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Impact of Pesticides Use in Cotton Areas of Korokoro Watershed (60.6 km^2) and Bafinkabougou on the Quality of Water and Sediments of Niger River (Koulikoro, Mali).

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ABSTRACT

Contamination of water and sediments of Niger River by pesticides used in Korokoro watershed (60.6 km^2, Mali) and Niger River outfall, was studied from 2009 to 2011. In these two localities, pesticides used frequently in cotton production have been surveyed near farmers. Sampling campaigns of water, water and sediments have been also carried out respectively in the watershed outlet and Niger River outfall. Chromatographic analyzes of overall samples showed a contamination of these by organochlorine pesticides due to agricultural waters drained from Korokoro watershed and those from external cotton fields of the watershed. Surface runoff can be the main source of this contamination.

Introduction

In West Africa, particularly in Mali, the economic development is based on some export crops such as cotton. Indeed, cotton also called "White Gold" is one of the main export crops of Mali and has been cultivated for over a century in Sahelian and Sudanian savannah areas of West Africa. Generally, the success of this crop is essentially linked to intensive use of chemical inputs, especially pesticides [1]. In Sahelian countries as Mali, cotton production has always required intensive use of pesticides. In Mali, the pesticides are frequently used in cotton areas of "Compagnie Malienne du Développement des Textiles (CMDT)" and "Office de la Haute Vallée du Niger (OHVN)". In these areas, 80% of pesticides used are insecticides (organochlorines, organophosphorus, etc.) [1]. However, it is known that intensive use of pesticides in agriculture can have adverse health effects on farmers where good practices (application rates, frequency of treatment etc.) are not sometimes applied as recommended [2-4]. As well as, the intensive use of such chemical products can contaminate surface also groundwater by pesticide residues. This contamination of these environmental matrices is generally linked to the use of pesticides which were already banned for agricultural use (e.g. organochlorine pesticides) because of their acute toxicity, potential persistence and bioaccumulation [3-7]. In addition, this contamination can also be linked to the agricultural land use [8 ;9]. Indeed, surface and groundwater are contaminated by soil during phytosanitary treatments and runoff process from the treated areas and also during infiltration process [10 ;11]. In fact, field plowing promotes pesticide residues which are both adsorbed on fine soil particles and accumulated in the surface horizon (0-20cm) to rise to soil surface or not and during significant rainfalls these pesticide residues are carried off by runoff and/or infiltration processes according to these rainfalls intensifications. Thus, through these runoff and/or infiltration processes, surface and groundwater can be contaminated by pesticides used in agriculture. Indeed, the U.S. Environmental Protection Agency (EPA) has reported at least the occurrence of 46 pesticides residues in groundwater and 76 in surface waterbodies after normal agricultural has been applied. The compounds mostly found were atrazine (herbicide) and endosulfan. (organochlorine pesticide) [12;13]. Generally, surface and groundwater are largely used for human consumption but today they are still contaminated worldwide by pesticides used in agriculture (e.g. cotton growth). Indeed, it has reported the occurrence of several pesticides residues in groundwater during the last 30 years in Europe [14-16], United States [17-19] and Africa [11;20]. In surface waters, it has been reported that pesticides residues are still detected 20 years after their use had been banned [21]. The contamination of these water resources is relating to the potential persistence of pesticides residues and this is very dangerous for human and environmental health because of the acute toxicity and bioaccumulation of these chemical compounds. Therefore, the fate of these pesticides residues in water resources (surface and groundwater) remains unknown in Mali where studies of these resources contamination by pesticide residues are still very limited [8]. Hence, the need to improve knowledge in order to protect people and environmental health. The aim of this study is to assess the impact of pesticides use in cotton areas of Korokoro watershed

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(60.6km2) and Bafinkabougou on the quality of water and sediments of Niger River (Koulikoro, Mali).

Material and methods

Study area

Korokoro Watershed (60.6 km^2) is located in Koulikoro region (Mali) between 12°42'N and 12°50'N, 7°22'W and 7°28'W. It is also located on the right bank of Niger River and situate at 70 km from the capitol of Mali (Bamako). Four villages or hamlets (Kodalabougou, Chonikoro, Sido and Fiéna) (Fig.1) have been followed from 2009 to 2011 in order to establish a balance on pesticides use in cotton production for several years and also studying the impact of pesticides use on the quality of water and sediments of Niger River. The climate of this watershed is characterized by a long dry season (November to May) and short rainy one (June to October). Annual rainfalls are variable according years (from 700 to 800 mm). Temperatures undergo little fluctuation however they are high in March and May (36°C to 40°C) and low from December to February (below 20°C). The soil compartment is dominated by three mainly soils, (i) Entisol (78.3%, of the watershed surface), (ii) Alfisol (18.7%) and (iii) Inceptisol (0.1%). Cotton fields that are subjected in this study are mainly located on Alfisol. Crops (cotton, sorghum, maize, millet etc.) occupy 25% of the watershed area [22]. Among these, cotton is mainly produced for the global market and requires always intensive use of chemical inputs such as insecticides (organochlorines, organophosphates and pyrethroids). These chemical products are used by farmers in order to control insect pests (e.g. *Helicoverpa armigera* and *Aphis gossypii*) and also increasing agricultural yields.

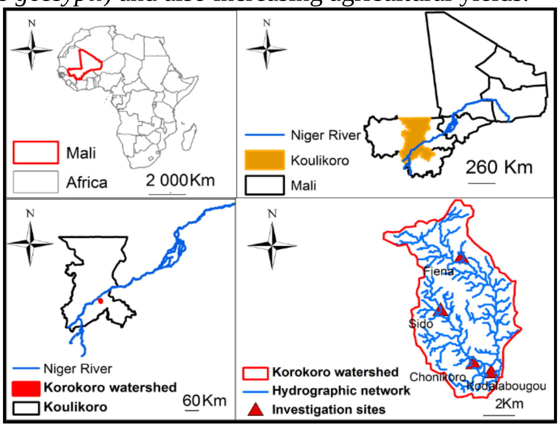

Figure 1. Korokoro watershed and the four investigative sites.

The area of Bafinkabougou and Niger River are located in the upstream part of Korokoro watershed (Fig.2).

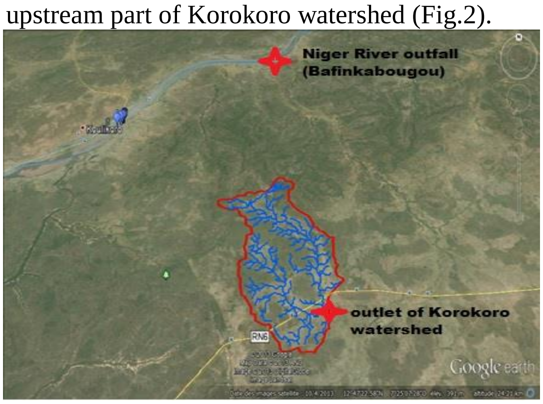

Figure 2. Location of Niger River outfall and outlet of Korokoro watershed.

However, Bafinkabougou is the outfall of Niger River, i.e. the meeting point of overall agricultural waters drained from the watershed as well as those from external fields of the catchment area, before diverting into Niger River. However, agricultural activities such as cotton production, market gardening, etc., are mainly practiced in Bafinkabougou.

Pesticides used in Korokoro watershed and Bafinkabougou

In order to assess the contamination of water and sediments of Niger River by agricultural waters drained from Korokoro watershed and those from outside fields of the watershed, it has been necessary to identify pesticides which are frequently used. in cotton production at the watershed and Niger River outfall (i.e. Bafinkabogou) scale. In both locations, surveys have been carried out near farmers from 2009 to 2011 and also monitored before, during and after each cotton cropping season. Pesticides used in agricultural activities have been released by using questionnaires. These questionnaires were addressed either individually either to groups as appropriate in order to know pesticide formulations, doses, frequency of phytosanitary treatments, periods of application, etc. Subsequently, the data collected from these surveys were later supplemented near the "Compagnie Malienne du Développement de Textiles (CMDT)".

Contamination experiments of water and sediments of Niger River by agricultural waters drained from Korokoro watershed and Bafinkabougou

In order to study the contamination of water and sediments of Niger River by agricultural waters drained from Korokoro watershed and those of external cotton fields of the watershed, three lysimeters (3m x 1m x 1m) have been installed at campus University of Bamako (June 16, 2009). The pedological material of lysimeters is from an alfisol of the watershed where cotton is cultivated since many years. Each box has two aluminum containers for respectively runoff and infiltration water collection.This experimental apparatus has been supplemented with a rain gauge. In order to know the initial soils contamination by pesticides residues, two tests were performed on each lysimeter box before experimentations. The tests were based on rain simulation for two events in each lysimeter box respectively on July 4 and 7, 2009. However, only runoff water samples could be collected and analyzed with a gas chromatograph. The results have not shown any contamination. Thus, during each raining season, the cotton has been grown in lysimeters in 2010 and 2011 and treated with endosulfan solution as well as phytosanitary treatments although its agricultural use has been banned worldwide.However, it has been chosen in this study for contamination tests because it is still used by some Malian farmers as Korokoro watershed ones in cotton production [23]. Cotton seeds were so sown in each lysimeter box respectively on July 10, 2010 and on August 6, 2011. After growthing, cotton plants have been treated with respectively two endosulfan applications (500 mg of applied matters) and one application (1,000 mg of applied matters). However, all agriculture practices (phytosanitary treatment, fertilizers application etc.) were referred to official recommendations in Malian cotton production area.

Protocol of sampling in lysimeters, Korokoro watershed outlet and Niger River outfall

At lysimeter boxes scale, runoff and infiltration samples were collected after each rainy season from July to August in 2010 and 2011 in order to assess their contamination level by endosufan residues. All water samples were collected always in amber glass bottles after each rainfall event which had caused runoff and/or infiltration.

Rainfall amounts were also measured as well as runoff and infiltration volumes after each rainfall event. The measurements have started on August 28, 2010 and August 24, 2011 after endosulfan application on cotton plants in each lysimeter box during 8 and 5 rainfall events respectively in 2010 and 2011.

At Korokoro watershed scale, all agricultural waters drained from cotton fields have been sampled at the outlet of the watershed (Kodalaboubou, Fig.1) in order to study on the one hand, the contamination level by pesticides frequently used in cotton production (endosulfan, cypermethrin, profenofos and atrazine). However, all water samples were taken in amber glass bottles previously decontaminated and transported in a cooler with cooling pads [24]. On the other hand, estimate pesticide residues amount (kg) transported by runoff process to Korokoro watershed outlet and also towards Niger River outfall. It has been also estimated pesticide residues annual fluxes (kg. year-1) based on pesticide residues amount (kg) expressed and rainfalls of this study area. As well as annual runoff (mm) on the watershed surface, flows (m3 s-1) and runoff volumes (m3) at the watershed outlet, have been estimated also during cotton campaigns in 2010 and 2011. However, all the measurements were carried out according to meteorological data provided by the synoptic station of Bamako (Mali). The data were mainly related to rainfalls (mm) and evaporations on Piche (mm) from 2009 to 2011.

At Niger River scale, water samples were taken at the outfall (i.e. Bafinkabougou, Fig.3) in order to study the impact of pesticides use in Korokoro watershed on the quality of water and sediments of Niger River. Water samples were taken at 2 m depth in the River with an automatic sampler (Niskin sampling bottle model 1010-1.2 to 40 L, Florida). This sampler was tied to a rope of 2 m in length and then immersed in water and pulled on about 10 m before released the first sampling. The other water samples were thus collected by applying this technic. Sediments were also collected at Niger River outfall on about 1 kilometer of distance. The samples were taken at 50 m from banks of Niger River with a metal bucket. The metal bucket was tied to a rope and pulled on about 10 m before carried out the first sampling. Thus, it was done for the other sediment samples. However, a composite sample was always made at each 100 meters. In laboratory and in order to ensure the stability of research molecules pesticide, all water and sediment samples were stored respectively at 4 °C and -20 °C before their analysis.

Figure 3. Sediment sampling points in Niger River (i.e. in Bafinkabougou, Google Earth, 2013).

Analysis of pesticides residues in samples from lysimeters, Korokoro watershed outlet and Niger River outfall

Samples from lysimeters have been subjected to endosulfan residues analyses but those from Korokoro watershed outlet and Niger River outfall have been analyzed for pesticides frequently used in cotton production through the watershed and Niger River outfall in 2010 and 2011 (endosulfan, cypermethrin, atrazine and profenofos).

Extraction and purification of active ingredient of pesticides in water and sediments

About water samples from lysimeters, Korokoro watershed outlet and Niger River outfall, three liquid-liquid extractions were released on each 500mL of water sample and 10% of hexane has been used as extraction solvent [25]. Anhydrous sodium sulphate (Na2SO4) was added in each sample in order to remove all water traces then all samples were filtered on filter papers. All filtrates obtained have been concentrated on a rotary evaporator (Büchi Rotavapor) to 1 mL and purified on nonpolar cartridges which were previously conditioned with 5 mL of hexane/diethyl ether (40:60, v/v) and 5 mL of hexane followed by sample deposit. Elution in each cartridge was carried out with 5 mL of hexane/diethyl ether in proportions respectively of 80:20 and 40:60 (v/v) then all extracts were concentrated again to 0.5 mL and completed to 1 mL with hexane then transferred into vial and analyzed with gas chromatographs.

All sediments samples collected in Niger River outfall have been before lyophilized (Alpha 1- 4 LD plus) during 48 hours, sieved with a wire sieve of 1 mm in diameter. Then, 5 g of each sample were introduced into each glass tube of centrifugation (50 mL) followed by 15 mL of acetone/hexane (50:50, v/v) and 10 µL of the solution of each internal standard. Then, all tubes were treated on ultrasonic bath (Branson 2510) for 20 minutes and centrifuged (Sigma 2-15) at 2500 rpm for 5 minutes. Each 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 Florisil cartridges (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 also 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.

Chromatographic analysis of water and sediments

For water samples, organochlorine pesticides (endosulfan, DDT etc.) and atrazine were analyzed with a gas chromatograph equipped with a micro electron capture detector (GC-µECD) but profenofos and cypermethrin were analyzed with a gas chromatograph with a nitrogen phosphorus detector (GC-NPD). Capillaries columns used in these analyses are HP-5 (length 30 m, 0.320 mm in diameter and 0.25 µm of film thickness) and DB-1701 for confirmation. Carrier gas (nitrogen) was high purity (99.8%). The injection was performed in splitless mode and the volume was set at 1 µL. Temperature program was set at 80°C for 2 min, 80°C to 150°C to 25°C mn-1, 150°C to 200°C to 3°C mn-1, 200°C to 280°C to 8°C mn-1 and at 280°C for 10 minutes. Temperatures of injector and detector were respectively set at 250°C and 300°C. All analyzed pesticides were identified and quantified by external calibration method.

Linearity (r^2> 0.996) was established for each compound with five points of standards solutions (from 0.0125 µg. mL-1 to 0. 125µg.mL-1). Detection and quantification limits (LOD, LOQ) were calculated according to the standard deviation, slope, dilution factor and the test volume for each pesticide standard.

Sediments samples have been analyzed with a gas chromatograph (Agilent Technologies, series 7890) associated to a mass spectrometer (5975C inert XL MSD). 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. The injection volume was release in splitless mode at 1 µL. Temperature program was set as described by [26]. Temperatures of source and quadruple were respectively 230°C and 150°C and solvent delay was set at 5 minutes. Pesticides residues have been identified and quantified by internal standard calibration method. Linearity (r^2 > 0.997) was carried out for each metabolite with eight points of 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 [27].

Quantification of endosulfan residues in runoff and infiltration water samples **at lysimeters scale**

Experiments performed at lysimeters scale aimed highlighting the contamination of water and sediments of Niger River by pesticides used in cotton production through Korokoro watershed and Bafinkabougou. During the experiments in 2010 (September, from 1 to 19, 2010), 8 rainfall events were recorded for a total of 307 mm of rainfalls and 9 significant water samples were also measured (6 for runoff and 3 for infiltration). In 2011 (from August 24 to September 13), 5 rainfall events were recorded. A total of 110 mm of rainfalls and 7 significant water samples were measured (3 for runoff and 4 for infiltration). All significant water samples measured in 2010 and 2011 were analyzed with a gas chromatograph in order to express endosulfan concentrations in runoff, infiltration and its exported amounts by rainfall events. At the end of each rainy season in 2010 and 2011, a mass balance was established. However, during these experiments, it has been supposed that endosulfan was degraded over time so, in runoff case, its concentrations havebeen calculated in 2010 and 2011 according to kinetic equation of first order:

$$C(T) = C_1 * e^{-KT} \quad (1)$$

with C (T) = endosulfan concentration as a function of time (T), C_1 = concentration measured at the first sampling day, K= (Log (2)/DT50), proportionality coefficient and DT50 = 86 days, endosulfan half-life [28].

In infiltration case, concentrations were expressed according to the mass conservation law. Thus, exported amount of endosulfan (µg) in runoff (∑Qruis) and infiltration (∑Qinf) were calculated and reported to applied amount (Qappl). Carry off processes by runoff or hydraulic erosion are calculated by multiplying each calculated concentration (Ci) by runoff volume Vi (n = 9 and 8 respectively in 2010 and 2011):

$$\sum Qruis = \sum_{i=1}^{n} C_i * V_i \quad (2)$$

As well as, amount (µg) of carry off matter by infiltration are calculated also by multiplying each calculated concentration (Ci') by infiltration volume Vi' (m = 18 and 6 respectively in 2010 and 2011):

$$\sum Qinf = \sum_{i=1}^{m} C'_i * V'_i \quad (3)$$

Results and discussion

Pesticides used in Korokoro watershed and Bafinkabougou

The surveys release in Korokoro watershed and Bafinkabougou from 2009 to 2011 have shown that farmers used several chemical families of pesticides (**Table 1**). The pesticides frequently used in cotton production are profenofos (Organophosphorus), cypermethrin (Pyrethroid) and endosulfan (Organochlorine). Among these, endosulfan is the pesticide which agricultural use has been banned worldwide due to its human toxicity and environmental persistence [29]. However, in Korokoro watershed and Bafinkabougou, these pesticides are distributed either by the local cotton company (i.e. CMDT) or purchased through the informal sector. Generally, in phytosanitary treatments, cypermethrin and profenofos are applied in liquid emulsifiable form or soluble concentrates but endosulfan is applied only in emulsifiable concentrates. During cotton production, phytosanitary treatments are performed from July to September of each cropping season and according also to the rainy season. However, the treatments frequency and the application rate are also set by the farmer following the degree of parasitic infestation on cotton plants.

Table 1. Main pesticides formulations used in Korokoro watershed and Bafinkabougou 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	Pyrethroid
		Monochrotophos	Organophosphate
Mistral 450 DP	Fongicide	Endosulfan	Organochlorine
		Chlorothalonil	Pyrethroid
Gazelle C 88 EC	Insecticide	Cypermetrin (72 gL^{-1})	Pyrethroid
		Acetamiprid*(16 gL^{-1})	Neonicotinoid
Thiofanex 500 EC	Insecticide	Endosulfan* (500 gL^{-1})	Organochlorine
Ténor 500 SC	Insecticide	Profenofos (500 gL^{-1})	Organophosphate
Cotogard 500 SC	Herbicide	Fluometuron	Phenylurea
		Prometryne	Triazine
Phaser	Insecticide	Endosulfan	Organochlorine
Emir 88 EC	Insecticide	Cypermetrin (72 gL^{-1})	Pyrethroid
		Acetamiprid (16 gL^{-1})	Neonicotinoid
Cyperfos 336	Insecticide	Cypermetrin (136 gL^{-1})	Pyrethroid
		Methamidophos (200 gL^{-1})	Organophosphate
Endosulfan 500 EC	Insecticide	Endosulfan *(500 gL^{-1})	Organochlorine
Malathion	Insecticide	Malathion	Organophosphate
Attakan C 344 SC	Insecticide	Cypermetrin* (144 gL^{-1})	Pyrethroid
		Imidacloprid (200 gL^{-1})	Neonicotinoid
Nomax 150 SC	Insecticide	Cypermetrin* (75 gL^{-1})	Pyrethroid
		Teflubenzuron (75 gL^{-1})	Benzoylurea
Calife 500 EC	Insecticide	Profenofos* (500 gL^{-1})	Organophosphate

Occurrence of endosulfan residues in runoff and infiltration water samples **at lysimeter boxes**

About the experiments release in lysimeters in 2010, 307 mm of rainfalls have been recorded as well as significant rainfalls of 52.5 mm, 101.4 mm, 37.8 mm and 28.2mm. These rainfalls were respectively occurred the fourth, sixth, seventh and ninth day after the first endosulfan application on cotton plants (August 28,2010) and were also followed by another one (62 mm) measured the eighth day after the second phytosanitary treatment (September 11,2010). Accordingly, high concentrations of endosulfan residues were more measured in runoff samples than infiltration ones. According to the established mass balance, endosulfan residues exported by runoff and infiltration processes are respectively 6.5 ± 2.9% and 0.1 ± 0.09%. It means that endosulfan exportation by water is rather than related to runoff than infiltration. Therefore, the use of endosulfan by certain farmers in cotton production can be a potential contamination risk for all watercourses at Korokro watershed and Niger River scale during significant rainfall events. However, higher concentrations measured during the experiments can be due to the fact that after application on cotton plants, a fraction of endosulfan can reach the soil and being adsorbed on fine soil particles and according to these significant rainfall events, being more transported by runoff process. In addition, during significant rainfall events, the raindrops can also impact the soil aggregates and favor slaking crusts formation which consequently reduce soil infiltration capacity and the roughness. Thus, soil surface becomes smooth and impermeable [30-32]. This phenomenon can thus limit infiltration and favor runoff. This can more explain the occurrence of higher concentrations of endosulfan residues in runoff samples than infiltration ones.

During 2011experiments, low rainfalls (110 mm against 307 mm in 2010) were recorded while significant rainfall events of 25, 32 and 24 mm were occurred respectively the first, fifth and tenth day after the single application of endosulfan on cotton plants (August 24, 2011). Consequently, low concentrations of endosulfan residues were measured in runoff and infiltration samples respectively. According to the established mass balance, the amount of endosulfan residues exported by runoff and infiltration processes are respectively 0.1 ± 0.09% and 0.2 ± 0.04%. These values are low compared to those obtained in 2010 because the rainfalls were low during the entire experiments period. However, even if the concentrations of endosulfan residues in 2011 are low, the results obtained in this study highlight further contamination of surface waters (e.g. Korokoro watershed and Niger River) and groundwater during significant rainfall events. It also means that continuous use of endosulfan in cotton production at Korokoro watershed and Bafinkabougou scale can be a potential contamination source for soil compartment and water resources in these two locations.

A**mounts (kg)** and **annual fluxes (kg.year^{-1})** of p**esticides residues carried off by agricultural waters to Korokoro watershed outlet from 2010 to 2011.**

Overall water samples collected in 2010 and 2011 at Korokoro watershed outlet were analyzed and the results showed only the occurrence of endosulfan residues in all drained waters. Indeed, a contamination with endosulfan residues was measured at 0.12 μg.L^{-1} whereas profenofos, cypermethrin and atrazine concentrations remained below the limit of detection (LOD). However, the non-detection of these pesticides may be related to their physico-chemical properties compared to those of endosulfan. Indeed, organochlorine pesticides (e.g. endosulfan) are known for their human and environmental toxicity and also potential persistence in environmental compartments (air, soil, sediments and water) [29]. However, we can observe that these results obtained at Korokoro watershed outlet are in perfect correlation with those obtained in lysimeter boxes. Indeed, experiments carried out in lysimeter boxes in 2010 and 2011 have shown that the use of endosulfan in cotton production at Korokoro watershed and Bafinkabougou scale is able to contaminate surface and groundwater. But, the results obtained in 2010 in lysimeters show clearly that surface water contamination by runoff process (6.5 ± 2.9%) is the most likely situation compared to groundwater contamination by infiltration process (0.1±0.09%). Thus, in order to estimate pesticide residues amount (kg) carried off by agricultural waters drained to Korokoro watershed outlet and pesticide residues annual fluxes (kg.year^{-1}), the results obtained in 2010 at lysimeters scale were used. Generally, lysimeter box and watershed do not function in the same way so a reduction coefficient (75%) has been applied on all the runoff performed on lysimeter boxes in order to take into account the watershed size effect on overall surface runoff [33]. Thus, from 2010 to 2011, it has been estimated respectively181 and 114 milliliters of water as annuals runoff on Korokoro watershed surface and annuals amounts of pesticide residues carried off by these runoff waters to the watershed outlet were respectively estimated at 1.3 and 0.8 kg. However, despite some favorable conditions for surface runoff (crust, strong slope, etc.), water amounts evaporating in the atmosphere can explain these values obtained in this study. Indeed, annuals evaporations measured on Piche show that water amounts evaporating in the atmosphere are significant and are often almost equal to rainfall ones (**Table 2**). These large evaporations may be due to the high temperatures and low air humidity which prevail during the long dry season (about 7 months) and also to the low density of vegetation cover. However, in a context of Sahelian climate such as that of Mali, these parameters can considerably influence runoff process as well as matter amounts (e.g. pesticide residues) transportable by runoff processes. Indeed, annuals pesticide residues fluxes estimated at Korokoro watershed outlet are generally low (0.2 kg.year^{-1}). However, these low values can be related to some natural environment parameters (vegetation cover, areas of depression, etc.) to which a fraction of endosulfan could have been adsorbed during water runoff. This fraction of endosulfan could also have settled on fine soil particles and then carried off by runoff process. In general, the most fraction of endosulfan may have remained strongly adsorbed in the soil compartment of Korokoro watershed because endosulfan, as organochlorine pesticides, is very persistent in air, water, sediment and soil of the environment [28].

Table 2. Annuals runoff (mm), flows (m^{3}s^{-1}), water volumes (m^3), amount and fluxes (kg.an^{-1}) of endosulfan residues (kg), rainfalls (mm) and evaporations on Piche (mm) from 2010 to 2011.

Year	Data provide by Bamako station			Values estimated at Korokoro watershed outlet				
	Rainfalls (mm)	**Number of rainfall month**	**Evaporation on Piche (mm)**	**Runoff on watershed (mm)**	**Water Volumes (m^3)**	**Flows (m^3 s^{-1})**	**Endosulfan amount (kg)**	**Fluxes (kg.an^{-1})**
2010	1164	8	908,9	181	10983000	0,5	1,3	0,2
2011	730	5	668,7	114	6885598	0,5	0,8	0,2

Contamination of water and sediments of Niger River by agricultural waters drained from Korokoro watershed and Bafinkabougou

All water samples collected in Niger River from 2010 to 2011 were analyzed and the results showed a water contamination of Niger River. Indeed, water samples of Niger River have been contaminated by the use of organochlorine pesticides in cotton production. The main contaminants are total HCH (α-HCH, lindane and Δ-HCH), DDT and its metabolites (p, p'-DDE and p, p'-DDD) and total endosulfan (α-endosulfan, β-endosulfan and endosulfan sulfate). The highest concentrations were measured for lindane (10 ng.L^{-1}), total endosulfan (1 to 8 ng.L^{-1}) and total DDT (0.1 to 0.7 ng.L^{-1}). However, profenofos, cypermethrin and atrazine were not detected in all the analyses performed while they were used in cotton production. Their non-detection in water samples of Niger River may be due to what has been described above in section 3.3. However, the contamination by total HCH and DDT is due to their ancient use in agriculture (e.g. Cotton growing) because they have not been found near farmers of Korokoro watershed and those of Bafinkabougou during the surveys in these two localities from 2009 to 2011. On the other hand, water contamination of Niger River by endosulfan residues is due to its recent use in cotton production at Korokoro watershed and Bafinkabougou scale according to surveys conducted in these both localities. But an ancient use of endosulfan is also possible because the investigations have also shown that organochlorine pesticides are used in these two localities before 2010 (**Table 1**). In sum, this contamination of Niger River is due to ancient and recent use of organochlorine pesticides in cotton production at Korokoro watershed and Bafinkabougou scale. Therefore, agricultural waters drained from Korokoro watershed and also those from external cotton fields of the watershed can be the main cause of Niger River contamination. In this study, the results obtained at Niger River are in perfect correlation with those found in lysimeter boxes in 2010 and also at Korokoro watershed outlet. However, the occurrence of organochlorine pesticides in water of Niger River is due to their potential persistence in aquatic ecosystems. In addition, it has been reported that many pesticides (e.g. organochlorine pesticides) can persist for long periods in an ecosystem and continuous to be detected in surface waters 20 years after their use had been banned [21].

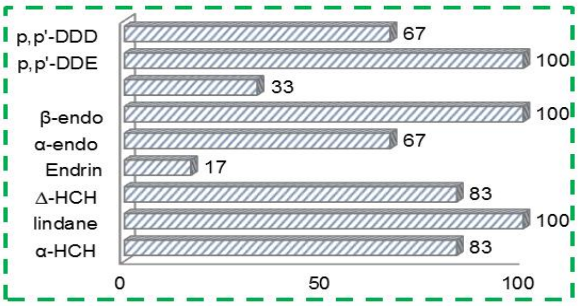

Figure 3. Detection frequency (%) of organochlorine pesticides measured in water samples of Niger River (i.e.in Bafinkabougou).

Generally, in Sahelian countries like Mali, surface waters such as Niger River are used for human consumption but their contamination by organochlorine pesticide residues is still a threat for human health and aquatic species of Niger River because of the acute toxicity and bioaccumulation potential of these pesticides. Organochlorine pesticides measured in water samples of Niger River are shown below in **Fig.3**

Similar contamination of Niger River water samples was also observed at overall sediments analyzed. Indeed, the results of the analyses showed that all sediments of Niger River were contaminated by past (DDT, lindane, HCHs, heptachlor) and recent (e.g. endosulfan) use of organochlorine pesticides in cotton production. As previously reported, profenofos, cypermethrin and atrazine were not detected in all sediments analyzed. The main contaminants are total HCH (α-HCH, β-HCH, lindane and Δ-HCH), DDT and its metabolites (p, p'-DDE and p, p'-DDD) and total endosulfan (α-endosulfan, β-endosulfan and endosulfan sulfate). The levels of these pesticides in sediments are mentioned as follows, total HCH, 1 to 21 µg.kg^{-1}, total DDT, 0.3 to 16 µg.kg^{-1} and total endosulfan, 6 to 191 µg.kg^{-1}. However, levels of DDT and its metabolites are lower than those (740 µg.kg^{-1}, 997 µg.kg^{-1} and 19.6 µg.kg^{-1}) measured respectively in Lake Kariba in Zimbabwe [34], Ebrié lagoon in Ivory Coast [35] and Agbassiandi river in Togo [36]. Similar situation was also observed for α-HCH (16 µg.kg^{-1}) and lindane (11 µg.kg^{-1}) measured in sediments in Togo [36]. But, the values of total endosulfan found in this study are still comparable to those (44.4 16 µg.kg^{-1}) measured in sediments in Togo [36]. According to hese results, the sediments contamination by past use of organochlorine pesticides seems to be more favourable but endosulfan recent use in Niger River market gardening environment is not dismiss as this has been reported in scientific works carried out in Burkina Faso [37] and Senegal [38]. However, the contamination of sediments by these pesticides can be mainly related to the transport of these pesticides residues by agricultural waters drained from Korokoro watershed and also those from cotton fields of the watershed area (e.g. Bafinkabougou). Indeed, water can carry off active ingredients amounts by surface runoff process toward Niger River even if some parameters such as the topography of environment, vegetation cover etc., can be major obstacles to this type of carry off. Also, the accumulation of these pesticides residues in sediments may be due to their higher capacity of persistence and hydrophobicity in aquatic environments [39]. Therefore, the aquatic species survival of Niger River is worrying because of the acute toxicity of these organochlorine compounds. The organochlorine pesticides measured in sediments of Niger River are shown below in **Fig. 4.**

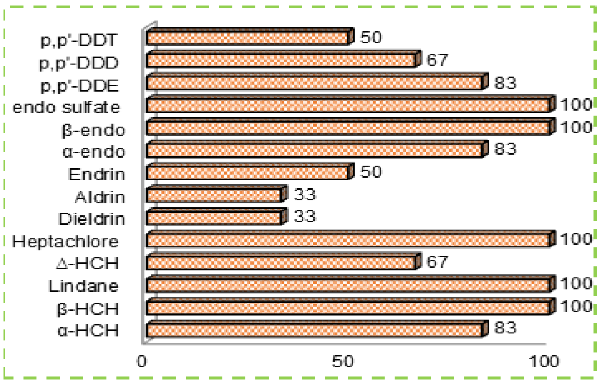

Figure 4. Detection frequency (%) of organochlorine pesticides measured in sediments of Niger River (i.e. in Bafinkabougou).

Conclusion

Surveys performed at Korokoro watershed and Bafinkabougou scale have shown that farmers used several pesticides families in cotton production.

However, experiments carried out in lysimeter boxes from 2010 to 2011 showed that the use of endosulfan in these both localities is able to contaminate surface and groundwater. But, the results obtained in 2010 confirmed exactly that surface water contamination by surface runoff is more likely than groundwater one by infiltration. Generally, these results are in perfect correlation with those found at Korokoro watershed and Niger River scale. Indeed, at Korokoro watershed outlet, the results obtained from 2010 to 2011 showed that agricultural waters drained from cotton fields were contaminated by endosulfan residues except for profenofos, cypermethrin and atrazine which were not detected although they were used in cotton production. At Niger River scale, contamination of water and sediments is the consequence of past and recent use of organochlorine pesticides in cotton production at the watershed and Bafinkabougou scale. Therefore, agricultural waters drained from Korokoro watershed and those from Bafinkabougou may be the main causes of this contamination. However, the occurrence of organochlorine pesticides in consume water and sediments is a potential risk for human and environmental health because of their degree of acute toxicity and bioaccumulation. Hence, the need for further research at Korokoro watershed and Bafinkabougou in order to sensitize farmers on the risks of human and environmental contamination by the use of organochlorine pesticides in agriculture as cotton growth. This can in long term reduce water and soil compartments contamination and also avoiding food products one.

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