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Pesticides Occurrence in an Alfisol of Sudano-Sahelian Agricultural Watershed (Korokoro, Mali)

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Abstract
Soil contamination by pesticides (organochlorine, organophosphates and pyrethroids) has been studied in the agricultural watershed (60.6 km^2) of Korokoro in Mali. Farmers of this watershed produce cotton and cereals (sorghum, maize, millet). Soil samples (0-20 cm) of an alfisol used for cotton cropping were collected at the end of the cropping seasons 2010 and 2011. Samples were analyzed by gas chromatography and mass spectrometer for quantifying the main pesticides (profenofos, acetamiprid, atrazine and cypermethrin) frequently used in the watershed and others organochlorine pesticides (DDT, endosulfan and HCH) that could be still detected. The results showed that soils were contaminated by DDT and its metabolites (0.1 to 3.5 $\mu g.kg^{-1}$) due to past agricultural uses for African migratory locust control while those of endosulfan sulfate (detection limit to 4.2 $\mu g.kg^{-1}$) and cypermethrin (2.5 to 6.2 $\mu g.kg^{-1}$) were due to their actual application on cotton. According to mass balances calculation cypermethrin residues are stocked in the soil compartment of the watershed after its application on cotton. This accumulation was evaluated at 13 ± 0.4% of applied quantities.
***Keywords**: contamination, Korokoro Watershed, pesticides, alfisol, Mali*

I. Introduction

Climatic conditions and pest pressure prevailing in Sub-Saharan Africa agriculture can justify the intensive use of pesticides in cotton cropping [1]. Pesticides are generally used to control parasitic infestation and to ensure good yields. In Mali, 80% of pesticides used in cotton cultivation are insecticides belonging mainly to families of organochlorines (endosulfan), organophosphates (profenofos, malathion), pyrethroids (cypermethrin) and neonicotinoids (acetamiprid) [2]. Among this group, organochlorines are persistent organic pollutants (POPs) which have been banned since 1970s throughout the world for agricultural use according to their toxicity, persistence in environment, low biodegradability, bioaccumulation and their endocrine action [3, 4]. However, their use continues in most developing countries in West Africa including Mali, due to absence of appropriate national regulations [5]. A better example in West Africa is endosulfan which was voluntarily removed in cotton production before 1980s and replaced by pyrethroïds but it was reintroduced since 1998 in Mali, Benin, Senegal, Burkina Faso and Cameroon due to resistance developed by pests (e.g. *Helicoverpaarmigera*) [6, 7]. It is known that intensive use of these pesticides in agriculture can have adverse health effects on farmers where good practices (application rates, frequency of treatment etc.) are rarely respected [8, 9, 10]. Following pesticides applications on crops sometimes, it is 0.1% of amount applied effectively reaches the pest [11], the rest (99.9%) is degraded or enters in soil, air and water through runoff, infiltration and volatilization and contaminates thus soils, sediments, surface water, groundwater and air [12, 13]. In Mali cotton zone, β-endosulfan was detected in soil samples at 65% for maximum level of 37 $\mu g.kg^{-1}$ [14]. According to some authors, endosulfan agricultural use is the source of soils contamination in some African countries as in Togo, Benin, Burkina Faso and Tanzania [15, 16, 17, 18]. Others contaminated soils by endosulfan and its degradation product (endosulfan sulfate) were also mentioned through many studies at different levels [19, 20, 21]. In general, Solid matrices contamination (soil and sediment) is linked to agricultural land use [22, 23]. In this context, soil compartment contamination by pesticides and their residues need today more better attention in West Africa and Mali in particular. The objective of this study is to assess the state of soil contamination of the small agricultural Korokoro watershed (a cotton production one) by organochlorine pesticides, organophosphates and pyrethroids.

II. Materials and methods

2.1 Study area

Korokoro watershed (60.6 km^2) is located between 12°42'N and 12°50'N and 7°22'W and 7°28'W in Koulikoro region on the right bank of Niger River at 70 km from Bamako **(Fig.1).** It is occupied by 10,000 inhabitants spread among four villages or farming hamlets (Kodalabougou, Chonikoro, Sido and Fiéna). In general, the watershed relief is dominated by sandstones hills (500 m), small cuirassed hills (300-400 m), glacis (200 m) and depressions. The climate is Sudano-Sahelian one, characterized by a long dry season (November to May) and a short rainy season (June to October). Annual rainfall is variable (from 700 to 800 mm) according years. Temperatures undergo little fluctuation.

However, they are high in March and May (36°C to 39°C) and low in December to February (below 20°C). The main soil compartment is dominated by three mainly soils which were identified and classified According to Soil Taxonomy of United State Agriculture Department (USDA). These soils are: Entisol (78.3%, of the watershed surface) Alfisol (18.7%) and Inceptisol (0.1%). Cotton fields that retain our attention here are mainly located on Alfisol. Crops (cotton, sorghum, maize, millet etc.) occupy 25% of the watershed area [24]. Cotton cropping requires the use of chemical inputs including insecticides (organochlorines, organophosphates and pyrethroids) to fight insects as *Helicoverpa armigera, Aphis gossypii etc*.

2.2 Used pesticides identification

In order to assess Korokoro watershed soils contamination, it has been necessary to identify pesticides used in cotton production at local scale. So, surveys have been conducted from 2009 to 20011 in 4 villages or hamlets (Kodalabougou, Chonikoro, Fiena and Sido) of the watershed **(Fig. 1).** A questionnaire was addressed to individually or groups in order to obtain required informations : pesticide formulations, doses frequency and period of their application during the cropping season. These surveys were later supplemented by informations from the Compagnie Malienne de Développement des Textiles (CMDT).

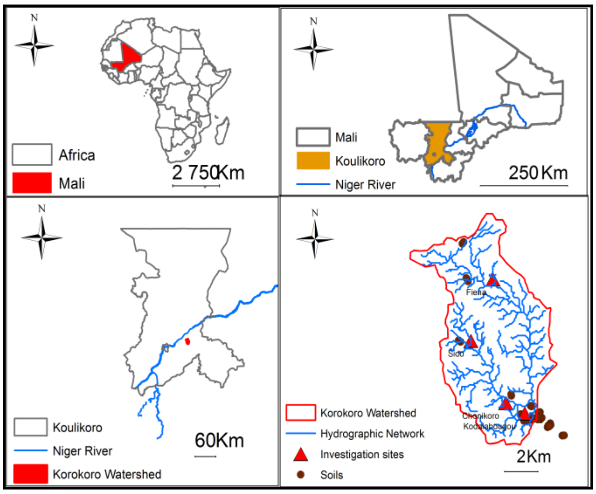

Fig.1 Investigation sites and sampling points in Korokoro watershed

2.3 Soil sampling

Soils sampling was conducted in investigative sites during 2010 and 2011 cropping seasons. This soil sampling was carried out according to Cissé and al, 2003 [25] and samples were collected in surface horizons (0-20 cm) at the end of cotton growing seasons**.** In August 3, 2010, soils were sampled in four cotton plots after pesticides applications in two sites. (**Table 4**): Kodalabougou (2 plots) and fiena (2 plots). However, in September 21, 2011, soil samples were taken in fourteen cotton plots after phytosanitary treatments in four sites (**Table 5**): Kodalabougou (9 plots), fiena (2 plots), Sido (1 plot) and Chonikoro (2 plots). Soils sampling was organized to share each plot into three parts in order to have composite samples for each part and representative ones from each plot in reference to AFNOR, 1999 [26]. All sampling points were georeferenced with a Garmin GPS 72 (**Fig. 1).** In laboratory, to ensure stability of pesticides residues, soil samples were frozen at -20 °C and they have been later transported from Bamako (Mali) to Paris (France) for analysis.

2.4 Particle size distribution and chemical analysis of soils

Particle size distribution analyzes were performed according to the international method with pipetting of Robinson whose principle is based on Stokes law. A test sample was realized with 20 g of soil previously treated with hydrogen peroxide for organic matter destruction and sodium hexametaphosphate for aggregates dispersion. Coarser fractions (coarse silt and sand) were obtained by dry sieving (sieves AFNOR of 50 µm and Prolabo of 2 mm) and the fine particles (clay and silt) were determined with the Robinson pipette. Five classes of particle sizes were considered: clay (< 2 µm), fine silt (2-20 µm), coarse silt (20-50 µm), fine sand (50 to 200 µm) and coarse sand (200 µm to 2 mm). Soil pH was measured in a suspension of soil/water 1/2.5 by the electrometric method of pH meter with glass electrode (Hach SENSION 156) and then pHKCl was determined after addition of 3.72 g of KCl in the above mixture followed by centrifugation at 2000 rpm min^{-1} for 1 hour. Organic carbon content of soil samples was determined by ANNE analytical method application (1945). Total phosphorus and total nitrogen were analyzed by an auto analyzer of type P-MANIFOLD BRAY after Kjeldahl mineralization. Exchangeable bases were determined by atomic absorption spectrometer (AAnalyst 200, PerkinElmer).

2.5 Pesticides analysis in soil samples

In scientific cooperation context, Korokoro watershed soils were transported from Bamako (Mali) to Paris (France) and were analyzed in Laboratoire Hydrologie and Environnement of UMR Metis at Université Pierre & Marie Curie. They were subjected to the same pesticides which were used in Korokoro watershed (cypermethrin, acetamiprid, atrazine, profenofos and endosulfan).

2.5.1 Reagents and standards

Solvents, acetone, n-hexane, isooctane, diethyl ether and ethyl acetate were supplied by Sigma-Aldrich GmbH Laborchemikalien as well as pesticide standards (atrazine, profenofos, cypermethrin, acetamiprid), internal standards solutions (PCB 30/107, 10 $ng.\mu L^{-1}$ in isooctane and triphenyl phosphate, 10 $ng.\mu L^{-1}$ in isooctane) and 16 organochlorine pesticides mix (2000 $ng.\mu L^{-1}$ in hexane/toluene 1:1, (v/v), LGC Standards). PCB 30 and 107 were used as internal standard to quantify organochlorines pesticides and atrazine but profenofos, cypermethrin and acetamiprid were quantified by triphenyl phosphate. Standards were high purity (99.7% to 99.9%, Dr. Ehrenstorfer, GmbH) and all solutions were stored in a refrigerator at 4°C.

2.5.2 Extraction and purification

Extraction and purification proceeding for the most pesticides (endosulfan, profenofos, cypermethrin, atrazine and acetamiprid) used in this study are inspired of others scientific works [27, 28]. Soil samples were lyophilized (Alpha 1- 4 LD plus) during 48 hours, sieved with a wire sieve of 1 mm in diameter. Then, 5 g of samples were introduced into each glass centrifugation tube of 50 mL followed by 15 mL of acetone/hexane (50:50, v/v) and 10 µL of the solution of each internal standard. Tubes were treated with ultrasonic bath (Branson 2510) for 20 minutes and then centrifuged (Sigma 2-15) at 2500 rpm for 5 minutes. Supernatant was transferred into amber glass tubes of 40 mL. Two extractions were thus carried out and followed by rinsing tubes with 5 mL of hexane while passing at vortex, centrifugation and decanting the supernatant as described above. Extracts were then concentrated under nitrogen flow (Alpha gas Smartop 1) to 2 mL and then purified on a Florisil cartridge (LC-Supelclean TM Florisil® SPE) which were conditioned beforehand with 10 mL of hexane/ethyl acetate. Extracts were added to each cartridge and eluted with 10 mL of the above mixture of 80:20 (v/v) in amber glass tubes of 15 mL. Five blanks were prepared with extraction solvent hexane/acetone (50:50, v/v) as samples for detection limit (LOD). Finally, all extracts were concentrated, transferred into vial and analyzed with a gas chromatograph associated to a mass spectrometer.

2.6 Chromatographic analysis

2.6.1 Soil analysis

Soils were analyzed with a gas chromatograph (Agilent Technologies, series 7890) associated to a mass spectrometer (5975C inert XL MSD) with detector, electron impact ionization (EI, 70 eV) and operating in a selective ion mode (SIM). Capillary column used is HP-5 (5% phenyl methyl Siloxan) of length 30 m, internal diameter 0.25 mm and 0.25 µm of film thickness. Carrier gas was helium of high purity (99.99%) and the flow rate was set at 1 $mL.mn^{-1}$. Injection was performed in splitless mode and injection volume was 1 µL. Temperature program was set as described by [29]. About the mass spectrometer, temperatures of source and quadruple were respectively 230°C and 150°C, solvent delay was set at 5 minutes. Pesticides which were analyzed by gas chromatography are presented in **Fig. 2**. They were identified by internal standard calibration method. Linearity (r^2 > 0.997) was performed for each pesticide with the calibration line of eight points with standards solutions from 2 to 200 ng. Detection and quantification limits (LOD, LOQ) were calculated respectively by multiplying by 3 and 10 standard deviation of blank replicas [30].

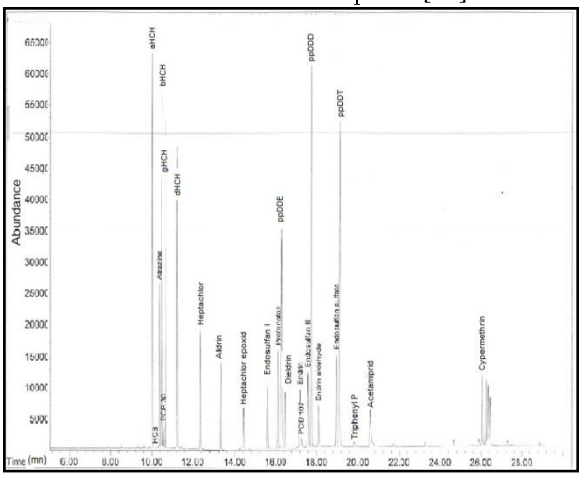

Fig.2: Pesticides analyzed by gas chromatography associated to a mass spectrometer

2.6.2 Recovery rate

To optimize extraction and purification methods, a spiking test was performed with three florisil cartridges (LC-Florisil® Supelclean TM, SPE) with a standard solution (1 ng.µL^{-1}) prepared with stock solutions (50 mg.L^{-1}) and solutions of internal standards (10 ng.µL^{-1}). Then, 50 µL of the standard solution were added into each cartridge and elution was carried out in triplicate with 10 mL respectively of hexane/acetate ethyl in the proportions 80:20; 50:50 and 20:80, (v/v). All extracts were subjected to the same analytical protocol as soil samples. Organochlorine pesticides, profenofos and cypermethrin were found more in the first fraction of hexane/acetate ethyl 80:20 (v/v) with a yield ranging from 48 to 105% according to pesticide. However, acetamiprid was not detected for this analytical method. Pesticides, retention time, internal standards, quantifier and qualifier ions (m/z), rate of recovery, limits of detection and quantification are listed in

Table 1.

2.7 Statistical analysis of data

Analysis was based on correlation search between pesticides contents, particle size distribution and physico-chemical properties of soil samples. This correlation was more studied in the second cropping season (2011 for 33 soil samples) than the first one (2010 for 16 soil samples). Analysis was performed with SPSS 13.0 software (Statistical Package for the Social Sciences). It was based on Pearson correlation coefficient (significance level α = 0.05). In calculation, zero was assigned to samples whose levels were below to the detection limit. However, quantification limit half value was attributed to samples whose contents were below to the quantification limit.

2.8 Estimation of pesticides residues stock in soils by mass balance method

The soil compartment contamination of Korokoro watershed by cypermethrin and profenofos was better assessed during 2011 cotton cropping season than 2010 one. In 2011, these two pesticides were the main compounds which were applied respectively in cotton fields from upstream to downstream of the watershed. In order to quantify residual amounts of these pesticides in the soil compartment of Korokoro watershed, apparent density of the first 20 cm of the topsoil was determined. Soil samples were collected in cylindrical tubes (20 cm x 6cm, in polyvinyl chloride) in each cotton field the before plowing and phytosanitary treatment. In laboratory, soils were dried in an oven (Heraeus instrument) at 105 °C for 24 hours, weighed (with the balance KERN 440-47) and apparent density of each soil was expressed (kg.dm^{-3}). An overall mass balance was established solely on various uses of cypermethrin in cotton production through the watershed in spite of its strong presence in all soil samples compared to profenofos, acetamiprid and atrazine which generally remained below to the detection limit (< LOD). Here, the assessment is done according to the quantities of cypermethrin used in cotton fields during the cropping season 2011 and its levels in soil samples (collected 3 months after it application on cotton). The mass balance was calculated using the following equation:

$$\sum Qstock = \sum Tmean\, x\, H\, x\, S\, x\, d$$

where **Qstock** is cypermethrin amount (µg) in stock through a given plot; **Tmean** is cypermethrin mean content (µg.kg^{-1}) in surface horizon (**H** = 0.2 m), plot surface **S** (m^{2}) and soil apparent density **d** (kg.dm^{-3}).

Table 1: Pesticides, retention time (min), quantifier and qualifier ions (m/z), limits of detection and quantification (LOD, LOQ, µg.kg^{-1}, dry weight) and recovery rate (%)

pesticides	Retention Time (mn)	Quantifier ion (m/z)	Qualifier ion (m/z)	Recovery rate (%)	LOD (µg.kg^{-1})	LOQ (µg.kg^{-1})
aHCH	10,003	181	183	68 ± 15	0,06	0,20
HCB	10,158	284	286	78 ± 17	0,01	0,02
atrazine	10,359	200	215	78 ± 20	0,25	0,84
bHCH	10,467	181	183	71 ± 16	0,06	0,18
PCB 30[a]	10,56	256	258	-	-	-
gHCH	10,653	181	183	72 ± 15	0,09	0,29
d-HCH	11,24	181	183	68 ± 15	0,08	0,28
heptachlore	12,344	272	274	54 ± 12	0,91	3,04
aldrin	13,308	263	265	74 ± 16	0,05	0,17
heptach epoxid	14,412	353	355	70 ± 16	0,05	0,15
endosulfan I	15,589	241	237	74 ± 17	0,21	0,70
p,p'-DDE	16,262	246	318	57 ± 21	0,01	0,02

dieldrin	16,467	263	139	76 ± 17	0,18	0,62
PCB 107[a]	17,267	326	328	84 ± 18	-	-
endrin	17,2	263	139	-	1,93	6,45
Endosulfan II	17,577	195	237	105 ± 23	0,03	0,09
p,p'-DDD	17,441	235	237	66 ± 14	0,01	0,03
endrin aldehyd	18,099	345	347	58 ± 13	0,01	0,04
endosulf sulfate	18,963	272	274	60 ± 9	0,07	0,23
p,p'-DDT	19,142	235	237	58 ± 9	0,06	0,21
profenofos	16,104	139	208	48 ± 11	0,81	2,70
Triphenyl phosph[b]	19,825	326	325	-	-	-
acetamiprid	20,583	152	126	nd	-	-
Cypermethrin	26,053	163	181	86 ± 36	1,48	4,92

a and b = internal standard; nd = not detecte

III. 3. Results

3.1 Pesticides used in Korokoro watershed

Pesticides used include mainly insecticides and secondary herbicides. Insecticides and herbicides are only used for cotton production. Surveys have shown that farmers used frequently profenofos, cypermethrin and endosulfan. Among this group, endosulfan is the pesticide which agricultural use has been banned or severely restricted in nearly 50 countries worldwide due to human toxicity and environmental persistence [31]. These pesticides are distributed either by cotton company or purchased through informal sector and they are applied generally in liquid emulsifiable form or soluble concentrates (cypermethrin and profenofos but cypermethrin is often used in combination with other active ingredients as acetamiprid and imidacloprid) but endosulfan is applied only in emulsifiable concentrates. In cotton production, cypermethrin is applied at 72 g.L^{-}1 but profenofos and endosulfans are applied at 500 g.L^{-1}. Insecticides treatments are performed in cotton fields from July to September. Frequency of treatment, interval between treatments (from one to two weeks) and application rate are set by farmer according to the degree of parasitic infestation of cotton plant during the cropping season. **Table 2** lists pesticides that are used in agricultural Korokoro watershed from 2009 to 2011.

Table 2: Main pesticide formulations used in Korokoro watershed from 2009 to 2011

Commercial specialty	Use	Active ingredients	Chemical family
Atrafor 500 SC	herbicide	Atrazine* (500 gL^{-1})	Triazine
Cytoforce 288 EC	insecticide	Cypermethrin Monochrotophos	Pyrethroid Organophosphate
Mistral 450 DP	fongicide	Endosulfan Chlorothalonil	Organochlorine Pyrethroid
Gazelle C 88 EC	insecticide	Cypermetrin (72 gL^{-1}) Acetamiprid*(16 gL^{-1})	Pyrethroid Neonicotinoid
Thiofanex 500 EC	insecticide	Endosulfan* (500 gL^{-1})	Organochlorine
Ténor 500 SC	insecticide	Profenofos (500 gL^{-1})	Organophosphate
Cotogard 500 SC	herbicide	Fluometuron Prometryne	Phenylurea Triazine
Phaser	insecticide	Endosulfan	Organochlorine
Emir 88 EC	insecticide	Cypermetrin (72 gL^{-1}) Acetamiprid (16 gL^{-1})	Pyrethroid Neonicotinoid
Cyperfos 336	insecticide	Cypermetrin (136 gL^{-1}) Methamidophos (200 gL^{-1})	Pyrethroid Organophosphate
Endosulfan 500 EC	insecticide	Endosulfan *(500 gL^{-1})	Organochlorine
Malathion	insecticide	Malathion	Organophosphate
Attakan C 344 SC	insecticide	Cypermetrin* (144 gL^{-1})	Pyrethroid

Nomax 150 SC	insecticide	Imidacloprid (200 gL^{-1})	Neonicotinoid
		Cypermetrin* (75 gL^{-1})	Pyrethroid
		Teflubenzuron (75 gL^{-1})	Benzoylurea
Calife 500 EC	insecticide	Profenofos* (500 gL^{-1})	Organophosphate

* Monitoring pesticides in the agricultural Korokoro watershed

3.2 Particle size distribution and chemical properties of soils

Results of soil samples analyzed are shown in **Table 3**. Analyses indicated that the alfisol of Korokoro watershed is characterized by the presence of two main texture classes which are loamy-sandy which is most observed at Kodalabougou (watershed outlet) and loamy-clay dominating in other three investigative sites (Chonikoro, Sido and Fiena). Particle size distribution in surface horizon (0-20cm) is quite variable within the watershed. Clay contents range from 14 to 25%. About chemical properties, it was observed an average acidity in all soil samples (pH < 7), low contents of organic matter (< 1%) and also in cation exchange capacity (CEC ≤ 8 meq/100g) and exchangeable bases (< 4 meq/100g).

3.3 Pesticides detected in soils

Soil contamination of Korokoro watershed was followed during 2010 and 2011cotton production. Cypermethrin, acetamiprid, atrazine, endosulfan and profenofos were monitored in cotton growing. The first analyses about some soils contamination have shown that these pesticides have not been previously used in cotton production except for organochlorine pesticides and cypermethrin for which values have been measured. During the first cropping season (in 2010), cotton growing was practiced in just two investigation sites of Korokoro watershed because of the low rainfalls which have been observed in entire the watershed. Thus, pesticides residues were analyzed in only 16 composites soil samples and maximum levels were observed for endosulfan (11 $\mu g.kg^{-1}$), cypermethrin (10 $\mu g.kg^{-1}$), endrin (7 $\mu g.kg^{-1}$) and DDT (4 $\mu g.kg^{-1}$). However, profenofos, acetamiprid and atrazine remained below to the detection limit. Pesticides contents ($\mu g.kg^{-1}$), detection frequencies (%), limits of detection and quantification (LOD, LOQ, $\mu g.kg^{-1}$, dry weight) are listed in **Table 4**. During the second season (in 2011), pesticides residues were analyzed in 33 composites soil samples which were collected from all investigation sites of Korokoro watershed. Pesticides which were detected in soils are mentioned in **Table 5**. Maximum levels were measured for cypermethrin (6.2 $\mu g.kg^{-1}$), endosulfan sulfate (4.2 $\mu g.kg^{-1}$) and DDT (3.5 $\mu g.kg^{-1}$) compared to profenofos, atrazine and acetamiprid which remained below to the detection limit (<LOD).

However, among these pesticides, cypermethrin is the most quantified compound in all soil samples. Its applied amounts in cotton fields of Korokoro watershed were estimated at 2520 g on 28 hectares in total. Stock of its residues in the soil compartment of the watershed after cotton cropping season (in 2011) were evaluated at 321.2 g which represented 13 ± 0.4% of applied quantities. But, levels of α-HCH, HCB, lindane, aldrin and endrin were below to the detection limit.

Table 3: Particle size distribution and chemical properties of topsoil (0-20 cm) in Korokoro watershed (September, 2011)

Characteristics	Investigation sites			
	Soils			
	Kodalabougou (n = 9)	Chonikoro (n = 2)	Sido (n = 1)	Fiéna (n = 2)
Clay(%)	14.4 ± 5.3	24.7 ± 10.6	19.1 ± 5.4	15 ± 8.0
Fine silt (%)	8.1 ± 5.3	13.2 ± 4.4	19.2 ± 16.6	12.4 ± 4.4
Coarse silt (%)	49.4 ± 8.9	53.3 ± 15.5	56.2 ± 18.3	50.6 ± 8.2
Fine sand (%)	27.5 ± 9.2	8.4 ± 1.7	4.8 ± 0.7	18.2 ± 8.2
Coarse sand (%)	0.6 ± 0.5	0.4 ± 0.3	0.8 ± 0.5	3.7 ± 2.1
OC (%)	0.2 ± 0.1	0.3 ± 0.2	0.2 ± 0.1	0.4 ± 0.2
OM (%)	0.4 ± 0.2	0.4 ± 0.3	0.4 ± 0.1	0.6 ± 0.4
total N (%)	0.04 ± 0.01	0.04 ± 0.01	0.04 ± 0.01	0.04 ± 0.01
total P ($mg.kg^{-1}$)	104.4 ± 39.3	129.4 ± 36.5	112.8 ± 9.4	116.1 ± 12.7

pHwater	6.5 ± 0.5	6.3 ± 0.2	5.9 ± 0.2	6.1 ± 0.2
pHKCl	5.5 ± 0.6	5.3 ± 0.2	4.9 ± 0.3	5.1 ± 0.2
app density (kg.dm^{-3})	1.4 ± 0.1	1.3 ± 0.2	1.2 ± 0.6	1.5 ± 0.1
Exchangeable bases				
CEC (meq/100g)	5.73 ± 1.68	6.84 ± 2.01	5.52 ± 0.79	4.96 ± 1.12
Ca++ (meq/100g)	3.05 ± 1.02	3.18 ± 0.42	3.11 ± 0.83	2.73 ± 0.35
Mg++ (meq/100g)	1.48 ± 0.52	1.69 ± 0.43	1.5 ± 0.42	1.36 ± 0.27
K+ (meq/100g)	0.19 ± 0.07	0.29 ± 0.08	0.17 ± 0.04	0.23 ± 0.05

OC = organic carbon; OM = organic matter; total N = total nitrogen; total P = total phosphorus; Ca = calcium;
CEC = cation exchange capacity; Mg = magnesium; K = potassium; app density = apparent density; "– "= not measured;
n = number of cotton fields

Table 4: Average contents (µg.kg^{-1}) of pesticides in top soil (0-20cm), limit of detection and quantification (LOD, LOQ, µg.kg^{-1}, dry weight), detection frequencies (%) (Korokoro watershed, Auguste 2010)

Invest sites	Plots code	dieldrin	endrin	α-endo	β-endo	endo sulfate	p,p'-DDE	p,p'-DDD	p,p'-DDT	profeno	cyperm	∑-endo	∑-DDT	p,p'-DDE/DDT
Kodalab	KBFD	trace	trace	<LOD	<LOD	trace	3,3 ± 0,9	0,3±0,3	0,5 ± 0,2	<LOD	<LOD	0.1	4	6,6
	KSD	0,7 ± 0,5	trace	trace	0,3 ± 0,3	0,3 ± 0,3	0,9 ± 0,4	<LOD	trace	<LOD	<LOD	0.9	1	9
Fiéna	FMD	trace	trace	trace	<LOD	<LOD	0,1 ± 0,02	<LOD	<LOD	<LOD	trace	0.4	0,1	-
	FDT	trace	7,1 ± 3,6	0,9 ± 1,1	5,2 ± 6,9	4,5 ± 6,3	1,9 ± 2,8	<LOD	trace	<LOD	10,1 ± 8,9	10.5	2	19
	Det freq (%)	**75**	**62,5**	**56,3**	**37,5**	**50**	**100**	**12,5**	**50**	-	**37,5**			
	LOD (µg.kg^{-1})	0,18	1,93	0,21	0,03	0,07	0,01	0,01	0,06	0,81	1,48			
	LOQ (µg.kg^{-1})	0,62	6,45	0,70	0,09	0,23	0,02	0,03	0,21	2,70	4,92			

endo sulfate = endosulfan sulfate ; Invest sites = investigation sites ; endo = endosulfan ; Kodalab = Kodalabougou ; Det freq (%) = detection frequency (%) ; profeno = profenofos ; cyperm = cypermethrin ; trace = value below quantification limit ; <LOD = value below detection limit; the sign – means value no determinat

Table 5; Average contents (µg.kg^{-1}) of pesticides in the topsoil (0-20cm), limit of detection and quantification (LOD, LOQ, µg.kg^{-1}, dry weight), detection frequencies (%) (Korokoro watershed, September 2011)

Investigative sites	Plots code	p,p'-DDE	p,p'-DDD	p,p'-DDT	endo sulfate	profeno	cyperm	∑-DDT	p,p'DDE/p,p'-DDT
	KBOD	1.3 ± 1.1	trace	0.2 ± 0.2	2.2 ± 2.2	trace	3.6 ± 1	1.5	6.5
	KKOD	0.7 ± 0.6	<LOD	0.1 ± 0.1	4.2 ± 4.2	<LOD	2.9 ± 1.9	0.8	7
	KKAD	2.1 ± 2	trace	0.1 ± 0.1	3.6 ± 3.6	<LOD	4.7 ± 0.2	2.2	21
	KDD	trace	<LOD	<LOD	0.1 ± 0.1	<LOD	3.7 ± 1	0.1	-
	KBAD	2.2 ± 1.1	0.1± 0.1	1.2 ± 1.0	<LOD	<LOD	4.8 ± 0.7	3.5	1.8
	KKED	1.6 ± 0.7	0.04± 0.03	0.1± 0.05	<LOD	trace	4.0 ± 0.4	1.7	16
Kodalabougou	KAD	trace	<LOD	<LOD	trace	trace	2.5 ±	0.1	-

							1.5		
	KTD	0.8 ± 0.4	<LOD	0.2± 0.1	<LOD	trace	4.5 ± 0.9	1	4
	KBFD	1.6 ± 0.7	0.04± 0.03	0.1± 0.05	<LOD	<LOD	4.0 ± 0.4	1.7	16
Chonikoro	CSD	1.1 ± 0.2	trace	0.2 ± 0.1	<LOD	<LOD	5.0 ± 0.9	1.3	5.5
	CAS	2.4 ± 0.4	<LOD	0.1 ± 0.1	2.2 ± 2.1	<LOD	5.3 ± 2.7	2.5	24
Sido	SBT	<LOD	<LOD	<LOD	<LOD	<LOD	4.5 ± 1.2	-	-
Fiéna	FSD	0.5 ± 0.4	<LOD	0.1 ± 0.1	3.3 ± 3.2	<LOD	6.2 ± 3	0.6	5
	FDT	<LOD	<LOD	<LOD	<LOD	<LOD	2.6 ± 0.5	-	-
	Det freq (%)	**84.8**	**27.3**	**60.6**	**30.3**	**18.2**	**100**		
	LOD (μg.kg^{-1})	0.07	0.01	0.003	0.02	0.88	0.59		
	LOQ (μg.kg^{-1})	0.24	0.03	0.01	0.06	2.93	1.96		

endo sulfate = endosulfan sulfate ; Det freq (%) = detection frequency (%) ; profeno = profenofos ; cyperm = cypermethrin ; trace = value below quantification limit ; <LOD = value below detection limit; the sign – means value no determinate.

IV. Discussions

4.1 Soil quality in the watershed

The variability of the topsoil content in clay appears to be related to the runoff and erosion which are also responsible of a high heterogeneity observed in the topsoil materials (clay and organic matter). Soil acidity is probably related to the sandstone origin of local soils and the loss of exchangeable bases (calcium, magnesium and potassium) due to crops nutrition needs and the low investments in fertilisers supply by farmers. These reasons added to hydraulic erosion and aeolian transport can also explain the low levels of organic carbon and matter in the topsoil [32]. For example, in Sahelian climate context and in particular Mali, aeolian transport is in most cases responsible for impoverishment of organic matter in topsoil [33]. However, low levels of organic matter in these soils are not favorable to pesticides degradation and this can further facilitate pesticides stockage.

4.2 Pesticides occurrence in soils

According to the results which were obtained during 2010 and 2011 cotton cropping season, the soil compartment of Korokoro watershed is contaminated by pesticides use. This contamination can be explained by two main factors: consequences of actual and past utilizations for cotton production. The past utilization concern organochlorine compounds (DDT and its metabolites, endrin, dieldrin, etc) which have not been identified during the surveys conducted in the present study. Similarly, the ratios between p,p'-DDE and p,p'-DDT are greater than 1 (**Tables 4 and 5**), it means that DDT has not been recently used in sampled fields. However, organochlorine pesticides presence in the soils of the watershed can thus be explained by a past utilization. Indeed, it is known that in Mali and other West Africa countries, important quantities of organochlorine pesticides have been used to fight African migratory locust control. Thus, soils contamination by these compounds can be justified by their persistence. Indeed, organochlorine pesticides are persistent in environment more than 30 years after the end of their use in agriculture [34, 35, 36]. Values which were obtained for these compounds in this study are similar to those indicated through others scientific works [37,38]. Also, their accumulation in the watershed soils can be due to the low levels of organic matter (less than1%) because organic matter presence is capitol to accelerate pesticides degradation process in soils [39]. Recent uses concern pesticides that have been frequently used in cotton growing during 2010 and 2011 in the watershed (endosulfan, cypermethrin,profenofos etc.). Among this group, cypermethrin was the most quantified compound in all soils (in 2011). Values obtained in this study for these compounds are comparable to those observed in others African countries where agricultural situation is similar to Malian one: Benin, Togo, Senegal and Burkina Faso. However, after 2011 cotton cropping season the mass balance which has been established showed that cypermethrin tends to be accumulating in the soil compartment of Korokoro watershed. This accumulation can be also explained by cypermethrin physico-chemical properties compared to those of profenofos. Indeed, profenofos is more volatile than cypermethrin (2.53 mPa against 0.00023 mPa) and degrades rapidly than cypermethrin (7 days against 69 days) [40]. So, soils contamination by cypermethrincan can be due to its extensive use on cotton plant during phytosanitary treatment (July-September) which could explain the high contents measured in soils. Similarly, Pearson correlation test (n =38; significance level α = 0.05) which has been achieved between pesticides levels, physico-chemical properties and soils particle size distribution (in 2011), showed in particularly positive correlation (r = 0.483) between cypermethrin and soil fine silt fraction (**Table 6**). Moreover, significant correlation (r = 0.484) was also observed between cypermethrin and p,p'-DDE (a metabolite of DDT). It can mean that cypermethrin is also a persistent compound in soil as this metabolite of DDT. However, an intensive application of cypermetrhin on cotton can be a health risk for farmers, soil compartment contamination and a factor of resistance development of insect pests level [41]. Cypermethrin levels which were obtained in this study are higher than those previously observed in others studies [42].

Table 6: Pearson correlation matrix (n = 38; α = 0.05, two-tailed test), pesticides contents, physico-chemical properties and particle size distribution

	pHeau	OC	OM	CEC	Clay	FSilt	CSilt	FS	CS	p,p'-DDE	p,p'-DDD	p,p'-DDT	endo sulfate	Profeno	Cyperm
pHeau	1														
OC	**-0,492**	1													
OM	**-0,494**	**1,000**	1												
CEC	-0,218	**0,501**	**0,502**	1											
Clay	**-0,642**	**0,582**	**0,585**	**0,734**	1										
FSilt	**-0,457**	**0,664**	**0,664**	**0,499**	**0,457**	1									
CSilt	0,171	**-0,458**	**-0,460**	**-0,608**	**-0,618**	-0,380	1								
FS	**0,482**	**-0,519**	**-0,519**	-0,262	-0,394	**-0,481**	-0,264	1							
CS	-0,112	0,265	0,265	-0,266	-0,174	0,048	0,008	-0,149	1						
p,p'-DDE	-0,161	0,364	0,363	0,237	0,435	0,284	-0,256	-0,152	-0,329	1					
p,p'-DDD	-0,077	0,432	0,430	-0,031	0,141	0,399	0,004	-0,328	-0,135	**0,797**	1				
p,p'-DDT	0,210	-0,210	-0,211	-0,207	-0,152	-0,252	0,045	0,203	-0,206	0,246	0,206	1			
endo sulfate	0,334	-0,366	-0,366	-0,032	-0,100	-0,318	-0,156	0,318	0,039	-0,078	-0,282	-0,076	1		
profeno	0,015	-0,082	-0,082	-0,060	-0,193	-0,377	0,132	0,182	-0,243	-0,195	-0,221	-0,054	-0,081	1	
Cyperm	-0,367	0,397	0,393	0,423	0,437	**0,483**	-0,171	-0,409	0,000	**0,484**	0,358	0,130	-0,019	-0,291	1

endo sulfate = endosulfan sulfate ; Cyperm = cypermethrin ; profeno = profenofos ; OC = organic carbon; OM = organic matter; CEC = cation exchange capacity; FSilt = fine silt; CSilt = coarse silt; FS = fine sand; CS = coarse san

V. Conclusion

Cotton farmers in Korokoro watershed commonly use chemical insecticides of various families. These pesticides are distributed either by cotton company or purchased through informal sector. However, this study has showed that soils of the watershed are contaminated by organochlorine pesticides due to past agricultural uses while those of endosulfan and cypermethrin are due to their actual application in cotton cropping. In sum, the presence of these pesticides in soils is due to their persistence and according to the low levels of organic matter. This can constitute a health and also environmental risk in Korokoro watershed. There is so a research need for better influence comprehension of soil quality and its hydraulic properties on pesticide transfer dynamic in soil compartment of the watershed.

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