



Water and soil compartments contamination by organochlorine pesticides in Malian cotton cropping system: experimental study in lysimeter boxes

A Maiga¹, D Diallo², H Blanchoud³, F Alliot³, A S Cisse¹ and M Chevreuil³

¹Department of Chemistry, Faculty of Sciences and Techniques, University of Sciences, Techniques and Technologies of Bamako.

²Rural Polytechnic Institute of Training and Applied Research.

³Laboratoire Hydrologie et Environnement, UMR Metis, Université Pierre & Marie Curie, 4, place Jussieu BC 105 75252 Cedex 05 Paris, France.

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ABSTRACT

Soil and water contamination by endosulfan, an organochlorine pesticide was experimented in lysimeters in 2010 and 2011. These lysimeters were filled in with alfisol brought from Korokoro watershed (60.6 km², Mali), a small agricultural one where cotton and cereals are the main crops. In the present experimentation, cotton was grown in lysimeters and treated with endosulfan which is frequently used in cotton production by some farmers although its agriculture use has been banned worldwide. After rainfall events subsequent to endosulfan application on cotton, runoff and infiltration were always sampled. Similarly, after each rainy season, composite soil samples were also collected in each lysimeter box. In 2010, soil samples were collected in surface horizon (0-20 cm) and depth one (20-40 cm) but in 2011, they were sampled in the whole soil profile about 1 m. Soils were analyzed by gas chromatography associated to a mass spectrometer at UMR Metis, Université Pierre et Marie Curie (France) but water ones were analyzed at University of Bamako (Mali). The results showed that soil and water are contaminated by endosulfan residues. Water contamination was mostly explained by runoff events in 2010 than 2011 ones ($6.5 \pm 2.9\%$ against $0.1 \pm 0.09\%$ of exported matters) but infiltration events in 2010 were low than those of 2011 ($0.1 \pm 0.09\%$ against $0.2 \pm 0.04\%$ of exported matters). However, in 2010 and 2011, endosulfan residues were more stocked in soil surface horizons ($22 \pm 15\%$ and $43.6 \pm 12.6\%$) than depth ones ($3 \pm 1.4\%$ and from $15.3 \pm 17.5\%$ to $28.5 \pm 24.8\%$).

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Introduction

In sub-Saharan Africa in particular Mali, agricultural development has conducted to an increasing use of chemical input such as pesticides. These practices can be one of the causes of water and soil compartments contamination of environment [1]. However, in the aim of global environmental protection, some scientists have performed experiments in controlled environment (as lysimeter boxes) and/or modeling studies to assess transferring possibilities of organic contaminants (as pesticides) towards surface and/or groundwater. Among these, experiments in lysimeter boxes have advantage to take into account all physico-chemical and biological processes relating to contaminants transfer phenomena but also to consider soil and climate parameters of studied environment. In addition, the lysimeter box can also facilitate further research on organic pollutants and also their contamination mechanisms. Through literature, we can observed that many scientific works were carried out on varied use of soil columns in order to evaluate pesticides potential to contaminate soil, surface water and groundwater [2-5]. Water resources in particular groundwater often intended for human consumption is contaminated by pesticides due to persistence and active substances transport through soil profile [6]. Indeed, various pesticides were detected in groundwater during the last 30 years in Europe [7-9], United States [10-12] and Africa [13-15]. However, experiments in laboratory or in controlled environment remain undeveloped in sub-Saharan Africa in particular Mali while water and soil compartments

contamination is a reality [16]. In this study, lysimeter boxes have been used to characterize vertical and horizontal transfer mechanisms of organic contaminants. That can contribute to understand soil and water contamination by pesticides at small agricultural watershed scale. Thus, the objective of this study is to study in lysimeter boxes the risk of water and soil compartments contamination by endosulfan (organochlorine pesticide) use in Malian cotton cropping zone.

Materials and methods

Lysimeter boxes

Three lysimeter boxes (3m x 1m x 1m) were installed on June 16, 2009 at Bamako University campus in order to study soil and water contamination by pesticides residues in controlled environment. The pedological material of these lysimeters is from an alfisol of the agricultural watershed of Korokoro (60.6 km², Mali) where cotton is cultivated since many decades (Table 1). Each box has two aluminum containers for respectively runoff and infiltration water collection. This experimental apparatus was completed with a rain gauge. In order to verify an eventual contamination of pedological material by pesticides (as endosulfan), a test was performed on each lysimeter box before experimentations. These tests consist to (i) rain simulation about two events in each lysimeter box respectively on July 4 and 7, 2009 with only runoff water collection and (2) runoff waters analyses with a gas chromatograph to search endosulfan and its metabolites. The results have not shown any contamination. That can be

Tele:

E-mail addresses: amaigaml2003@yahoo.fr

explained by the precautions which have been taken to avoid lysimeters filling with contaminated material.

Cotton cropping and endosulfan application in lysimeters

In 2010 and 2011, cotton has been grown in lysimeters in order to study soil and water compartments contamination by endosulfan (organochlorine pesticide) which agricultural use has been banned through the world but it is still used in cotton production by some Malian farmers as Korokoro watershed ones [17]. Thus, cotton seeds were sown in each lysimeter box respectively on July 10, 2010 and on August 6, 2011. In 2010, cotton plants have been treated with two endosulfan applications (250 mg per treatment): the first on August 28, 2010 and the second on September 11, 2010. But in 2011, only one endosulfan treatment about 1,000 mg has been applied on the cotton plants according to the low rainfall recorded this year and its consequence on cotton growing cycle. However, all agriculture practices (phytosanitary treatment, fertilizers application etc.) were referred to official recommendations in Malian cotton production area.

Water and soil sampling in lysimeter boxes

Soil and water were sampled after each rainy season (July-August) in order to assess their contamination level by endosulfan residues in 2010 and 2011. Thus, water samples were collected always in amber glass bottles after each rain event which had caused runoff and/or infiltration. Rainfall amount was also measured as runoff and infiltration volumes after each event. Measurements have started on August 28, 2010 and August 24, 2011 after endosulfan application on cotton in each lysimeter box. They have been spread on 8 and 5 rainfall events respectively in 2010 and 2011 for 36 and 21 collected water samples. However, all samples have not been analyzed by gas chromatography because of losses observed during sampling and storage. About soil compartment, in 2010, soil was taken on a square of side 10 cm and depth 10 cm to measure the apparent density. Thus, it was dried in an oven (Heraeus, instrument) at 105 °C for 24 hours and weighed with a balance (KERN 440-47). Six composites soil samples were also collected after the rainy season (March 13, 2011) respectively in surface horizon (0-20 cm) and subsurface one (20-40 cm) in order to measure endosulfan residues. But, in 2011, fifteen composites soil samples were sampled on the whole soil profile about 1 m in each lysimeter box and also soil apparent density has been measured in each 20 cm horizon (January 22, 2012). In laboratory, to ensure stability of endosulfan residues, soils were always frozen at -20 °C and water ones were also conserved in a refrigerator at 4 °C. Soil samples were transported each year from Bamako (Mali) to Paris (France) for analysis and water ones were analyzed at Bamako University.

Endosulfan residues analysis in soil and water

Water samples were analyzed in Laboratoire Central Veterinaire of Bamako (Mali) and soil samples were transported to Paris and were analyzed in Laboratoire Hydrologie et Environnement of UMR Metis at Université Pierre & Marie Curie (France). These matrices (soil and water) were subjected to endosulfan residues analyses.

Reagents and standards

Solvents, acetone, n-hexane, isooctane, diethyl ether and ethyl acetate were supplied by Sigma-Aldrich GmbH Laborchemikalien, as well as internal standards solutions (PCB 30/107, 10 ng.µL⁻¹ in isooctane) and the mix of 16 organochlorine pesticides (2000 ng.µL⁻¹ in hexane/toluene 1:1, (v/v), LGC Standards). PCB 30 and 107 were used as internal standard to quantify endosulfan and its metabolites (α, β and endosulfan sulfate). These standards were high purity (99.7% to

99.9%, Dr. Ehrenstorfer, GmbH) and all solutions were stored in a refrigerator at 4 °C.

Extraction and purification

In reference to (Tadeo and al, 2008; Li and al, 2010) [18, 19], 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.

However, three liquid-liquid extractions were performed on each 500 mL water sample of runoff and infiltration with 10% of hexane as extraction solvent according to [20]. Anhydrous sodium sulphate (Na₂SO₄) was added in each sample before filtered through filter paper. Then, filtrates were concentrated in 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 extracts were concentrated to 0.5 mL and completed to 1 mL with hexane then transferred into vial and analyzed with a gas chromatograph.

Chromatographic 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.min⁻¹. The injection volume was performed in splitless mode at 1 µL. Temperature program was set such as described by [21]. About the mass spectrometer, temperatures of source and quadrupole were respectively 230°C and 150°C, solvent delay was set at 5 minutes. Endosulfan residues were identified and quantified by internal standard calibration method. Linearity (r² > 0.997) was performed for each metabolite 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 [22].

But, water samples were analyzed with a gas chromatograph equipped with micro electron capture detector (GC-µECD). Capillaries columns used were HP-5 (length 30 m, 0.320 mm in diameter and 0.25 µm of film thickness) for analyses and DB-1701 for confirmation. Carrier gas (nitrogen) was high purity (99, 8%). The injection volume was set as

described above. Temperature program was established as follows, oven initial temperature was set at 80°C for 2 min, 80°C to 150°C to 25°C min⁻¹, 150°C to 200°C to 3°C min⁻¹, 200°C to 280°C to 8°C min⁻¹ and at 280°C for 10 minutes. Temperatures of injector and detector were respectively set at 250°C and 300°C. Endosulfan metabolites were identified and quantified by external calibration method. Linearity ($r^2 > 0.996$) was established for each product 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 standard deviation, slope, dilution factor and test volume for each pesticide standard.

Estimation of endosulfan residues in runoff, infiltration and soil by mass balance method

In this study, experiments in lysimeters aimed to understand dynamic of soil and water contamination by endosulfan. During experiments in 2010 (September 1-19), 8 rainfall events were recorded as well as 307 mm in total and 36 water samples but only 9 samples of 500 mL (6 of runoff and 3 of infiltration) of main rainfalls (September 1 and 19, 2010) were selected to be analyzed by gas chromatography in order to express first concentrations in runoff, infiltration and endosulfan exported quantities by rainfall events. Then, concentrations and quantities of exported matter of samples (volumes < 500 mL or lost, 27 in total) not analyzed by gas chromatography were estimated in order to optimize mass balances according to similar and previously scientific works carried out in lysimeters [23, 24]. However, in 2011 (from August 24 to September 13), 5 rainfall events were recorded with 110 mm in total and 21 water samples but only 7 samples (3 of runoff and 4 of infiltration) of main rainfalls (August 29 and September 03, 2011) were also analyzed as described above. Concentrations and quantities of exported matter of samples (14 in total) not analyzed by gas chromatography were estimated as in 2010. During experiments, it has supposed that endosulfan was degraded over time so, in runoff case, concentrations of water samples not analyzed by gas chromatography were calculated in 2010 and 2011 according to kinetic equation of first order:

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

with $C(T)$ = endosulfan concentration as a function of time (T), C_1 = concentration measured at the first sampling day, $K =$

proportionality coefficient and $K = \frac{\text{Log}(2)}{DT \ 50}$ ($DT50 = 86$ days, endosulfan half-life, PPDB, 2009). In infiltration case, concentrations were expressed according to mass law conservation.

However, in 2010, endosulfan residues have also been quantified in six composite soil samples collected respectively in surface horizons (0-20 cm) and depth ones (20-40 cm) but in 2011, they have been sampled in the whole soil profile about 1 m in each lysimeter box. Thus, exported quantities of endosulfan residues (µg) in runoff ($\sum Q_{ruis}$), infiltration ($\sum Q_{inf}$) and stock in soil ($\sum Q_{stock}$), were calculated and reported to applied quantities (Q_{appl}). Exportation processes by runoff and erosion are calculated by multiplying each calculated concentration (C_i) by runoff volume V_i ($n = 9$ and 8 respectively in 2010 and 2011):

$$\sum Q_{ruis} = \sum_{i=1}^n C_i \times V_i \quad (2)$$

As well as, quantities (µg) of exported matter by infiltration are calculated also by multiplying each calculated concentration

(C_i) by infiltration volume V_i ($m = 18$ and 6 respectively in 2010 and 2011):

$$\sum Q_{inf} = \sum_{i=1}^m C_i \times V_i \quad (3)$$

Quantities (µg) of stock matter in lysimeters soil are calculated based on endosulfan contents T (µg.kg⁻¹) in soils analyzed, horizons ($H = 0.2$ m), lysimeters surface ($S = 3$ m²) and soil apparent density d (kg.dm⁻³):

$$\sum Q_{stock} = \sum_{i=1}^k T \times H \times S \times d \quad (4)$$

where k is the number of composite soil samples collected ($k = 6$ and 15 respectively in 2010 and 2011).

Results

Endosulfan residues in runoff and infiltration samples

During experimentation in 2010, the main rainfall events recorded were 52.5 mm, 101.4 mm, 37.8 mm and 28.2mm. They were respectively measured the fourth, sixth, seventh and eighth day after the first endosulfan application on cotton (August 28, 2010) and were also followed by another one (62 mm) occurred on the eighth day after the second treatment (September 11, 2010) (**Fig.1**). However, estimated concentrations of endosulfan were calculated according to the method described above. Thus, high concentrations of endosulfan residues were more obtained in runoff samples than infiltration ones. After the rainy season and according to mass balance calculation, matter quantities exported by runoff and infiltration are respectively $6.5 \pm 2.9\%$ and $0.1 \pm 0.09\%$. Concentrations distribution and matter quantities measured in analyzed samples (9 in total) by gas chromatography are mentioned in **Table 2**.

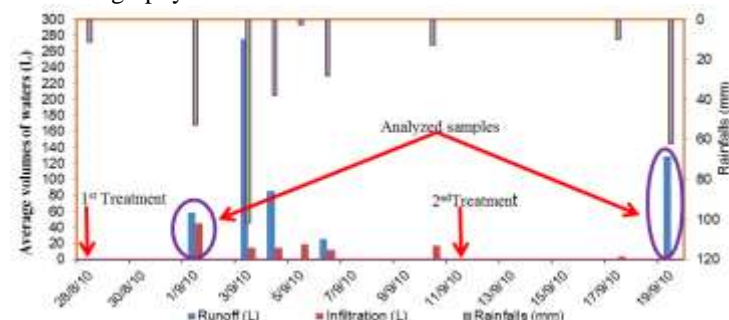


Figure 1: Daily rainfall distribution, runoff and infiltration volumes, endosulfan application period on cotton and samples analyzed (cropping season in 2010)

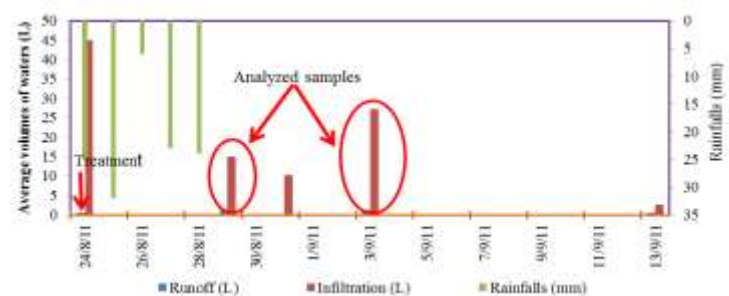


Figure 2: Daily rainfall distribution, runoff and infiltration volumes, endosulfan application period on cotton and samples analyzed (cropping season in 2011)

But, in 2011 experiments, the rainfalls recorded (110 mm in total) were lower than 2010 ones (307 mm in total) although some quantities (25, 32 and 24 mm) were measured respectively the first, fifth and tenth day after endosulfan application on cotton (August 24, 2011) (**Fig. 2**).

Table 1. Some properties of Alfisol under cotton cropping in Korokoro watershed (Mali)

Horizons	App density (gcm ⁻³)	Clay (<2µm)	FS (%)	CS (%)	FS (%)	CS (%)	OC (%)	OM (%)	Total P (mg.kg ⁻¹)	pHwater	pHKCl	P (%)	K (m.s ⁻¹)
0-20 cm	1.3	11.3	19.1	26.4	16.3	26.9	1.3	2.3	255	6.2	5.5	50.9	5.8.10 ⁻⁶
20-45 cm	1.4	28.6	7.7	23.6	14.7	25.5	1.0	1.7	233.8	4.9	4.8	47.2	
45-100 cm	1.5	32.8	7.2	24.2	12.5	23.4	0.9	1.6	212.5	5.0	4.8	43.4	

OC = organic carbon ; OM = organic matter ; K(m.s⁻¹)= permeability studied only in surface horizon (0-20 cm) ; FS = fine silt ; CS = coarse silt ; FS = fine sand ; CS = coarse sand ; Total P = total phosphorus ; P (%) = porosity ; App density = apparent density

Table 2. Concentration of endosulfan (α, β and endosulfan sulfate) in analyzed samples (cropping season in 2010)

Samples analyzed date		Runoff			Infiltration		
		lysimeter 1	lysimeter 2	Lysimeter 3	Lysimeter 1	lysimeter 2	lysimeter 3
	After the first treatment						
	Water Volumes (L)	26.5	90	58.8	45	45	45
Sept 1 st , 2010	Concentration (µg.L ⁻¹)	25	85.1	100	1.8	0.2	2.2
	Quantity (µg)	662.5	7659	5880	81	9	99
	After the second treatment						
Sept 19, 2010	Water Volumes (L)	127	121	139	-	-	-
	Concentration (µg.L ⁻¹)	7.3	2.9	12.3	nm	nm	nm
	Quantité (µg)	927.10	350.90	1709.70	nm	nm	nm

The sign - means that no infiltration; nm = not measured

Table 3. Concentrations of endosulfan (α, β and endosulfan sulfate) in samples analyzed (cropping season in 2011)

Samples analyzed date		Runoff			Infiltration		
		lysimeter 1	lysimeter 2	Lysimeter 3	lysimeter 1	lysimeter 2	Lysimeter 3
August 29, 2011	Water Volumes (L)	-	-	-	76*		
	Concentration (µg.L ⁻¹)	nm	nm	-	20.6		
	Quantity (µg)	nm	nm	-	1566.4		
Sept 03, 2011	Water Volumes (L)	0.9	2	1.4	30	32	20
	Concentration (µg.L ⁻¹)	nd	93.9	nd	20.6	8	18
	Quantity (µg)	nd	190	nd	616.8	255.7	360

* = infiltrated samples mixture; nd = not determinate; nm = not measured; the sign - means no runoff

In contrast, low concentrations of endosulfan residues were measured in runoff and infiltration water samples (Table 3). According to mass balance established, quantities of exported matter by runoff and infiltration are respectively $0.1 \pm 0.09\%$ and $0.2 \pm 0.04\%$.

Endosulfan residues in soil

In 2010, measurements of endosulfan residues show more quantities in surface horizons of lysimeters 1 and 2 than lysimeter 3. In the two first lysimeters, quantities of top horizons were higher than the sub-horizons ones except in lysimeter 3. According to mass balance calculation, contents were more accumulated in surface horizons (0-20 cm) than depth ones (20-40 cm) and values measured in these horizons are respectively $21.9 \pm 14.8\%$ and $2.8 \pm 1.4\%$ (Fig.3). However, matter quantities lost either by volatilization or degradation or retained in soil and unextractable were estimated at $68.6 \pm 14.9\%$.

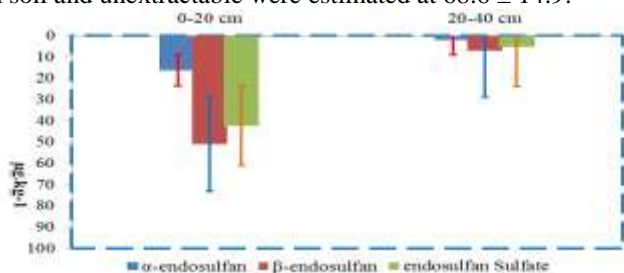


Figure 3: Endosulfan average contents in surface horizons (0-20 cm) and depth ones (20-40 cm) (cropping season in 2010)

In 2011, according to low rainfalls recorded (110 mm), endosulfan residues were more measured in lysimeters soils than in 2010. However, in the whole soil profile about 1 m, its contents were variable but more stocked in surface horizons than depth ones and according to mass balances established, these quantities range from $43.6 \pm 12.6\%$ (horizons of 0-20 cm) to $8.6 \pm 6.9\%$ (horizons of 80-100 cm) (Fig.4). As well as matter quantities lost either by volatilization or degradation or retained in soil and unextractable were estimated at $28.5 \pm 24.8\%$.

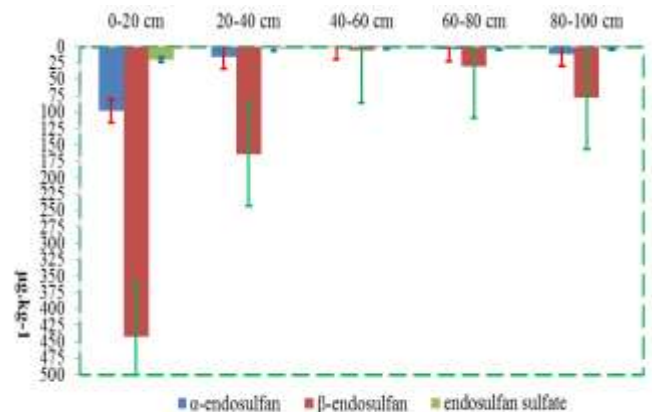


Figure 4: Endosulfan average contents distribution in the whole soil profile about 1 m (cropping season in 2011)

Discussions

Endosulfan occurrence in runoff and infiltration

In 2010 experiments, the results showed that endosulfan residues were more transported by runoff ($6.5 \pm 2.9\%$) than infiltration ($0.1 \pm 0.09\%$). This can mean that endosulfan exportation by water is rather than related to runoff than infiltration process. This water contamination by runoff process can be mainly due to some parameters such as slaking crust, low slope and low vegetation cover of cotton plant in lysimeters. Indeed, after the first and second endosulfan application on cotton (August 28, 2010 and September 11, 2010), according to the significant rains which were followed and the raindrops impact on the soil aggregates, these factors can favor slaking crusts formation which consequently can reduce soil infiltration capacity and the roughness. Thus, soil surface becomes smooth and impermeable [25-27]. This phenomenon can therefore limit infiltration and favor runoff. What can explain the higher concentrations of endosulfan in runoff samples than infiltration ones. These concentrations observed may also be due to the fact that after endosulfan application on cotton, this pesticide can also reach the soil and be adsorbed on fine soil particles and according to these significant rainfall events, it can be transported by runoff. In contrast, the low rains recorded in 2011 have rather than contributed to reduce runoff and infiltration processes so that they have not allowed to properly following endosulfan transport by runoff or infiltration. Endosulfan residues were so lowly estimated in runoff ($0.1 \pm 0.09\%$) and infiltration ($0.2 \pm 0.04\%$) according to mass balance established and this can so explain the low concentrations levels obtained in water samples. However, in a context of Sahelian climate in particular Mali, the results of this study are different from those obtained in regions of temperate climates or Mediterranean but they nevertheless remain comparable to similar and previous scientific works carried out [28, 29].

Endosulfan occurrence in soil

Experiments carried out in 2010 and 2011 have highlighted soil compartment contamination by endosulfan residues. According to mass balances calculation, endosulfan residues are more accumulated in surface horizons than depth ones. This can be explained by several factors including organic matter content.

Indeed, better organic matter presence in surface horizons can be the source of endosulfan adsorption in these horizons [30, 31]. This adsorption can therefore explain endosulfan residues stock in soil surface horizons of lysimeters. This accumulation can also be due to physico-chemical properties of this pesticide. Indeed, endosulfan as organochlorine pesticides is very persistent in soil [32]. However, its contents in depth horizons can also mean that it can be mobile in soil and this mobility seems to be favored by soil moisture and this can contribute to contaminate groundwater. Thus, at agricultural watershed scale, the use of endosulfan can cause soil compartment contamination and also groundwater.

Conclusion

Experiments carried out in lysimeter boxes in 2010 and 2011 have allowed to highlight the risk of soil, surface water and groundwater contamination by endosulfan. In 2010, endosulfan residues were more transported by runoff than infiltration according to significant rainfall events occurred after the first and second application of this pesticide on cotton. Thus, a possible water contamination by runoff appears to be more favorable compared to infiltration. But, the low total rainfall recorded in 2011, have not clearly favored the contamination process by runoff and infiltration. However, soil compartment was contaminated by endosulfan residues which rather than tend to be accumulating in surface horizons than depth ones. In sum,

these results confirm that endosulfan use in agriculture can be a source of water and soil compartments contamination. There is so a research further need for better comprehension on water and soil compartments contamination by pesticide transfer dynamic in lysimeter boxes.

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