is (MCL) the highest level of a contaminant that is allowed in drinking water. Among the pesticides detected in water atrazine and lindane have MCL set by the US EPA. The MCLs for atrazine and lindane are 3.0 ppb and 0.2 ppb, respectively. Water residues detected in this study do not exceed the drinking water Maximum Contaminant Level (MCL) of the US EPA for atrazine (1.4 ppb) and lindane (below the quantification limit).

Further residue studies in other agricultural areas of Mali are needed in order to assess the levels of pesticide residues in Malian soils, water and living organisms.

Chapter 5

Summary and Conclusions

This study has examined Malian farmers' knowledge, attitudes and practices regarding pesticide usage and identified various pesticides in soil and water from four cotton growing areas. The farmer survey indicates that pesticides are intensively used in cotton growing areas in Mali. Crop rotation is frequently practiced in the southern part of Mali and cotton is the major crop grown. Most of the cotton farmers had a low education level. The majority of farmers were trained on pesticide application techniques and pesticide disposal. However, the survey results have shown that despite their training, sometimes growers did not use pesticides in an appropriate manner. The survey identified various concerns regarding personal safety and environmental safety. Highly toxic pesticides are used by farmers with insufficient personal protective equipment. A total of 20 pesticides were used in the cotton growing areas during the past ten years. However, a majority of the farmers were not certain about the names of the pesticides nor were they able to provide specific information regarding the formulations of pesticides they had used. Endosulfan was the most frequently used pesticide followed by profenofos, cypermethrin, monocrotophos, and chlorpyrifos. Herbicides didn't appear to be used extensively in the four regions. The lack of personal protective equipment use is of concern and reflects not only low education level, but also low socio-economic level (poverty). Even farmers who were aware of the risks of exposure during pesticide application did not have the financial resources to purchase protective equipment. Since cotton growers are organized into Village Associations, a solution to this problem could be to have each Association provide a few complete sets of protective equipment which could be shared by the farmers. In conclusion, since failure to use appropriate protective clothing or to adopt adequate mixing application, storage, and pesticide disposal procedure may result into elevated health risks, there is a need for farmers' pesticide safety education. Pesticide safety training will improve farmers' understanding of the risks associated with pesticide use and, as a result, they will acquire better knowledge and attitudes regarding proper pesticide application, storage and disposal. The use of

highly toxic pesticides should be restricted if adequate personal protective equipment cannot be provided to farmers.

Numerous studies have demonstrated the persistence of organochlorine pesticides in soils from past agricultural usage in the United States, Canada (Bidelman and Leone, 2004) and worldwide (Gong et al., 2004). Although the levels were low, results from this study are not exceptional, since we detected pesticide residues in 46 of the 60 soil samples from Malian cotton growing areas. Seven pesticides or their metabolites were detected in soil samples and included: endosulfan I, endosulfan II, endosulfan sulfate, p,p-DDD, p,p-DDE, p,p-DDT and profenofos. The high persistence of a pesticide like DDT is evidenced by residues detected in soil samples with no history of DDT application during the past ten years. The concentrations of pesticide residues detected in this study are relatively low compared to other studies. The results of our study suggest that contamination by pesticides in the four cotton growing areas is not as severe as might be anticipated. However, this study was limited to a small number of farmers in only one phase of the growing season. At the same time, the significance of identifying endosulfans and DDTs in soils and water in close proximity to human and animal populations should not be discounted. The soil residues detected in the Kita and San regions were below the quantification limit and below residues levels detected in Koutiala and Sikasso. Koutiala, the oldest cotton growing area, appeared to have the highest frequency of residue detection observed in the study areas; the highest residues concentrations were also observed in this region. Eight pesticides were detected in water samples and included: γ -BHC or lindane, endosulfan I, endosulfan II, endosulfan sulfate, dieldrin, p,p-DDD, p,p-DDE and atrazine. All pesticides detected in the water samples had concentrations below the quantification limit except for atrazine (1.4 ppb) which was detected in one sample (surface water sample).

Further residues studies in other agricultural areas of Mali are needed in order to assess the levels of pesticide residues in Malian soils, water and living organisms.

Appendices

Appendix I: CMDT letter of support and soil permit

Appendix I-i. Soil permit for transport, storage, and processing of samples obtained from foreign region.

Soil Permit

Permit Number: S-60500

UNITED STATES DEPARTMENT OF AGRICULTURE
Animal and Plant Health Inspection Service
Plant Protection and Quarantine

Issued To: Virginia Technical University, Department of Entomology
(Donald E. Mullins)
352 Litton Reaves, Pesticide Residue Laboratory
Blacksburg, Virginia 24061
TELEPHONE: (540) 231-6443

Under the authority of the Federal Plant Pest Act of May 23, 1957, permission is hereby granted to the facility/individual named above subject to the following conditions:

1. Valid for shipments of soil not heat treated at the port of entry, only if a Compliance Agreement (PPQ Form 519) has been completed and signed. Compliance Agreements and Soil Permits are non-transferable. If you hold a Soil Permit and you leave your present employer or Company, you must notify your local USDA office promptly. A copy of this permit must accompany all shipments.
2. To be shipped in sturdy, leakproof, containers.
3. To be released without treatment at the port of entry to permittee or authorized user.
4. To be used only for analysis and only in the facility of the permittee at Virginia Technical Institute, Pesticide Residue Laboratory, located in Blacksburg, Virginia.
5. No use of soil for growing purposes is authorized, including the isolation or culture of organisms imported in soil.
6. All unconsumed soil, containers, and effluent is to be autoclaved, incinerated, or heat treated by the permittee at the conclusion of the project as approved and prescribed by PPQ.
7. This permit authorizes shipments from all foreign sources, including Guam, Hawaii, Puerto Rico, and the U.S. Virgin Islands through any U.S. port of entry.

Expiration Date: DECEMBER 31, 2007

WARNING: Any alteration, forgery, or unauthorized use of this Federal form is subject to civil penalties of up to \$250,000 (7 U.S.C. s 7734(b)) or punishable by a fine of not more than \$10,000, or imprisonment of not more than 5 years, or both (18 U.S.C. s 1001).

PPQ FORM 525B (8/94)

PART 1 - PERMITTEE

Appendix I-ii. Copy of letter of support for field research.

CMDT
DIRECTION DES RESSOURCES HUMAINES

Bamako, le **03 JUIN 2003**

N° 0072 /SD

NOTE DE SERVICE

Objet :

Autorisation de recherches

Madame Safiatou BERTHE DEM, Etudiante de l'Institut Polytechnique de Virginie (USA) Option : Chimie Environnementale, est autorisée à faire des recherches à la CMDT sur le thème :

« Etude environnementale des résidus de pesticide dans les sols et les eaux : cas de quatre régions agricoles du mali ».

- Lieu : DPA (DR K1a ,Skso ,San, Kita)
- Période : du 10/06 au 24/07/03

Le Chef de Division Liaison Recherche Accompagnement est chargé de lui faciliter les recherches et de fournir à l'intéressée, les renseignements et documents nécessaires à l'élaboration du thème cité ci-dessus.

Il reste entendu que la prise en charge des frais de stage sera assurée par le Projet USAID LCV.

Ampliations :

- PDG/ CS
- PI/DR/K1a/ Skso/San Kita
- Hc DC/DR

Le Directeur des Ressources Humaines

Appendix II: Sample of survey questionnaire used when interviewing farmers in cotton growing regions of Mali

Questionnaire

Date:

1-Site Description

Sample ID if field sampled:

Village:

Region:

Longitude:

Latitude:

Elevation:

Unusual events:

2-Landowner

Name:

Education:

1- Coranic:

2- Elementary School:

3- High School:

4- University:

5- No education:

6-Other:

3-Field Description

Visual:

Slope %:

Vegetation:

Dimensions (estimates):

Hectares:

Meters:

How far is the nearest water supply in the field?

1- 0-10 m

2- 10-50 m

3- 50-100m

4- 100-500m

5- >500m

4-Present Management

Cropping System:

Irrigation:

Amount and timing:

Unusual Events:

(Plowing, change in field size)

Other:

5-Past Management History

Cropping System: Rotation?

Irrigation:

Amount and timing:

Unusual Events:

Plowing, change in field size:

Other:

6-Pesticides Use

Supplier of pesticides

- 1- Government (specify)
- 2- CMDT
- 3- Private applicators
- 4- Other (please specify)

Name and Formulation of pesticides used during the last ten years

Where do you get information about the proper pesticide to use on your cotton?

- 1- Pesticide dealer
- 2- Extension specialists from CMDT
- 3- Other (specify)

Who is in charge of pesticide application?

- 1- Yourself, family member or employee
- 2- Professional agricultural consultant
- 3- Extension service
- 4- Other (specify)

Volume of pesticides used per year on target crop(s) = cotton:

- 1- <5L
- 2- 5-20L
- 3- 20-50L
- 4- 50-100L
- 5- >100L

Products Name:

Do you make dilutions of pesticides solution

- 1- Yes
- 2- No

Pesticides/water ratio:

Date of the most recent pesticide application:

Name and Formulation of the most recent Pesticide used:

Normal frequency of pesticide applications per product (cotton) and per season:

- 1- One application
- 2- 2-4 applications
- 3- 5-8 applications
- 4- 8-10 applications
- 5- >10 applications

Who tell you to apply pesticides when you have a pest problem in your field?

- 1- Pesticide dealer
- 2- Extension specialists from CMDT
- 3- Other

How many applications of which pesticides did the farmer apply this year before the sampling date?

Names:

Number of applications

- 1- 0
- 2- 1-3
- 3- 4-5
- 4- ≥ 6

How far are pesticides mixing areas from a water supply?

- 1- 0-10 m
- 2- 10-50 m
- 3- 50-100m
- 4- 100-500m
- 5- >500m

What types of protective equipment do you use when applying pesticides in your cotton field?
(Please specify)

What type of pesticide application equipments do you use in your field? (Please specify)

Who is in charge of pesticides mixing?

- 1- Yourself, family member or employee
- 2- Professional agricultural consultant
- 3- Extension service
- 4- Other (specify)

Do you use any of the following as a regular precaution when applying pesticides?

- 1- Goggles or face shield
- 2- Rubber gloves
- 3- Rubber boots
- 4- Long sleeve clothing

5- Other (specify)

Do you take into account the wind direction and strength when you apply pesticides?

1- Yes

2- No

7-Pesticide Storage

How are pesticides stored in the farm?

1- Locked in a building

2- Stored in the open

3- Other (please specify)

How far are pesticides stored from a water supply?

1- 0-10 m

2- 10-50 m

3- 50-100m

4- 100-500m

5- >500m

How long are unused pesticides stored in the farm?

1- <=1 year

2- 2-3 years

3- 4-5 years

4- >5 years

Inventory of all pesticides stored at the time of sampling and expiration dates

8-Disposal

Is there any approved pesticide containers disposal procedures that you follow?

1- Yes

2- No

How do farmers get information about containers disposal?

1-Governmental Agencies

2-Suppliers

3-Cooperatives “Associations Villageoises”

4-Other

How does the farmer dispose of empty pesticide containers?

1-Burn

2-Bury

3-Left in the field

4-Recuperate by individuals for reuse purpose

5-Recuperate by extension agents or governmental agents

6- Other (please specify)

What do you do with rinsing solutions?

9-Training

Have you ever received any training on pesticides application techniques?

1- Yes

2- No

Who train you on pesticides application techniques?

- 1- Extension specialists from CMDT
- 2- Other (please specify)

Have you ever received any training on pesticides disposal

- 1- Yes
- 2- No

Who train you on pesticides disposal?

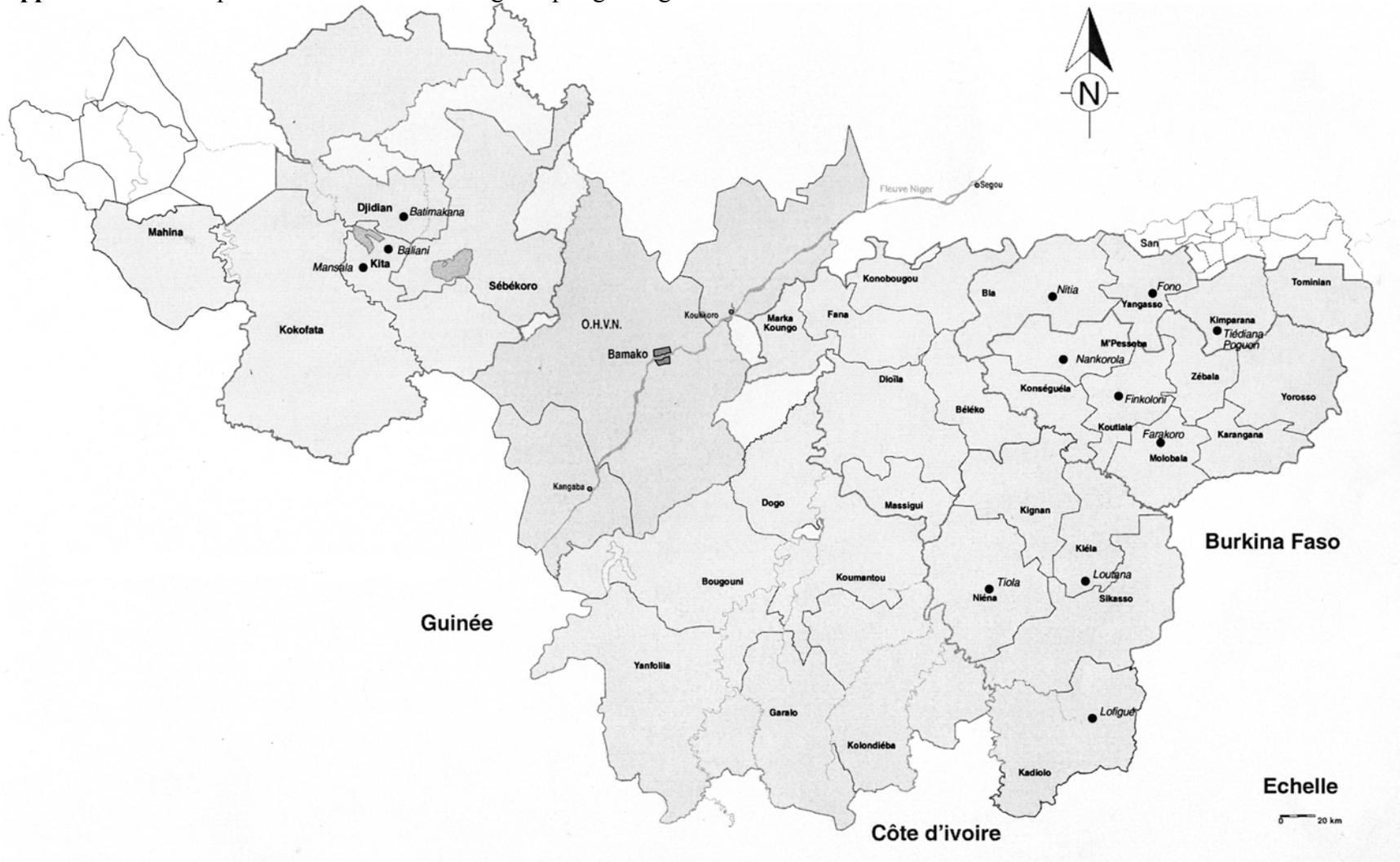
- 1- Extension specialists from CMDT
- 2- Other (please specify)

Appendix III: Maps of sampling sites of cotton growing regions in Mali

Appendix III-i. Map of Mali showing sampling regions.



Appendix III-ii. Map of southern Mali showing sampling villages.



Appendix IV: Analytical Methods

Appendix IV-i. Multi-residue extraction method for soil samples.

Spikes And Recoveries:

Blank 25 g Control Soil.

STANDARDS: As required.

SPIKES: As required.

Review materials safety data sheets for each chemical used in this method.

Materials:

Sand (previously cleaned and checked on the GC)

Sodium sulfate and saturated sodium sulfate

Acetone:hexane (1:1, v/v)

15% methylene chloride in hexane

Column Preparation:

1. Weigh out 25 g of soil into a sample bottle. Add spike at this point.
2. Add 25 g sand. Add 50 g of Sodium Sulfate. Mix. (When necessary, to facilitate mixing, the sample bottle may be placed on a roller or, after manual shaking, allow the sample to stand for about 20 minutes.)
3. Place a small glass wool pledget in the bottom of a 250 mL bulb column. Carefully transfer the sample mixture to the column.
4. Triple rinse the sample flask with small amounts (3 to 5 mL) of hexane each time. Transfer each rinsing to the top of the soil in the bulb column.
5. Elute the column with 250 ml of 1:1 Acetone-Hexane. Try to maintain a flow rate of 3-5 mL/min. Collect the eluate in a 500 mL Erlenmeyer flask.

Extraction:

6. Evaporate sample on rotary evaporator to approximately 100 mL.
7. Transfer sample to a 500 mL separatory funnel. Add 300 mL distilled water and 25 mL saturated sodium sulfate to the separatory funnel.
8. Shake vigorously for 2 minutes. Allow layers to separate for 10 minutes.
9. Drain the aqueous layer (bottom layer) into a beaker and transfer the hexane (top layer) to a 250 mL separatory funnel.
10. Return the aqueous layer to the 500 mL separatory funnel.
11. Re-extract the aqueous layer with 40 mL of 15% methylene chloride in hexane. Shake vigorously for 2 minutes. Allow layers to separate for 10 minutes.
12. Discard the aqueous (bottom) layer and transfer the organic layer (top) to the 250 mL separatory funnel.
13. Add 100 mL distilled water to the combined organic layers. Gently wash the solvent extracts for 30 seconds.
14. Discard the aqueous layer (bottom).

15. Drain the organic layer through a sodium sulfate column into a 250 mL Erlenmeyer flask (ground glass top).
16. Evaporate almost to dryness on rotary evaporator.
17. Rinse down the sides of the flask with 20 mL of hexane. Return flask to rotary evaporator and continue to evaporate sample to approximately 1 mL. Transfer quantitatively (1 to 2 mL each transfer) with a minimum of 10 mL hexane through a small sodium sulfate column into a 15 mL centrifuge tube.
18. Evaporate on N₂ evaporator to 0.5 mL.
19. Re-dilute sample to exactly 2 mL (or suitable volume, as determined by particulate matter and color of the sample) with hexane and vortex.
20. Place tubes in a rack and label the rack with the Source or Project name, "GENERAL EXTRACTION SOIL- READY FOR GC".

GC Parameters:

Agilent GC Model 6890, column RTX-5: 30m x 0.25mm x 0.25 μ m df; oven temperature 90°C for zero minute, 30°C/min to 190°C held for 20 minutes, 20°C/min to 275°C held for 10 min, injector (splitless mode) temperature 250°C; carrier gas (UHP Helium) at a constant flow of 1.1 mL/min; detector (μ ECD U2180) temperature 350°C; make up gas UHP nitrogen at 60 mL/min.

Sources:

Organochlorine Insecticides in Soils and Housedust. Section 11A, pp. 1-8. 1979. Analysis of Pesticide Residues in Human and Environmental Samples, USEPA Health effects research lab, Environ. Tox. Div., Research Triangle Park, NC (April 1998).

Organochlorine and Organophosphorus Insecticides in Bottom Sediments, Section 11 B, pp. 1-6. 1980. Analysis of Pesticide Residues in Human and Environmental Samples, USEPA Health Effects Lab, Environ. Tox. Div., Research Triangle Park, NC.

Appendix IV-ii. Multi-residue extraction method for water samples.

Procedure works well for most chlorinated hydrocarbons, organic phosphates, herbicides (including acid herbicides), and carbamates, with detection on EC Ni₆₃ detector and organophosphates confirmed on flame photometric detector.

Standards: As required.

Spikes: As required.

Review Materials Safety Data Sheets (MSDS) for each chemical used in this method.

General Extraction:

Measure exactly 900 mL of sample. Filter, if necessary, through S&S fast flow filter paper into a 1000 mL graduated cylinder. If sample does not total 900 mL, record the amount of sample (needed for calculation later) and make up to 900 mL with distilled water.

Transfer the sample to a 1000 mL separatory funnel.

Add 5-10 g sodium sulfate (Na_2SO_4) and shake to dissolve. (Granulated Na_2SO_4 that has been ground to a powder will dissolve quicker.).

Add 100 mL methylene chloride. Shake vigorously 2 min. Let separate for 10 min.

Draw methylene chloride (bottom layer) through a Na_2SO_4 column into a 500 mL Erlenmeyer flask.

Repeat extraction two more times with 100 mL methylene chloride. Let separate for 10 min and draw the methylene chloride through the same Na_2SO_4 column into the sample flask.

When both of the methylene chloride layers have been combined, add 5 drops of keeper solution to the sample flask. Evaporate the sample on a rotary evaporator to approximately 5 mL. Add 15-20 mL hexane to the sample flask and continue evaporation to approximately 2 mL. Remove sample from rotary evaporator and immediately rinse down the sides of the flask with hexane.

Transfer quantitatively with hexane (4 or 5 times with approx. 2 mL solvent each time) into a calibrated centrifuge tube.

Evaporate to 0.5 mL on a nitrogen evaporator. This step is necessary to remove any traces of methylene chloride.

(If further cleanup is necessary, see source method for preparation of silica gel column.).

Dilute samples to 2 mL with hexane. Vortex.

Label rack, or specific centrifuge tubes, "GENERAL EXTRACTION-READY FOR GC," when finished. Store in refrigerator until ready to analyze.

SOURCE:"The sampling and analysis of water for pesticides". Section 10 A, pp. 1-26 and section 10 B, pp. 1-6. Manual of Analytical Methods for the Analysis of Pesticides in Human and Environmental Samples, (Randall R. Watts, Ed.). EPA-600/8-80-038. 1980.

Appendix IV-iii. Solvents distillation standard operating procedures.

SOP 4.18 Solvent Stills (Revision #1).

Purpose: To ensure the proper operation of stills in the laboratory.

Scope: Pesticide Residue Laboratory conducting studies under the SOPs, including the IR-4 Minor Use Pesticide Program.

Procedures:

1. Set up stills for distillation.
 - a. Wear safety glasses. Turn on hood fan and light.
 - b. Add no more than eight liters (8L) of solvent to be distilled to a twelve liter (12L) boiling flask.
 - c. Add boiling chips to the boiling flask.
 - d. When distilling hexane, add a small piece of sodium metal, unless an undeteriorated piece is already present. Sodium metal is stored under oil. Keeping the sodium under oil, use a scalpel to carefully cut a cube of sodium approximately 0.5 inches on a side. Use forceps to transfer the

sodium to the hexane in the boiling flask. Sodium metal should not be exposed to water due to the reactive (explosive) properties of the metal.

- e. Connect the condenser to the boiling flask using an adaptor and slowly turn on the cold water supply to the condenser.
 - f. Plug AC power supply (rheostat) into electrical outlet and turn on power switch.
 - g. Lower the hood sash to within six inches of the fully closed position.
 - h. Collect at least 100 mL of distilled solvent in a graduated cylinder before connecting the condenser to the collection flask. Discard the collected solvent following SOP 11.1.
 - i. Monitor the temperature to ensure that it does not exceed the boiling point of the solvent being distilled. If this occurs, the solvent must be redistilled.
2. Shut-down of stills after distillation.
- a. Turn off rheostat power switch.
 - b. Unplug rheostat from the electrical outlet. Always turn off the power before unplugging the unit to avoid sparks which could result in a fire or explosion.
 - c. Turn off condenser water, hood fan, and hood light.
 - d. Distilled solvents are stored in four liter (4 L) bottles. Before use, the bottles should be rinsed twice with the redistilled solvent. The solvent used for rinsing is considered waste and should be disposed of appropriately. See SOP 11.1.
3. Evaluation of purity of laboratory distilled solvents.
- a. Transfer approximately 150 mL of the distilled solvent to an Erlenmeyer flask and evaporate to dryness using a rotary evaporator according to SOP 4.17.
 - b. Rinse the sides of the dry Erlenmeyer flask with approximately 3 mL of previously tested hexane.
 - c. Using a gas-liquid chromatograph equipped with an electron capture detector, establish the appropriate sensitivity by injecting a concentration of 0.02 ng/ μ L (or less) hexachlorobenzene (HCB). The volume to inject should be 1 μ L for capillary columns and 2 μ L for packed columns. Adjust the attenuation to achieve at least a 75% full-scale deflection of the HCB peak.
 - d. Inject 5 L of the sample (step b). If there are peaks larger than 20% full-scale deflection using the conditions established in step c, the solvent is rejected.
 - e. Graphs from these tests are kept in the current Solvent Check Folder in 352 Litton Reaves Hall. At the end of the calendar year, these graphs are transferred to files and stored.

4. When necessary, dismantle and clean the distilling apparatus following appropriate glassware cleaning procedures. Refer to SOP 6.3.

Appendix IV-iv. Cleanup method of sand for soil extraction.

Summary:

Sand is “washed” with distilled water, acetone, methylene chloride, and hexane to remove organic materials that may interfere with GC analysis following soil extraction.

Safety Precautions:

Review Materials Safety Data Sheets (MSDS) For each chemical used in this method.

Preparation:

1. Purchase play sand (50 lbs) at Lowe’s Hardware for about \$3.00.
2. Assign a unique number to the sand in the chemical inventory logbook.
3. Transfer the sand to clean, glass bottles and add a chemical label with the assigned number to each bottle. Add a second label that says, “Not Clean.”

Sand Cleanup:

1. Partially fill a small plastic dishwashing pan with distilled water.
2. Transfer sand to a Tyler Standard sieve #00 or other fine mesh sieve.
3. Place sieve in water and stir with hands to rinse. Replace distilled water as necessary until the rinse water is clear. Multiple rinsings may be necessary.
4. Using funnel, transfer sand to glass bottle with green plastic mesh sleeve to continue cleanup steps. This “sleeve” allows the bottle to fit in clamps on the shaker table.
5. Add 250 mL lab-distilled acetone to bottle. Shake on table for about 30 minutes.
6. Decant acetone into waste hood container, record amount, and repeat one more time.
7. Add 250 mL methylene chloride to sand in bottle and shake on table for about 30 minutes. Decant methylene chloride into waste hood container, record amount, and repeat one more time.
8. Add 250 mL hexane to sand in bottle and shake on table for about 30 minutes as before. When finished, collect hexane by draining through sodium sulfate column into a 500 mL Erlenmeyer flask.
9. Evaporate the hexane to dryness using rotary evaporator.
10. Rinse down the sides of the flask with hexane and quantitatively transfer to a centrifuge tube up to about 10 mLs.
11. Evaporate to 2 mLs using nitrogen evaporator.

GC Check:

1. Check sand “extract” on GC using similar parameters that will be used during analysis of

soil extracts.

2. Evaluate chromatograms to determine if the cleanup steps were adequate. If yes, transfer the cleaned sand to a tray and dry in oven. When dry, transfer sand to clean, dry bottle with the chemical label and mark as, "Lab Sand- CLEAN." If no, continue with additional rinse steps until the sand "extract" chromatogram is satisfactory.

Appendix V: Pesticides retention time, method detection limit and recovery

Appendix V.i. Retention time of the pesticides on an RTX-5 capillary column.

Compound	Retention time ¹ (minutes)	Method Quantification Limit (ng/g)	% Recovery \pm SD ²
α -BHC	8.66	6.4	54 \pm 13
β -BHC	9.65	6.4	43 \pm 8
γ -BHC (lindane)	9.84	6.4	42 \pm 10
δ -BHC	10.87	6.4	95 \pm 21
Heptachlor	13.42	6.4	27 \pm 8
Aldrin	15.81	6.4	63 \pm 12
Heptachlor epoxide	19.51	6.4	49 \pm 11
γ -chlordane	22.21	6.4	52 \pm 9
Endosulfan I	23.72	6.4	52 \pm 10
α -chlordane	24.06	6.4	47 \pm 7
Dieldrin	25.43	6.4	69 \pm 37
p,p-DDE	25.43	6.4	40 \pm 9
Endrin	26.32	6.4	20 \pm 7
Endosulfan II	26.69	6.4	46 \pm 10
p,p-DDD	26.94	6.4	71 \pm 21
Endrin aldehyde	27.19	6.4	62 \pm 12
Endosulfan sulfate	27.78	6.4	72 \pm 29
p,p-DDT	27.87	6.4	99 \pm 5
Endrin ketone	28.95	6.4	37 \pm 2
Methoxychlor	29.29	6.4	32 \pm 23
Dichlorvos	4.19	40	71 \pm 18
Mevinphos	5.04	40	57 \pm 26
Demeton-o	6.14	40	45 \pm 25
Ethoprop	7.39	40	103 \pm 39
Naled	7.81	40	110 \pm 44
Phorate	8.39	40	168 \pm 74
Diazinon	10.16	40	90 \pm 22
Disulfoton	10.54	40	46 \pm 28
Methyl parathion	12.89	40	110 \pm 74
Fenthion	13.80	40	80 \pm 30
Ronnel	13.80	40	80 \pm 30
Chlorpyrifos	16.40	40	93 \pm 41
Trichloronate	17.54	40	77 \pm 25

Appendix V.i. (Continuation) Retention time of the pesticides on an RTX-5 capillary column.

Compound	Retention time ¹ (minutes)	Method Quantification Limit (ng/g)	% Recovery \pm SD ²
Stirofos	24.01	40	89
Tokuthion	25.14	40	90 \pm 26
Merphos	25.47	40	82 \pm 41
Fensulfothion	26.83	40	125 \pm 71
Sulprofos	27.40	40	64 \pm 33
Azinphos methyl	30.11	40	173 \pm 84
Coumaphos	32.30	40	160 \pm 137
TEPP	7.29	40	205
Sulfotepp	7.91	40	648
Monocrotophos	7.99	40	507
Dimethoate	8.94	40	53
Malathion	15.4	40	209
Parathion	16.41	40	154
EPN	29.11	40	172
Atrazine	9.15	400	51 \pm 4
Profenofos	25.79	8	87 \pm 25
Cypermethrin	33.96 ³	500	112 \pm 12

¹GC parameters: Agilent GC Model 6890, column RTX-5: 30m x 0.25mm x 0.25 μ m df; oven temperature 90°C for zero minute, 30°C/min to 190°C held for 20 minutes, 20°C/min to 275°C held for 10 min, injector (splitless mode) temperature 250°C; carrier gas (UHP Helium) at a constant flow of 1.1 mL/min; detector (μ ECD U2180) temperature 350°C; make up gas UHP nitrogen at 60 mL/min.

²Mean percent recovery \pm Standard Deviation of the mean based on n = 3 replicates for all pesticides but n = 1 replicate for stirofos, TEPP, sulfotepp, monocrotophos, dimethoate, malathion, parathion and EPN.

³Retention reported is for the first peak of cypermethrin.

Appendix VI: Physico-chemical characteristics and sampling locations of soil samples from four cotton growing regions in Mali

Appendix VI-i. Soil samples: physico-chemical characteristics, geographic coordinates and current crop (Kita region).

Samples #	Crops	Geographic coordinates (UTM)		Texture	Percent Organic matter	Percent Clay	pH
		Longitude	Latitude				
Kibi01	Bushes and forage	29 452312 E	1451887 N	Silt	1.1	5.80	5.4
Kibi02	Nothing	29 452275 E	1452338 N	Sandy-loam	0.9	13.90	6.2
Kibi03	Cotton	29 452520 E	1452519 N	Sandy-loam	1.0	12.20	6.3
Kibi04	Sorghum	29 451908 E	1451130 N	Sandy-loam	0.9	14.80	6.3
Kibi05	Cotton	29 451545 E	1450511 N	Sandy-loam	0.6	9.80	7.1
Kima01	Bushes and forage	29 428559 E	1443575 N	Loam	1.7	14.90	6.6
Kima02	Cotton	29 429444 E	1439404 N	Loam	1.1	12.00	6.7
Kima03	Millet	29 429269 E	1439454 N	Sandy-loam	0.9	10.50	5.9
Kima04	Cotton	29 428522 E	1443536 N	Sandy-loam	1.2	12.90	6.1
Kima05	Cotton	29 430410 E	1440462 N	Loam	1.3	16.20	6.5
Kiba01	Bushes and forage	29 457589 E	1466590 N	Sandy-loam	1.1	9.60	5.9
Kiba02	Sorghum	29 457511 E	1466503 N	Sandy-loam	0.7	8.20	5.5
Kiba03	Cotton	29 457345 E	1466655 N	Sandy-loam	0.6	8.20	6.1
Kiba04	Peanuts	29 457113 E	1466258 N	Sandy-loam	0.9	7.90	5.6
Kiba05	Sorghum	29 457261 E	1466241 N	Sandy-loam	1.1	9.40	5.8

Appendix VI-ii. Soil samples: physico-chemical characteristics, geographic coordinates and current crop (Sikasso region).

Samples #	Crops	Geographic coordinates (UTM)		Texture	Percent Organic matter	Percent Clay	pH
		Longitude	Latitude				
Silo01	Bushes and forage	30 206906 E	1177876 N	Sandy-loam	2	12.60	5.3
Silo02	Cotton	30 204275 E	1177339 N	Loam-sandy	1.2	4.50	5.8
Silo03	Cotton	30 207066 E	1177929 N	Sandy-loam	1.3	11.50	5.3
Silo04	Corn	30 204902 E	1180396 N	Sandy-loam	1.5	5.20	5.8
Silo05	Corn	30 204004 E	1177374 N	Loam-sandy	1.1	5.60	6.1
Siti01	Bushes and forage	29 794039 E	1260684 N	Sandy-loam	1.1	8.50	5.7
Siti02	Cotton	29 794099 E	1260934 N	Sandy-loam	1	8.70	6.1
Siti03	Sorghum	29 794263 E	1261016 N	Sandy-loam	0.7	6.10	6.1
Siti04	Cotton	29 794594 E	1260953 N	Loam-sandy	0.6	6.50	5.6
Siti05	Corn	29 794848 E	1260917 N	Sandy-loam	1.1	7.80	5.8
Sila01	Bushes and forage	30 209634 E	1285359 N	Loam	1.2	13.70	5.5
Sila02	Cotton	30 210087 E	1284256 N	Sandy-loam	0.8	9.20	6.0
Sila03	Corn	30 209892 E	1284653 N	Sandy-loam	0.9	12.50	5.3
Sila04	Cotton	30 209756 E	1285332 N	Sandy-loam	0.9	13.20	6.4
Sila05	Cotton	30 209345 E	1285591 N	Loam	1	13.70	5.8

Appendix VI-iii. Soil samples: physico-chemical characteristics, geographic coordinates and current crop (Koutiala region).

Samples	Crops	Geographic coordinates (UTM)		Texture	Percent Organic matter	Percent Clay	pH
		Longitude	Latitude				
Kofi01	Bushes and forage	30 227604 E	1354796 N	Sandy-loam	1.3	9.20	5.2
Kofi02	Corn	30 228712 E	1356729 N	Loam-sandy	0.3	5.40	5.7
Kofi03	Cotton	30 230036 E	1355202 N	Loam-sandy	0.2	5.60	5.7
Kofi04	Cotton	30 227999 E	1355613 N	Sandy-loam	0.5	7.60	5.8
Kofi05	Cotton	30 227977 E	1355710 N	Loam-sandy	0.3	5.60	6.2
Kona01	Forage	30 198512 E	1401355 N	Sandy-loam	0.3	8.60	5.5
Kona02	Sorghum	30 199491 E	1401476 N	Loam-sandy	0.2	6.10	5.6
Kona03	Corn	30 198515 E	1401484 N	Sandy-loam	0.3	8.20	6.1
Kona04	Cotton	30 198781 E	1401355 N	Loam-sandy	0.3	0.07	5.7
Kona05	Millet	30 199150 E	1401377 N	Loam-sandy	0.3	6.40	5.2
Kofa01	Bushes and forage	30 246649 E	1351908 N	Loam-sandy	0.5	7.30	5.3
Kofa02	Cotton	30 247017 E	1352386 N	Loam-sandy	0.5	6.70	5.2
Kofa03	Millet	30 247020 E	1352354 N	Loam-sandy	0.4	6.70	5.7
Kofa04	Corn	30 246979 E	1352154 N	Loam-sandy	0.4	6.90	5.6
Kofa05	Cotton	30 245954 E	1351195 N	Sandy-loam	1	7.80	6.2

Appendix VI-iv. Soil samples: physico-chemical characteristics, geographic coordinates and current crop (San region).

Samples	Crops	Geographic coordinates (UTM)		Texture	Percent Organic matter	Percent Clay	pH
		Longitude	Latitude				
Sati01	Bushes and forage	30 292519 E	1411546 N	Sandy-loam	0.8	14.90	5.4
Sati02	Corn	30 293215 E	1412849 N	Sandy-loam	0.4	9.00	6.4
Sati03	Corn	30 293161 E	1412812 N	Sandy-loam	0.8	7.10	7.2
Sati04	Millet	30 292887 E	1412609 N	Sandy-loam	0.6	8.40	6.8
Sati05	Cotton	30 292893 E	1412539 N	Sandy-loam	0.9	9.30	6.4
Safo01	Bushes and forage	30 241970 E	1436380 N	Loam	1.5	26.50	5.5
Safo02	Cotton	30 243960 E	1440591 N	Sandy-loam	0.3	7.10	6.6
Safo03	Millet	30 244061 E	1440727 N	Sandy-loam	0.5	7.30	6.6
Safo04	Corn	30 243987 E	1440769 N	Sandy-loam	0.3	6.70	6.9
Safo05	Cotton	30 241953 E	1436852 N	Loam-sandy	0.3	6.10	6.7
Sagn01	Bushes	30 199000 E	1438424 N	Sandy-loam	0.5	9.60	5.0
Sagn02	Corn	30 200350 E	1437220 N	Loam-sandy	0.3	5.00	6.3
Sagn03	Cotton	30 200388 E	1437242 N	Loam-sandy	0.5	4.00	5.8
Sagn04	Millet	30 200223 E	1437190 N	Loam-sandy	0.3	4.90	6.1
Sagn05	Cotton	30 200166 E	1437113 N	Loam-sandy	0.3	3.50	5.8

Appendix VI-v. Water samples: geographic coordinates, pH and temperature.

Sample #	Geographic coordinates (UTM)		pH ¹	Temperature °C
	Longitude	Latitude		
Well01	30 229791 E	1355461 N	5.3	30°6
Well02	30 228094 E	1355819 N	5.37	30°8
Well03	30 227595 E	1354609 N	5.39	31°6
Well04	30 199937 E	1401394 N	5.96	32°5
Well05	30 200288 E	1401630 N	4.89	31°8
Well07	30 245941 E	1351287 N	6.53	30°8
Bani River	30 185342 E	1462279 N	7.18	29°4
Kouoro River ²	30 206899 E	1330400 N	6.5	Not measured

¹pH measured with pH meter at all sites but Kouoro.

²pH measurement was completed with strips Panpeha™ paper strips from Sigma-Aldrich. Water temperature not measured at this site (pH meter out of order).

Appendix VII: Residues detected in soil samples from four cotton growing regions of Mali

Appendix VII-i. Residues detected in soil samples from the Kita region.

Field# →	Kibi01	Kibi02	Kibi03	Kibi04	Kibi05	Kima01	Kima02	Kima03	Kima04	Kima05	Kiba01	Kiba02	Kiba03	Kiba04	Kiba05
Pesticide detected	all values reported in ng/g dry weight														
Endosulfan I	ND ¹	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	<MQL	ND
Endosulfan II	ND	<MQL ²	<MQL	<MQL	ND	<MQL	<MQL	<MQL							
Endosulfan sulfate	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
p,p-DDD	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
p,p-DDE	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
p,p-DDT	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Profenofos	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

¹ND = Not Detected.

²Method Quantification Limit (MQL) = 6.4 ng/g dry weight for all pesticides detected except for profenofos which quantification limit is 8 ng/g.

Appendix VII-ii. Residues detected in soil samples from the Sikasso region.

Field# →	Silo01	Silo02	Silo03	Silo04	Silo05	Siti01	Siti02	Siti03	Siti04	Siti05	Sila01	Sila02	Sila03	Sila04	Sila05
Pesticide detected	all values reported in ng/g dry weight														
Endosulfan I	ND	<MQL	<MQL	<MQL	ND	ND	ND	ND	<MQL	ND	ND	<MQL	ND	<MQL	ND
Endosulfan II	<MQL	<MQL	<MQL	<MQL	<MQL	ND	<MQL	<MQL	17	8	<MQL	18	<MQL	26.4	<MQL
Endosulfan sulfate	ND	17	<MQL	31	ND	ND	<MQL	<MQL	28	18	ND	49	74	40.8	<MQL
p,p-DDD	ND	<MQL	ND	<MQL	<MQL	ND	<MQL	ND	ND	<MQL	ND	ND	ND	ND	ND
p,p-DDE	ND	<MQL	ND	<MQL	20	ND	<MQL	ND	ND	<MQL	ND	<MQL	<MQL	<MQL	<MQL
p,p-DDT	ND	ND	ND	ND	<MQL	ND									
Profenofos	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

¹ND = Not Detected.

²Method Quantification Limit (MQL) = 6.4 ng/g dry weight for all pesticides detected except for profenofos which quantification limit is 8 ng/g.

Appendix VII-iii. Residues detected in soil samples from the Koutiala region.

Field# →	Kofi01	Kofi02	Kofi03	Kofi04	Kofi05	Kona01	Kona02	Kona03	Kona04	Kona05	Kofa01	Kofa02	Kofa03	Kofa04	Kofa05
Pesticide detected	all values reported in ng/g dry weight														
Endosulfan I	<MQL	ND	<MQL	ND	ND	<MQL	ND	ND	10						
Endosulfan II	<MQL	<MQL	10	<MQL	ND	10	ND	<MQL	37						
Endosulfan sulfate	ND	ND	ND	ND	ND	ND	9	14	14	<MQL	ND	14	<MQL	<MQL	49
p,p-DDD	ND	<MQL	ND	<MQL	ND	<MQL	<MQL								
p,p-DDE	<MQL	121	<MQL	ND	<MQL	11									
p,p-DDT	ND	11	ND												
Profenofos	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

¹ND = Not Detected.

²Method Quantification Limit (MQL) = 6.4 ng/g dry weight for all pesticides detected except for profenofos which quantification limit is 8 ng/g.

Appendix VII-iv. Residues detected in soil samples from the San region.

Field# →	Sati01	Sati02	Sati03	Sati04	Sati05	Safo01	Safo02	Safo03	Safo04	Safo05	Sagn01	Sagn02	Sagn03	Sagn04	Sagn05
Pesticide detected	all values reported in ng/g dry weight														
Endosulfan I	ND	ND	ND	ND	ND	ND	<MQL	ND	ND	ND	ND	ND	ND	<MQL	<MQL
Endosulfan II	ND	ND	ND	ND	<MQL	ND	<MQL	ND	ND	<MQL	ND	<MQL	ND	<MQL	<MQL
Endosulfan sulfate	ND	ND	ND	ND	<MQL	ND	<MQL	ND	ND	<MQL	ND	<MQL	<MQL	ND	<MQL
p,p-DDD	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
p,p-DDE	ND	<MQL	<MQL	<MQL	<MQL	ND	ND	ND	<MQL	ND	ND	<MQL	<MQL	ND	ND
p,p-DDT	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Profenofos	ND	<MQL	<MQL	ND	<MQL	ND	<MQL								

¹ND = Not Detected.

²Method Quantification Limit (MQL) = 6.4 ng/g dry weight for all pesticides detected except for profenofos which quantification limit is 8 ng/g.

Appendix VII-v. Residues detected in water samples.

Field# →	Well 01 Finkoloni	Well 02 Finkoloni	Well 03 Finkoloni	Well 04 Nangorola	Well 05 Nangorola	Well 07 Farakoro	River at Bani Bridge	River at Kouoro Bridge
Pesticide detected	all values reported in parts per billion (ppb)							
gamma-BHC	ND ¹	ND	ND	ND	ND	ND	ND	<MQL
endosulfan I	<MQL ²	<MQL	<MQL	<MQL	<MQL	<MQL	ND	ND
endosulfan II	<MQL	<MQL	ND	ND	<MQL	<MQL	<MQL	ND
endosulfan sulfate	<MQL	ND	ND	ND	ND	<MQL	<MQL	<MQL
dieldrin	ND	ND	ND	ND	<MQL	ND	ND	ND
p,p-DDD	ND	ND	ND	<MQL	<MQL	ND	<MQL	ND
p,p-DDE	ND	ND	<MQL	<MQL	<MQL	<MQL	<MQL	<MQL
p,p-DDT	ND	ND	ND	ND	ND	ND	ND	ND
atrazine	ND	ND	ND	ND	ND	ND	<MQL	1.4

¹ND = Not Detected.

²Method Quantification Limit (MQL) = 0.1 ppb for all pesticides detected except for atrazine which quantification limit is 1.1 ppb.

Appendix VII-vi. Pesticides applied during the past ten years and residues detected in soil samples from the Kita region.

Sample #	Pesticides applied during the past ten years	Pesticides detected in samples
Kibi 01	None	ND
Kibi 02	cypermethrin, profenofos, dimethoate, endosulfan	endosulfan II ¹
Kibi 03	Unknown	endosulfan II ¹
Kibi 04	cypermethrin, profenofos, dimethoate endosulfan	endosulfan II ¹
Kibi 05	Unknown	ND ²
Kima 01	None	ND
Kima 02	Unknown	ND
Kima 03	atrazine, endosulfan, cypermethrin	ND
Kima 04	endosulfan, cypermethrin	ND
Kima 05	Unknown	ND
Kiba 01	None	ND
Kiba 02	endosulfan, cypermethrin	ND
Kiba 03	Unknown	endosulfan II ¹
Kiba 04	endosulfan, cypermethrin	endosulfan I ¹ , endosulfan II ¹
Kiba 05	Unknown	endosulfan II ¹

¹Pesticide residues detected below the quantification limit.

²Residues Not Detected.

Appendix VII-vii. Pesticides applied during the past ten years and residues detected in soil samples from the Sikasso region.

Sample #	Pesticides applied during the past ten years	Pesticides detected in samples
Silo 01	None	endosulfan II ¹
Silo 02	endosulfan	endosulfan I ¹ , endosulfan II ¹ , p,p-DDD ¹ , p,p-DDE ¹ endosulfan sulfate ²
Silo 03	Unknown	endosulfan I ¹ , endosulfan II ¹ , endosulfan sulfate ¹
Silo 04	endosulfan, cypermethrin, monocrotophos	endosulfan I ¹ , endosulfan II ¹ , p,p-DDD ¹ , p,p-DDE ¹ endosulfan sulfate ²
Silo 05	endosulfan, cypermethrin, monocrotophos	endosulfan II ¹ , p,p-DDD ¹ , p,p-DDE ² , p,p-DDT ¹
Siti 01	None	ND ³
Siti 02	endosulfan, cypermethrin	endosulfan II ¹ , p,p-DDD ¹ , p,p-DDE ¹ , endosulfan sulfate ¹
Siti 03	Unknown	endosulfan II ¹ , endosulfan sulfate ¹
Siti 04	endosulfan, cypermethrin	endosulfan I ¹ , endosulfan II ² , endosulfan sulfate ² endosulfan II ² , p,p-DDD ¹ , p,p-DDE ¹ , endosulfan sulfate ²
Siti 05	Unknown	endosulfan II ² , p,p-DDD ¹ , p,p-DDE ¹ , endosulfan sulfate ²
Sila 01	None	endosulfan II ¹
Sila 02	endosulfan, cypermethrin, monocrotophos, profenofos	endosulfan I ¹ , endosulfan II ² , p,p-DDE ¹ endosulfan sulfate ²
Sila 03	atrazine, endosulfan, cypermethrin, monocrotophos, profenofos	endosulfan II ¹ , p,p-DDE ¹ , endosulfan sulfate ²
Sila 04	endosulfan, cypermethrin,	endosulfan I ¹ , endosulfan II ² , p,p-DDE ¹ , endosulfan sulfate ²
Sila 05	Unknown	endosulfan II ¹ , p,p-DDE ¹ , endosulfan sulfate ¹

¹Pesticide residues detected below the quantification limit.

²Pesticide residues detected above the quantification limit.

³Residues Not Detected.

Appendix VII-viii. Pesticides applied during the past ten years and residues detected in soil samples from the Koutiala region.

Sample #	Pesticides applied during the past ten years	Pesticides detected in samples
Kofi 01	None	endosulfan I ¹ , endosulfan II ¹ , p,p-DDE ¹
Kofi 02	Unknown	endosulfan II ¹ , p,p-DDD ¹ , p,p-DDE ² , p,p-DDT ²
Kofi 03	cypermethrin, endosulfan	endosulfan I ¹ , endosulfan II ² , p,p-DDE ¹
Kofi 04	Unknown	endosulfan I ¹ , endosulfan II ¹ , p,p-DDD ¹ , p,p-DDE ¹
Kofi 05	Unknown	endosulfan I ¹ , endosulfan II ¹ , p,p-DDD ¹ , p,p-DDE ¹
Kona 01	endosulfan, cypermethrin, chlorpyrifos, profenofos dimethoate, monocrotophos	endosulfan I ¹ , endosulfan II ¹ , p,p-DDD ¹ , p,p-DDE ²
Kona 02	endosulfan, cypermethrin, chlorpyrifos, profenofos, dimethoate	endosulfan I ¹ , endosulfan II ¹ , p,p-DDD ¹ , p,p-DDE ¹ endosulfan sulfate ²
Kona 03	endosulfan, cypermethrin, chlorpyrifos, profenofos, dimethoate	endosulfan I ¹ , endosulfan II ¹ , p,p-DDD ¹ , p,p-DDE ¹ endosulfan sulfate ²
Kona 04	endosulfan, cypermethrin, chlorpyrifos, profenofos, dimethoate, monocrotophos	endosulfan I ¹ , endosulfan II ¹ , p,p-DDD ¹ , p,p-DDE ¹ endosulfan sulfate ²
Kona 05	endosulfan, cypermethrin, chlorpyrifos, profenofos, dimethoate	endosulfan II ¹ , p,p-DDD ¹ , p,p-DDE ¹ , endosulfan sulfate ¹
Kofa 01	Unknown, no pesticide applied since 8 years	p,p-DDD ¹ , p,p-DDE ¹
Kofa 02	endosulfan, cypermethrin, profenofos	endosulfan I ¹ , endosulfan II ² , p,p-DDD ¹ , p,p-DDE ¹ endosulfan sulfate ²
Kofa 03	Unknown	endosulfan sulfate ¹
Kofa 04	Unknown	endosulfan II ¹ , p,p-DDD ¹ , p,p-DDE ¹ , endosulfan sulfate ¹
Kofa 05	endosulfan, cypermethrin, profenofos	endosulfan I ² , endosulfan II ² , p,p-DDD ¹ , p,p-DDE ² endosulfan sulfate ²

¹Residues detected below the quantification limit.

²Residues detected above the quantification limit.

Appendix VII-ix. Pesticides applied during the past ten years and residues detected in soil samples from the San region.

Sample #	Pesticides applied during the past ten years	Pesticides detected in samples
Sati 01	None	ND
Sati 02	Unknown	p,p-DDE ¹ , profenofos
Sati 03	Unknown	p,p-DDE ¹ , profenofos
Sati 04	Unknown	p,p-DDE ¹
Sati 05	Unknown	p,p-DDE ¹ , endosulfan II ¹ , endosulfan sulfate ¹ , profenofos
Safo 01	None	ND ²
Safo 02	Unknown	endosulfan I ¹ , endosulfan II ¹ , endosulfan sulfate ¹
Safo 03	Unknown	ND
Safo 04	Unknown	p,p-DDE ¹
Safo 05	endosulfan, profenofos, cypermethrin, chlorpyrifos	endosulfan II ¹ , endosulfan sulfate ¹
Sagn 01	None	ND
Sagn 02	Unknown	p,p-DDE ¹ , endosulfan II ¹ , endosulfan sulfate ¹
Sagn 03	cypermethrin, endosulfan, profenofos	p,p-DDE ¹ , endosulfan sulfate ¹
Sagn 04	Unknown	endosulfan I ¹ , endosulfan II ¹
Sagn 05	Unknown	endosulfan I ¹ , endosulfan II ¹ , endosulfan sulfate ¹ , profenofos

¹Pesticide residues detected below the quantification limit.

²Residues Not Detected.

Appendix VIII: List of acronyms

BNDA	Banque Nationale de Développement Agricole/National Bank for Agricultural Development
CILSS	Comité Inter-états de Lutte contre la Sécheresse dans le Sahel/Inter-governmental Permanent Committee to combat of Drought in the Sahel
CFDT	Compagnie Française pour le Développement des Textiles / The French Company for Textile Development
CMDT	Compagnie Malienne pour le Développement des textiles/ The Malian Company for Textile Development
CVL	Central Veterinary Laboratory
DGRC	Direction Générale de la Réglementation et du Contrôle
DNA	Direction Nationale de l'Agriculture
DNACPN	Direction Nationale de l'Assainissement et du Contrôle des Pollutions et des Nuisances
DNAMR	Direction Nationale de l'Appui au Monde Rural
DNH	Direction Nationale de l'Hydraulique
ETL	Environmental Toxicology Laboratory
FAO	Food and Agriculture Organization of the United Nations
IER	Institut d'Economie Rurale
IPM	Integrated Pest Management
LCV	Laboratoire Central Vétérinaire (same as Central Veterinary Laboratory)
LEC	Lutte Etagée Ciblée
MCL	Maximum Contaminant Level
MDL	Method Detection Limit
MQL	Method Quantification Limit
PRL	Pesticide Residues Laboratory
OHVN	Opération Haute Vallée du Niger
USDA	United States Department of Agriculture
USAID	United States Agency for International Development
USEPA	United States Environmental Protection Agency
WHO	World Health Organization

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