

Spatial Availability of Nitrogen and Pesticides in the Surface Layers of Agricultural Soils of Tropical Hydrosystems in the Wet Season: Case of the Béré Watershed in Côte d'Ivoire (West Africa)

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Abstract

The objective of this study was to assess the contribution of the spatial organization of cropping systems and the physicochemical properties of surface layers of the agricultural zones soils in tropical hydrosystems to the spatial availability of nitrogen and pesticides during the wet season, such as the Béré watershed (BW) in Côte d'Ivoire. For this purpose, after mapping the spatial distribution of the BW cropping systems based on the likelihood classification methodology of satellite images of the study area, 27 samples from the 0 - 20 cm horizon of the soil surface layers of the agricultural areas were taken during the wet and agricultural season of the year 2016. The Kjeldahl method has been used to evaluate the total nitrogen concentration and high-performance liquid chromatography (HPLC) chain made it possible for the analysis of pesticide residues in the soil solutions. Geostatistical analysis and processing of spatial data and physicochemical and agrochemical soil parameters revealed that two major agricultural areas stand out in the BW, namely the Béré upstream watershed (BUW) dominated at 32.65% by annual croppings (maize, cotton, rainfed or lowland rice, market gardening, etc.) and the Béré downstream watershed (BDW) by large areas of perennial croppings (cashew nuts, cocoa, etc.), *i.e.* 21.47%. Agricultural soils in BW are usually of the moderately desaturated ferralitic type with a low acid pH and a quite strong temperature, such as those of tropical soils' characteristics. However, agricultural soils in the BUW are cha-

racterized by higher proportions of sand and coarse sand. The parameters such as total porosity, cation exchange capacity, clay, organic matter, silt, fine silt, coarse silt, and potassium ions, are higher in the soils of the agricultural area of the BDW. Moreover, soils in the agricultural areas of the BUW are less rich in total nitrogen ($0.84 \text{ g}\cdot\text{kg}^{-1}$) in contrast to those of the BDW ($1.2 \text{ g}\cdot\text{kg}^{-1}$). On the other hand, the median concentrations of total pesticides remain very high in the BUW ($193.80 \text{ }\mu\text{g}\cdot\text{kg}^{-1}$) in front of those of the BDW ($94.81 \text{ }\mu\text{g}\cdot\text{kg}^{-1}$). In addition, the biological family of herbicides was the most notable in BW. The chemical families of triazines (100% detection; $79.37 \text{ }\mu\text{g}\cdot\text{kg}^{-1}$) are the most important in the agricultural area of the BUW with the very significant presence of active molecules of pesticides such as simazine (92.86% detection; $13.17 \text{ }\mu\text{g}\cdot\text{kg}^{-1}$). However, in the BDW, urea substitute (100% detection; $44.02 \text{ }\mu\text{g}\cdot\text{kg}^{-1}$) dominate, including the active substance chlortoluron (84.62% detection; $10.12 \text{ }\mu\text{g}\cdot\text{kg}^{-1}$). The presence and abundance of nitrogen and pesticides in the soils of the agricultural areas of BW are strongly linked to the intensive use of these agrochemicals in cropping systems in recent decades in West African countries, even though most of the active molecules found are forbidden in several countries, especially in European countries. These are applied to tropical agricultural soils with physico-chemical characteristics favorable to their retention in wet weather, as confirmed by the case of BW's agricultural soils. Therefore, the BW's water resources present worrying risks of contamination during rainy events that deserve to be assessed and monitored. Hence the need to take mitigating measures to this effect in order to preserve the quality of the environment.

Keywords

Agrochemical Products, Soils Contamination, Water Resources Pollution, West Africa Tropical Hydrosystems, Béré Watershed, Côte d'Ivoire

1. Introduction

In recent decades, in addition to the expansion of cropping systems, most modern methods of cropping protection in the world and especially in West Africa have increasingly relied on the use of plant protection products and chemical fertilizers for rapid development and an increase in agricultural production to meet the food needs linked with high population growth in developing countries [1] [2] [3] [4] [5]. However, the intensive use of agrochemicals in agriculture poses a serious medium-term threat to the quality of the environment and health risks [6] [7] [8] [9]. Indeed, the soils of hydrosystems constitute the compartment of the environment that is heavily contaminated by these agrochemicals, even though they constitute the interface of interactions with other compartments of the environment [10] [11] [12]. In addition, water resources and food products, especially those in developing countries in West Africa that do not have permanent quality monitoring, remain the environmental

compartments most exposed to the increasing contamination of soils by nitrogen and pesticides [13]-[19]. On the other hand, the transfer of these agricultural pollutants to the water resources of a catchment area appears to be more important during flood periods, in both dissolved and particulate form, depending on several control factors [20] [21] [22]. In Côte d'Ivoire, according to the Ministry of Agriculture and Rural Development [23], the agricultural sector plays a major role in the national economy, accounting for around 27% of Gross Domestic Product (*GDP*) and provides employment for two-thirds of the working population. Although recent, the development of this sector and the desire to increase yields has led to intensive use of nitrogen fertilizers and plant health products in recent years. This situation also raises many concerns about the quality of the environment and the health exposure of the population [24] [25] [26] [27] [28]. In addition, several studies carried out recently using multi-criteria spatial analysis methods showed the vulnerability and risk of widespread diffuse pollution of soil and water resources by nitrates and pesticides [29] [30] [31]. The studies carried out by [32] have therefore identified the Béré watershed (BW) as an area with a high potential risk of surface water pollution by nitrate and pesticides. Thus, in view of this worrying situation, it was necessary to ensure the quality of BW's soils in order to take measures to prevent environmental risks linked to the contamination of water resources by diffuse agricultural pollution. To this end, the public authorities needed to know the level of contamination of the agricultural soils of BW by nitrogen and pesticides. This included understanding the conditions that would facilitate or limit the contamination of soil and water in tropical hydrosystems during the wet season. Consequently, this work is of great interest and constitutes a prerequisite for good preservation of the environment through proposals for more rational use of these agrochemicals in the agrosystems of developing countries. It is with this in mind that this study was initiated in order to assess the contribution of the spatial organization of cropping systems and the physicochemical characteristics of the surface layers of soils in the agricultural zones of tropical hydrosystems to the spatial availability of nitrogen and pesticides in wet season soils such as the BW in Côte d'Ivoire. More specifically, the aim was to 1) establish the spatial distribution of the agricultural areas of the BW; 2) characterize the physicochemical parameters of the soil surface layers of the agricultural areas; 3) establish the spatial distribution of the concentrations of total nitrogen and pesticides available in these areas; 4) determine the influence of the spatial distribution of cropping systems and the physicochemical properties of the soils of the agricultural areas of the BW on their availability of total nitrogen and pesticides.

2. Materials and Methods

2.1. Study Area Data

The Béré watershed (BW) is an agro hydrosystem located in the central-western

part of the Republic of Côte d'Ivoire, precisely on the right bank of the Marahoué River, which is an affluent of the great Bandama River. The BW is located between longitudes 143,594.39 - 188,848.55 m East and latitudes 834,843.247 - 960,487.927 m North according to the UTM projected geographic coordinate system of Zone 30 North WGS 84 (**Figure 1(A)**). Indeed, the BW covers an area of 3610.56 km² with a perimeter of 376.63 km and a relief that is not very uneven (191 - 461 m). The Béré River is the main permanent watercourse with its outlet located at longitude 1,615,527.98 m East and latitude 834,927.851 m North. The BW is in a tropical climate of transition between equatorial and sub-Saharan climate. According to the analysis of rainfall data from 1951 to 2016, the average annual rainfall on the BW is estimated at 1197.675 ± 12.80 mm (**Figure 1(B)**). The highest average annual rainfall (1205.360 - 1215.077 mm) is observed in the north-western and central-western parts of the BW with an average temperature of 17.445°C. While the lowest rainfall (1160.021 - 1174.055 mm) falls in the South with an average temperature of 22.50°C. The overall rainfall trend has been drier since 1960. In addition, a large rainy season is observed from April to October in BW followed by a large dry period from November to March. In the BW, the soil is essentially composed of ferralitic soils that are moderately desaturated, with hydromorphic soils in places [33] resulting from the alteration of a geological context dominated by heterogeneous granitoids with biotites, schist and Grauwackes flyschist formations and sub-alkaline granitoids with two (2) mica [34] (**Figure 1(C)**, **Figure 1(D)**). According to the National Institute of Statistics (INS), the BW has a population of more than 357,000 inhabitants, 65% of whom are young people in the 6 to 40 age group [35]. These young people, therefore, constitute a significant part of the local workforce for the development of the economy of this Region, which is essentially based on agricultural activities.

2.2. Spatial Characterization of Béré Watershed Cropping Systems

The spatial characterization of the cropping systems of the Béré watershed (BW) has been obtained following the elaboration of the land use map from satellite images of Landsat 8 OLI-TIRS 197-54 and 197-55 scenes from January 05, 2017, with a resolution of 30 m. To do this, these scenes were first pre-processed, including radiometric calibrations and rapid atmospheric corrections, before being mosaiced into a single image on which the likelihood classification methodology was applied under the ENVI software as followed by several researchers [32] [36] [37] [38] [39] [40]. In addition, at the end of the supervised classification, a confusion matrix was developed in order to obtain clarification on the treatment and to validate the choice of training areas. This is the Kappa coefficient and the Overall Accuracy coefficient of treatment. Thus, the BW land use and occupation map was drawn up and exported under the ArcMap of ArcGIS software for the continuation of the spatial analyses and treatments used for the spatial characterization of the BW cropping systems.

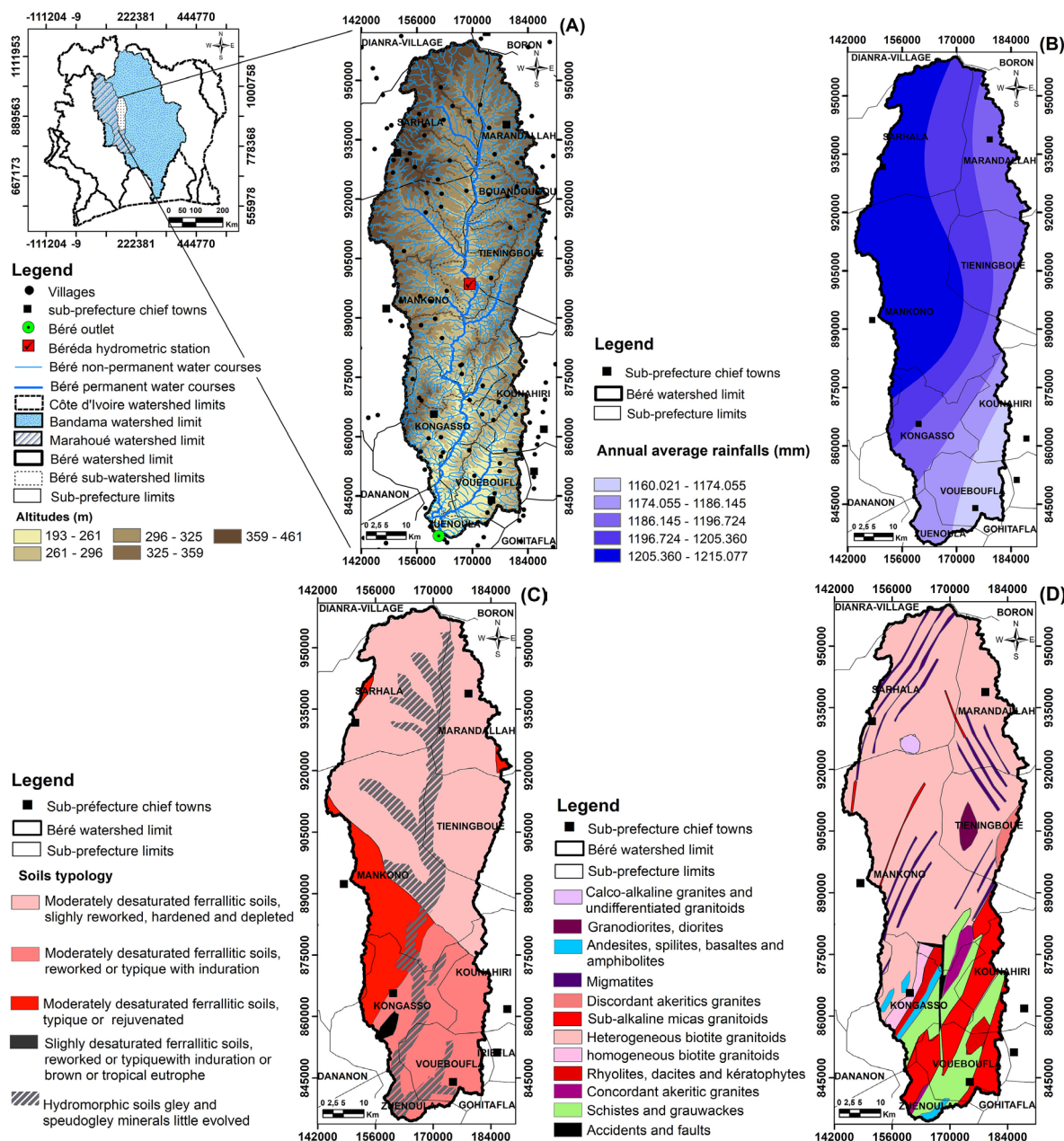


Figure 1. Béré watershed (BW) environmental data: Geolocation, altitudes and hydrographic network (A), Annual average rainfalls (B), Digitalized soil sketch (C) and Digitalized geologic sketch (D).

2.3. Agricultural Soils Sampling

The stratified random stratified exploratory sampling method was applied at the Béré watershed (BW) scale [11] [41] (Figure 2(A)). In fact, according to the “Law of the Quart” adopted by the [42] and [43], the area encompasses the Béré watershed (BW) has been stratified by a regular mesh of 14×15 km (210 km^2) representing about 6% of its total surface area (3610.56 km^2). Thus, a reduced number of 27 meshes integrating the boundaries of the BW could be visited (Figure 2(B)). However, depending on accessibility and cropping speculations, 27 cultivated plots could be identified using a GARMIN Etrex 30 Global Posi-

tioning Satellite (*GPS*) device for the systematic mixed sampling of 27 composite soil samples during the wet season agricultural period of the year 2016. These were made up of 9 simple samples from the surface layers at depths of 0 - 20 cm from separate sampling sites adapted to the size of the agricultural plot using a decameter [44] [45] (**Figure 2(C)**). On average, a mass of around 0.5 kg of composite soil samples was obtained using a manual 50 cm auger with a regular mesh size adapted to the size of the agricultural plot. In addition, all the BW soil samples obtained were packed in coded polystyrene plastic bags, then wrapped in aluminum foil, and packaged to be taken to the laboratory in accordance with NF ISO 10381-1 to 2 standards. In accordance with these standards, the soil samples taken from the plots of land were kept in the ambient air for a maximum of one month before being analyzed by a physicochemical laboratory.

2.4. Analysis of Physicochemical Parameters, Nitrogen and Pesticides of the Agricultural Soils

The Physicochemical parameters of the composite soil samples from plots in the agricultural zones of the Béré (BW) catchment area analyzed in the laboratory are granulometry, total porosity, temperature, exchangeable bases Sodium (Na^+), Calcium (Ca^{2+}), Potassium (K^+), and Magnesium (Mg^{2+}), hydrogen potential (pH), cation exchange capacity (CEC) and organic matter. The granulometric analysis was carried out using the Robinson pipette method according to the NF X31-107 standard. Following the determination of the granulometric composition of the soils, a textural classification of the soils was carried out according to the United States Department of Agriculture (*USDA*) Texture Triangle [46].

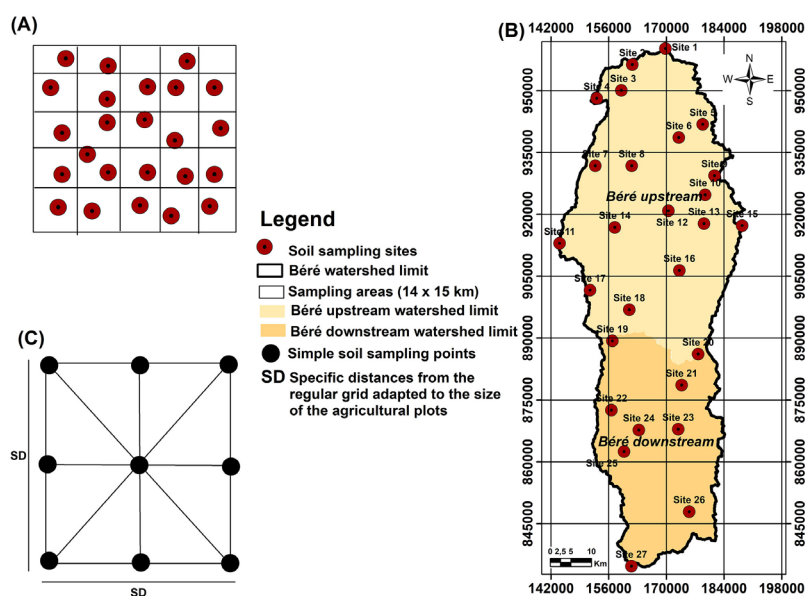


Figure 2. Ofsampling plan of surface layers 0 - 20 cm of agricultural Béré watershed (BW): Probabilistic sampling plan of the stratified random type (A), Stratified random distribution of the composite soil sampling sites in the 14 × 15 km grid (B) and Arrangement of the points sampling simple soil in a regular grid adapted to the size of the agricultural plots (C).

The total porosity was determined by the method of water saturation of the soil sample in accordance with the international standard NF ISO 5017. Soil temperatures and pH were measured automatically in-situ using a Cobra 4 PHYWE multi-parameter thermal probe according to the international standard NF ISO 10390. The concentrations of the exchangeable bases Na^+ , Ca^{2+} , K^+ and Mg^{2+} in the various soil samples were obtained from the atomic absorption spectrometer reading of the extractant solution of the exchangeable bases followed by determination of the cation exchange capacity of the various soils by the Metson method according to the NF X 31-108 standard. The analysis of organic carbon was carried out according to the international standard NF ISO 10694. The organic carbon content obtained made it possible to evaluate the concentration of soil organic matter according to Equation (1).

$$\text{MO} = 1724 \times \text{COrg} \quad (1)$$

where, MO: Organic Material ($\text{g}\cdot\text{kg}^{-1}$); COrg: Organic Carbon ($\text{g}\cdot\text{kg}^{-1}$).

The Kjeldahl method according to the international standard NF ISO 13878 made it possible to evaluate the total nitrogen concentration of the soils. In addition, the ratio of the carbon (C%) and nitrogen (N%) contents made it possible to determine the C:N ratio. Concerning pesticides, the first step consisted of preparing soil samples after adding a dichloromethane solution to the soil grind sieved at $250\ \mu\text{m}$. The dry residue obtained after soil preparation was recovered in a flask following a liquid-liquid/solid-liquid extraction by mechanical agitation with methanol before passing to the purification phase of the extract of the residue recovered on C18 (18 carbon) cartridges mounted on a rotary evaporator (BUCHI) equipped with a pressure controller (V-880), a Rotavapor (R-15), a water bath (B-491) and a vacuum pump (V-700) to concentrate the solutions extracted from the soil samples [47]. In order to do this, the eluates are collected in different vials for injection and quantification. The chromatographic conditions that allowed the identification and quantification of the pesticide molecules are as follows: Column type: Shim pack VP-ODS ($250\ \text{L} \times 5\ \text{mm}$); Injection volume: $20\ \mu\text{l}$; Flow rate: $20\ \mu\text{l}/\text{min}$; Mobile phase: 80% acetonitrile and 20% H_2O ; Elution mode: Isocratic; Wavelength (λ): Emission (254 nm) and Extraction (205 nm); Final time: 56 mn. Standard solutions (Standards) of most of the pesticides had been previously prepared and then injected several times in the SHIMADZU type HPLC composed of a tank (TRAY), a degasser (DGU-20A5), an automatic sampler (SIL-20A), a type oven (CTO-20A) and a UV/VIS detector (SPD-20A), a pump (LC-20AT). This allowed calibration from the surfaces or peak heights and retention times of the recorded standards using a computer equipped with LC Solution software. After calibration, the samples has could be injected and quantified in the SHIMADZU type high-performance liquid chromatography (HPLC) chain by observing the chromatogram of pesticide residues obtained in the analyzed soil solutions. Final time: 56 mn. Based on the retention time and concentration in comparison with the chromatogram of the standard (Standard), the presence or absence of pesticide active substances from the chemical families sought in the BW samples was determined. A substance identified during the analysis of the samples corresponds

to the substance of the calibration (Standard) if and only if both substances have the same retention time. The detection and quantification limits for the chemical families of pesticides sought in solid matrices are 0.01 and 0.032 $\mu\text{g}\cdot\text{kg}^{-1}$ for organophosphates and chloroacetamides respectively; 0.007 and 0.022 $\mu\text{g}\cdot\text{kg}^{-1}$ for organochlorines, alkylchlorophenoxys, phosphonoglycines, carbamates, urea substitute, phenylurea, triazines, and oxazoles; 0.012 and 0.039 $\mu\text{g}\cdot\text{kg}^{-1}$ for pyrethroids.

2.5. Data Processing

The univariate statistical analyses of the data in this study consisted first of all of the normality tests following the Shapiro-Wilk test and comparison tests using the Kruskal-Wallis and Mann-Whitney U tests on the data spread over the two agricultural areas of BW. Also, the median values and ranges (minimum and maximum) of the data from the samples as well as the detection frequencies of active pesticide materials were determined. All statistical tests, calculations, and graphical analyses were carried out using the R software. Also, multivariate statistical analyses were carried out. A Principal Component Analysis (*PCA*), using the R software, was applied to discriminate the relationships between the physicochemical properties of soils in the agricultural areas of BW. The effect of environmental factors on nitrogen and pesticide abundance was analyzed using Redondance Analysis (*RDA*). To do this, the relevance of this analysis was verified using a Monte-Carlo permutation test on 499 random permutations. In order to reduce the amplitude of the fluctuations and ensure the linearity of the relationships between the variables, the pollutant densities (*X*) were subjected to a logarithmic transformation and then expressed in $\log(X + 1)$. The Redondance Analysis (*RDA*) was performed using CANOCO software. Inverse Distance Weighting (*IDW*) was used for the spatial analysis of data for the whole Béré watershed (BW) [41]. Thus, the estimate of the spatial variable was calculated using the values of 12 control points measured in the vicinity and assigning them weight as a function of distance (Equation (2)). In addition, the IDW method provides iso-values classes in a circular manner around the observation points during spatial interpolation but retains the integrity of the nominal values of the attributes obtained during laboratory analysis for each of the sampled points. The spatial interpolations of the variables according to the IDW method were performed using the ArcGIS software.

$$Z(S_n) = \sum_{\alpha=1}^n \omega_{\alpha} Z_{\alpha} \quad (2)$$

where, $Z(S_n)$: Estimated value at coordinates (x_n, y_n); α : Number of support points selected; ω_{α} : Weight assigned to the control point Z_{α} for example, proportional to $1/d, 1/d^2, \dots, 1/d^n$, where d is the distance between $Z(S_n)$ and Z_{α} ; Z_{α} : Value of attribute of the control point.

Moreover, the overall indicator of validation of interpolated data used in this study is the Root Mean Square Error (*RMSE*) [10] [41]. *RMSE* is the difference between the estimated value and the measured value at a few points in the domain (Equation (3)). To overcome difficulties in interpreting the values, the *RMSE* has been normalized to be expressed as a percentage of the mean value of

the observations.

$$\text{RMSE} = \frac{1}{Z_m} \sqrt{\frac{1}{n} \sum_{k=1}^n (Z'(X_k) - Z(X_k))^2} \quad (3)$$

where, Z_m : Average value of the measured points; n : Number of measured values whose values are estimated; $Z'(X_k)$: Estimated point value X_k ; $Z(X_k)$: Measured point value X_k .

3. Results and Discussion

3.1. Results

3.1.1. Spatial Distribution and Characteristics of Béré Watershed Cropping Systems

The Béré watershed (BW) land-use map (LU) of January 2017 presented by **Figure 3** displays 07 classes with variable surface proportions for a global classification precision of 80.26% and a Kappa coefficient of 73.95%. In fact, almost half of the BW territory (45.9%) was made up of large farming areas divided into two distinct large farming areas, the Béré upstream watershed (BUW) (30.14%) and the Béré downstream watershed (BDW) (15.76%) in the agricultural zone of the BUW (Marandallah, Sarhala, Tiéningboué, and Mankono), the majority of the agricultural exploitations of annual types (maize, cotton, rainfed or lowland rice, market gardening, etc.) were developed, *i.e.* about 32.65% of its 2268.85 km² surface area. However, in the agricultural zone of the BDW (Kongasso, Kounahiri, Vouéboufla, and Zuenoula), one finds mainly large areas of perennial croppings (cashew nuts, cocoa, etc.) representing 21.47% of its surface area of 1340.46 km².

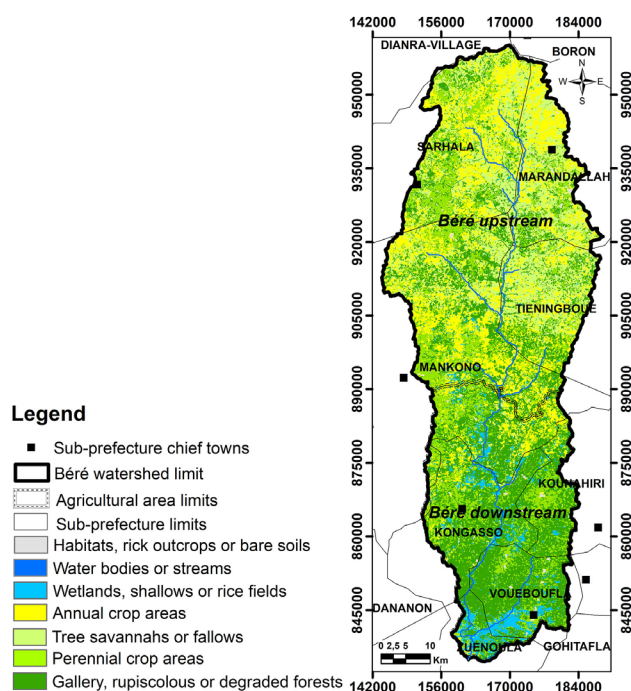


Figure 3. Béré watershed (BW) land use map from the scenes 197-54 and 197-55 of the Landsat 8 OLI-TIRS satellite images of 30 meters resolution of January 05, 2017.

3.1.2. Spatial Distributions of Physicochemical Parameters in the Surface Layers of Béré Watershed Agricultural Areas Soils

The analysis of the physicochemical parameters of the soils in the agricultural areas of the Béré watershed (BW) has made it possible to characterize the aptitude of the surface layers of these soils for the retention and/or transfer of nitrogen and pesticides in the wet season. The values of the physicochemical parameters of the agricultural soils of the BW do not differ significantly from one station to another (Kruskal-Wallis test; $p > 0.05$). Thus, the values of these parameters were grouped into agricultural zones, Béré upstream watershed (BUW) and Béré downstream watershed (BDW), in order to assess the different inter-zone fluctuations (**Figure 4**). **Figures 4(A)-(C)** show spatial variations in the proportions of clays, silts, and sands, respectively, in the 0 - 20 cm horizon of soils in the agricultural areas of the BW. Overall, the median clay, silt, and sand contents of soils in the agricultural areas of BW respectively between 6.50% to 38.49%, 2.28% to 26.23%, and 36.3% to 87.69% with Root Mean Square Error (RMSE) spatial interpolations of 4.11%, 5.84%, and 2.74% respectively. The soils of the agricultural zone of the Béré downstream watershed (BDW) present median contents of clays (30%) and silts (15%) more important notably in the southern part in Vouéboufla and Kounahiri where the ranges of variations of clays (31.21% - 38.49%) and silts (20.60% - 26.23%) were observed the highest. On the other hand, the agricultural area of the Béré upstream watershed (BUW) concentrates a higher median proportion of sands (76%) especially in Sarhala and Marandallah (75.40% - 87.89%). The comparison test of U Mann-Whitney shows a significant difference between the clay, silt, and sand contents of the BUW and BDW soils ($p < 0.05$). Thus, the soils in the agricultural area of the BUW have a silty-sandy texture and those of the BDW correspond to the silty-clay-sandy texture. The total soil porosities of the agricultural areas of the BW range from 29.41% - 37.49% with a spatial RMSE interpolation of 0.29% (**Figures 4(D)**). Soils in the BUW agricultural area are less porous (32.9%) with more minimal total porosity values located in the Sarhala, Mankon, and Marandallah area (29.41% - 32.93%). The maximum porosities are recorded in the agricultural soils of Vouéboufla, Kounahiri, and Zuenoula localities (34.29% - 37.49%) of the BDW agricultural zone which presents more porous agricultural soils with a median value of total porosities of 34.7%. The Mann-Whitney U Test at $p < 0.05$ shows that there is a significant difference between the total porosities of the two agricultural areas of the BW. Temperatures in the 0 - 20 cm horizon of the soils in the agricultural areas of the BW range from 17.30°C to 29.89°C (RMSE = 0.30%) (**Figures 4(E)**). The highest agricultural soil temperatures are noted in Mankono (24.86°C - 29.89°C) while the lowest is found in Sarhala (17.30°C - 23.22°C). The median agricultural soil temperature in BDW is 24.40°C and that of BUW is 22.05°C. However, the median temperatures of the agricultural areas of the BUW do not differ significantly from each other according to the Mann-Whitney U-Test whose significance value $p > 0.05$. **Figure 4(F)** shows the spatial distribution of the hydrogen potentials (pH) of the 0 - 20 cm

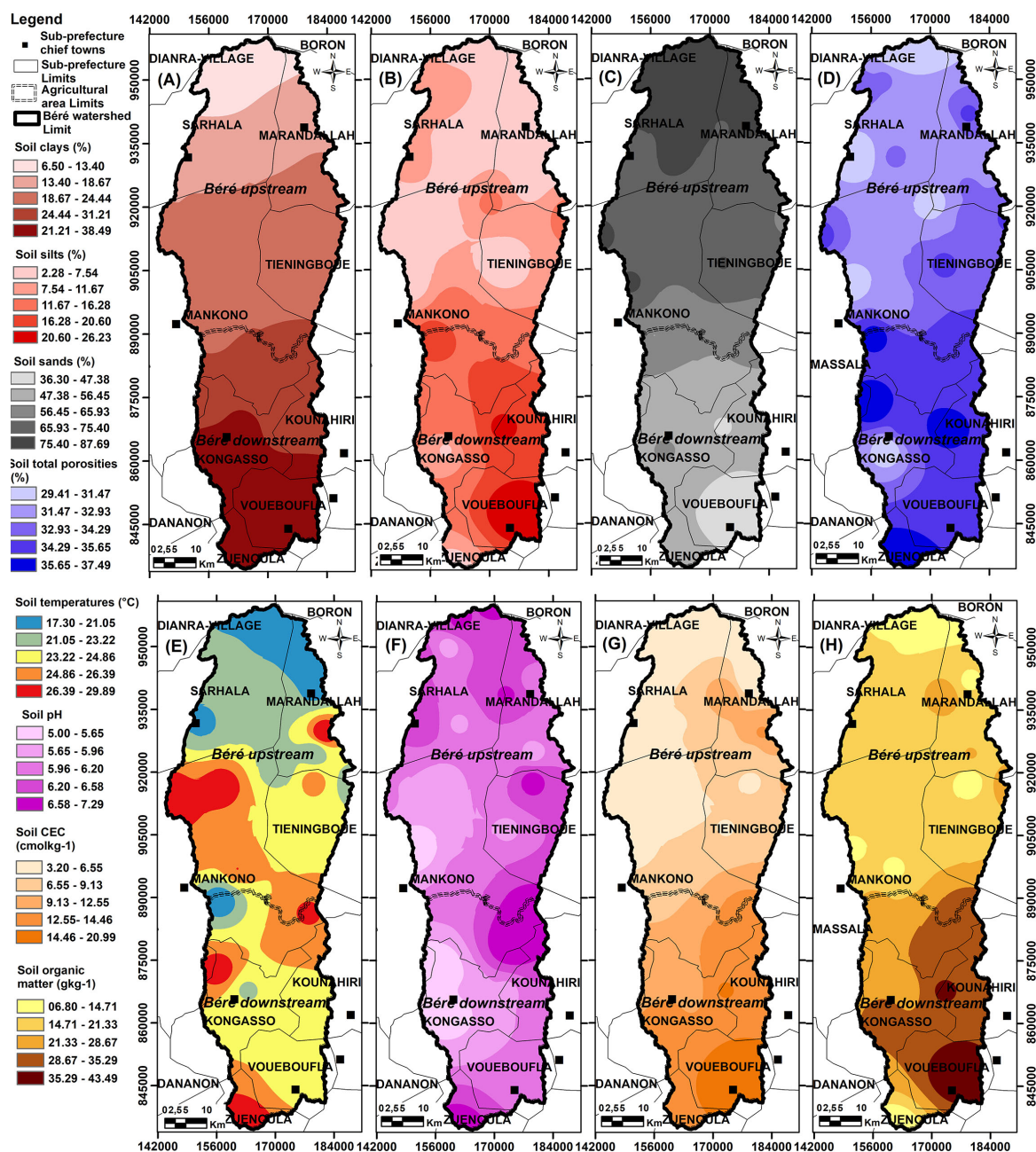


Figure 4. Spatial distributions of physical and chemical parameters in the surface layers (0 - 20 cm) of agricultural soils Béré watershed (BW): Clay (A), silt (B), Sand (C), Total porosity (D), Temperature (E), Hydrogen potential (pH) (F), Cation Exchange Capacity (CEC) (G) and Organic Matter (MO) (H).

horizon of the soils in the agricultural areas of the BW. The pH values of the agricultural soils fluctuate between 5 and 7.29 on the BW with an RMSE spatial interpolation of 0.28%. The agricultural soils of the BUW and the BDW show respectively weakly acidic pH values of 6.05 and 6.00 quite similar from one area to the other (U Mann-Whitney test, $p > 0.05$). On the other hand, the agricultural soils of the south-east of Mankono, Tiénigoué, Sarhala, and Marandallah (6.20 - 7.29) are those that are more weakly alkaline contrary to those of central

Mankono and Kongasso (5.0 - 5.96) which remain weakly acidic. The spatial variation of the Cation Exchange Capacity (CEC) in the 0 - 20 cm horizon of the soils of the agricultural areas of the BW is presented by **Figure 4(G)**. CEC values are between 3.20 and 20.99 $\text{cmol}\cdot\text{kg}^{-1}$ (RMSE = 4.86%). The locality of Sarhala record the minimum CEC values (3.20 - 9.13 $\text{cmol}\cdot\text{kg}^{-1}$), whereas Vouéboufla, Kongasso and Kounahiri record the maximum values (12.53 - 20.99 $\text{cmol}\cdot\text{kg}^{-1}$). The median CEC values are higher in the BDW agricultural zone (10 $\text{cmol}\cdot\text{kg}^{-1}$) and low in the BUW agricultural zone (5.76 $\text{cmol}\cdot\text{kg}^{-1}$) (U Mann-Whitney test, $p < 0.05$). The organic matter (MO) contents in the 0 - 20 cm horizon of the soils of the agricultural areas of the BDW vary between 06.80 and 43.49 $\text{g}\cdot\text{kg}^{-1}$ (**Figure 4(H)**). The interpolation (RMSE) of soil concentrations of agricultural areas in MO over the whole BW is about 7.367%. Sarhala's agricultural soil concentrations in MO are the lowest (6.80 - 21.33 $\text{g}\cdot\text{kg}^{-1}$) while those of Vouéboufla are the highest (28.67 - 43.49 $\text{g}\cdot\text{kg}^{-1}$). The agricultural zone of BDW (26.60 $\text{g}\cdot\text{kg}^{-1}$) is richer in MO while that of BUW is poorer in MO (15.5 $\text{g}\cdot\text{kg}^{-1}$). Agricultural soil contents in the BUW differ significantly from those in the BDW (U Mann-Whitney test, $p < 0.05$).

3.1.3. Spatial Distributions of Total Nitrogen and Pesticides Concentrations in the Surface Layers of Agricultural Soils

The spatial variation of total nitrogen concentrations in the 0 - 20 cm horizon of soils in the agricultural areas of the Béré watershed (BW) is presented by **Figure 5(A)**. Overall, a variation in total nitrogen concentration ranging from 0.30 to 1.99 $\text{g}\cdot\text{kg}^{-1}$ is observed in the agricultural soils of the BW with a spatial interpolation RMSE equal to 7.93%.

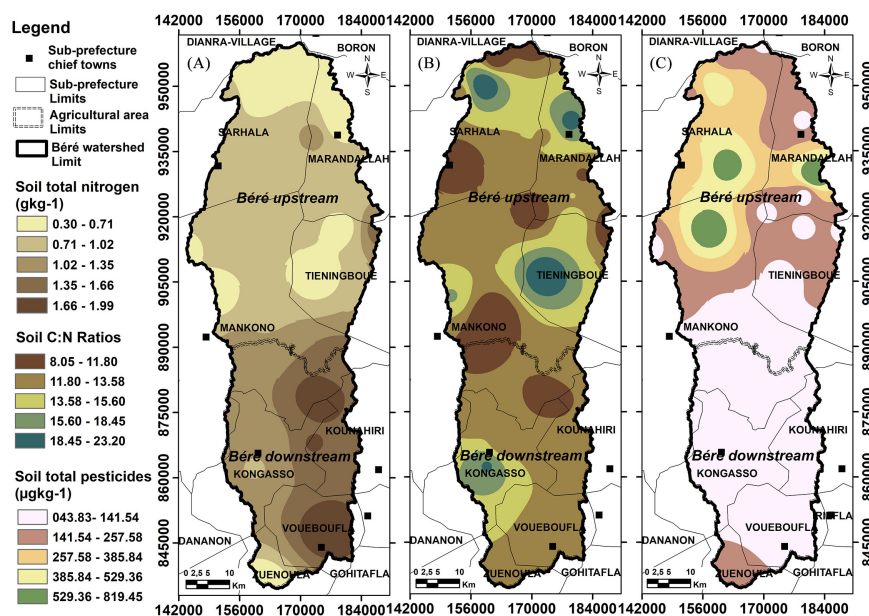


Figure 5. Spatial distributions of total nitrogen (A), carbon to nitrogen (C:N) ratios (B), and total pesticides concentrations (C) in the surface layers (0 - 20 cm) of agricultural soil of Béré watershed (BW).

The total nitrogen concentrations are lower ($0.30 - 1.02 \text{ g}\cdot\text{kg}^{-1}$) in the agricultural soils of Sarhala and Marandallah localities. On the other hand, they are higher ($1.35 - 1.99 \text{ g}\cdot\text{kg}^{-1}$) in Vouéboufla, Kounahiri and Kongasso. The Béré upstream watershed (BUW), with a median total nitrogen content of $0.84 \text{ g}\cdot\text{kg}^{-1}$, remains the poorest agricultural area in terms of nitrogen, whereas, in the Béré downstream watershed (BDW) agricultural area, agricultural soils are the richest with a median total nitrogen content of around $1.2 \text{ g}\cdot\text{kg}^{-1}$. The determined C:N ratio values of the agricultural soils in BW fluctuate between 8.05 and 23.20 following an RMSE spatial interpolation of 1.57%. The Variations in the total nitrogen content of agricultural soils in the BUW and BDW indicate a significant difference in concentrations between the two agricultural areas (U Mann-Whitney test; $p < 0.05$). The spatialization of the carbon: nitrogen (C:N) ratio of the 0 - 20 cm horizon of the soils of the agricultural areas of the BW is presented by **Figure 5(B)**. The median C:N ratios of the agricultural soils of the BUW (12.42) and the BDW (12.61) are roughly similar. However, the values of the C:N ratios of the most basic agricultural soils ($8.06 - 13.58$) are noted in the north-western and south-eastern parts of the BW. On the other hand, the highest C:N ratio values ($15.60 - 23.20$) are found in the central-eastern, northern and south-western parts of the BW. Indeed, the U Mann-Whitney comparison test shows that there is no significant difference between the C:N ratios of these two agricultural areas of the BW (U Mann-Whitney test, $p > 0.05$). The analysis of **Figure 5(C)** presenting the spatial variation of total pesticide concentrations found in the 0 - 20 cm horizon of the soils of the agricultural areas of the BW shows that, in general, the concentrations of the latter fluctuate between 43.83 and $819.45 \text{ }\mu\text{g}\cdot\text{kg}^{-1}$ according to an RMSE interpolation of 5.16%. These concentrations are more important in the majority of the agricultural soils of the BUW with a median concentration of total pesticides of $193.80 \text{ }\mu\text{g}\cdot\text{kg}^{-1}$ especially in its north-western part (Sarhala) where the maxima reach the concentration range of $385.84 - 819.45 \text{ }\mu\text{g}\cdot\text{kg}^{-1}$. On reforestation, most of the agricultural soils of the BDW (Mankono, Kongasso, and Kounahiri) have lower total pesticide concentrations ($43.83 - 141.54 \text{ }\mu\text{g}\cdot\text{kg}^{-1}$) with a median concentration of $94.81 \text{ }\mu\text{g}\cdot\text{kg}^{-1}$. The Mann-Whitney U-Test with ($p < 0.05$) shows that there is a significant difference between the total pesticide concentrations in the two agricultural areas of the BW. **Table 1** shows the distributions of detection frequencies and concentrations of biological families, chemical families, and active ingredients of pesticides found in agricultural soils in the 0 - 20 cm horizon of the Béré watershed (BW). At the level of the biological families of pesticides, the median concentrations and the frequencies of detection follow the order of importance: herbicides > insecticides > fungicides whatever the agricultural zone of the BW. Herbicides are most notable in the BUW (100%; $134,035 \text{ }\mu\text{g}\cdot\text{kg}^{-1}$) with a variation in concentrations from 41.10 to $799.47 \text{ }\mu\text{g}\cdot\text{kg}^{-1}$. The BUW is also the agricultural area where fungicides are least encountered ($<0.022 - 21.56 \text{ }\mu\text{g}\cdot\text{kg}^{-1}$) with a median concentration of $5.75 \text{ }\mu\text{g}\cdot\text{kg}^{-1}$ and a detection frequency of 69.23%. About to the chemical families of pesticides found in the soils of the BW agricultural.

Table 1. Distributions of detection frequencies and concentrations of biological families, chemical families and active ingredients of pesticides found in agricultural soils in the 0 - 20 cm horizon of the Béré watershed (BW).

		Agricultural areas							
		Béré upstream watershed (BUW)				Béré downstream watershed (BDW)			
		<i>Minima</i>	<i>Median</i>	<i>Maxima</i>	<i>Detection %</i>	<i>Minima</i>	<i>Median</i>	<i>Maxima</i>	<i>Detection %</i>
Pesticide biological families	Herbicides ^a	41.10	134.04	799.47	100	17.40	65.29	182.16	100
	Insecticides	0.09	17.29	168.77	100	0.09	12.6	39.74	100
	Fungicides	<0.022	5.75	21.56	85.71	<0.022	8.71	17.71	69.23
Pesticide chemical families	Organophosphates	<0.032	17.29	44.64	85.7	<0.032	12.60	36.13	92.3
	Organochlorines	<0.022	0.09	3.84	57.1	<0.022	0.09	3.23	53.8
	Alkylchorophenoxys	<0.022	<0.022	3.23	42.9	<0.022	<0.022	4.03	46.2
	Phosphonoglycines	<0.022	<0.022	2.85	42.9	<0.022	<0.022	3.03	46.2
	Carbamates	<0.022	<0.022	138.75	14.3	<0.022	<0.022	22.08	7.69
	Urea substitutes	11.59	52.14	303.75	100,00	1.01	44.02	76.96	100
	Phenylureas	<0.022	5.50	195.47	71.4	<0.022	3.44	12.17	92.3
	Chloroacetamides	0.07	9.81	16.59	100	0.07	10.31	22.79	100
	Triazines ^a	7.70	79.37	292.43	100	<0.022	5.23	112.15	69.2
	Oxazoles	<0.022	5.75	21.56	85.7	<0.022	8.71	17.71	69.2
	Pyrethroids	<0.039	<0.039	3.1	42.9	<0.039	<0.039	2.73	46.2
Pesticides active matters	Parathion-methyl	<0.032	3.00	7.74	78.57	<0.032	2.45	4.17	53.85
	Chlorfenvinphos ^a	<0.032	8.94	11.45	85.71	<0.032	3.98	17.13	53.85
	Parathion-ethyl	<0.032	1.10	20.13	57.14	<0.032	2.33	15.32	69.23
	Profenofos	<0.032	<0.032	4.21	35.71	<0.032	<0.032	3.4	38.46
	Chlorpyrifos ethyl	<0.032	<0.032	5.00	42.86	<0.032	<0.032	3.87	53.85
	Paraquat	<0.032	<0.032	3.98	42.86	<0.032	<0.032	3.47	53.85
	Organochlorines								
	Endosulfan	<0.022	0.09	3.84	57.14	<0.022	0.09	3.23	61.54
	Alkylchorophenoxys								
	2,4 D	<0.022	<0.022	3.23	42.86	<0.022	<0.022	4.03	53.85
	Phosphonoglycines								
	Glyphosate	<0.022	<0.022	2.85	42.86	<0.022	<0.022	3.03	53.85
	Carbamates								
	Aldicarb	<0.022	<0.022	138.75	14.29	<0.022	<0.022	22.08	7.69
	Chlorpropham	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Metoxuron	<0.022	6.66	53.05	64.29	<0.022	5.70	9.99	76.92
	Methabenzthiazuron	<0.022	5.48	12.25	71.43	<0.022	8.32	18.01	69.23
	Chlortoluron	<0.022	8.53	218.32	78.57	<0.022	10.12	18.92	84.62
	Monolinuron	<0.022	0.37	14.16	50.00	<0.022	<0.022	14.16	30.77
	Isoproturon	<0.022	0.71	11.21	78.57	<0.022	<0.022	15.05	46.15
	Metobromuron	<0.022	<0.022	28.33	42.86	<0.022	2.01	20.09	69.23
	Linuron	<0.022	7.94	24.73	64.29	<0.022	<0.022	12.84	38.46
	Fenuron	<0.022	<0.022	15.33	35.71	<0.022	<0.022	9.32	7.69

Continued

Phenylureas	Buturon	<0.022	0.53	56.91	50.00	<0.022	<0.022	9.27	30.77
	Monuron	<0.022	3.39	138.56	50.00	<0.022	1.17	12.17	76.92
	Diuron	<0.022	<0.022	17.97	14.29	<0.022	<0.022	0.12	7.69
Chloroacetamides	metolachlore	<0.032	6.25	16.03	71.43	<0.032	0.07	6.07	53.85
	Metazachlor	<0.032	0.93	11.02	78.57	<0.032	10.31	19.34	61.54
Triazines	Simazine ^a	<0.022	13.17	203.91	92.86	<0.022	<0.022	27.25	46.15
	Cyanazine	<0.022	<0.022	18.35	42.86	<0.022	<0.022	18.35	15.38
	Atrazine	<0.022	1.12	24.67	50.00	<0.022	<0.022	9.49	23.08
	Propazine	<0.022	2.61	13.13	64.29	<0.022	<0.022	17.31	23.08
	Terbuthylazine	<0.022	1.35	45.77	57.14	<0.022	2.11	31.12	53.85
	Prometryn	<0.022	6.21	95.89	85.71	<0.022	0.44	33.13	53.85
	Terbutryn	<0.022	<0.022	90.3	28.57	<0.022	<0.022	11.42	15.38
Oxazoles	Vinclozolin	<0.022	5.75	21.56	85.71	<0.022	8.71	17.71	69.23
Pyrethroids	Cypermethrin	<0.039	<0.039	2.06	42.86	<0.039	<0.039	1.95	46.15
	Lambda Cyhalothrin	<0.039	<0.039	1.04	42.86	<0.039	<0.039	0.94	46.15

a: Significant difference between the concentrations of the biological and chemical families as well as the active ingredients in the two agricultural areas (Test U Mann-Whitney at $p < 0.05$).

areas, the detection frequency pairs and median concentrations of triazines (100%; 79.37 $\mu\text{g}\cdot\text{kg}^{-1}$), urea substitute (100%; 52.14 $\mu\text{g}\cdot\text{kg}^{-1}$) and organophosphates (85.7%; 17.29 $\mu\text{g}\cdot\text{kg}^{-1}$) are successively the most important in the agricultural area of the BUW with concentrations between 7.70 - 292.43 $\mu\text{g}\cdot\text{kg}^{-1}$, 11.59 - 303.75 $\mu\text{g}\cdot\text{kg}^{-1}$ and <0.032 - 44.64 $\mu\text{g}\cdot\text{kg}^{-1}$ respective. At the level of the BDW, the order of abundance of the values of the chemical families is as follows: urea substitute (100%; 44.02 $\mu\text{g}\cdot\text{kg}^{-1}$) > organophosphates (92.3%; 12.60 $\mu\text{g}\cdot\text{kg}^{-1}$) > chloroacetamides (100%; 10.31 $\mu\text{g}\cdot\text{kg}^{-1}$) with values that fluctuate respectively between 1.01 - 76.96 $\mu\text{g}\cdot\text{kg}^{-1}$, <0.032 - 36.13 $\mu\text{g}\cdot\text{kg}^{-1}$, 0.07 - 22.79 $\mu\text{g}\cdot\text{kg}^{-1}$. However, whatever the agricultural area, carbamates, phosphonoglycines, alkylchlorophenoxys and pyrethroids remain successively very weakly present and quantified in agricultural soils. The lowest values for carbamates (7.69%; <0.022 $\mu\text{g}\cdot\text{kg}^{-1}$), phosphonoglycines (46.2%; <0.022 $\mu\text{g}\cdot\text{kg}^{-1}$), alkylchlorophenoxys (46.2%; <0.022 $\mu\text{g}\cdot\text{kg}^{-1}$) and pyrethroids (46.2%; <0.039 $\mu\text{g}\cdot\text{kg}^{-1}$) are observed in the agricultural area of the BDW with concentrations varying respectively between <0.022 - 22.08 $\mu\text{g}\cdot\text{kg}^{-1}$, <0.022 - 3.03 $\mu\text{g}\cdot\text{kg}^{-1}$, <0.022 - 4.03 $\mu\text{g}\cdot\text{kg}^{-1}$ and <0.039 - 2.75 $\mu\text{g}\cdot\text{kg}^{-1}$. On the other hand, only the median values of the concentrations of the chemical families of the biological families of herbicides and triazines differ significantly in the soils of the two BW agricultural areas (Test U Mann-Whitney; $p < 0.05$). With regard to the distribution of detection frequencies and concentrations of the active matters of the pesticides found in the 0 - 20 cm horizon of the soils of the agricultural areas of the BUW, it appears that the highest pairs of detection frequencies and concentrations of the active molecules in the agricul-

tural soils of the BUW concern primarily simazine molecules (92.86%; 13.17 $\mu\text{g}\cdot\text{kg}^{-1}$), chlorfenvinphos (85.71%; 8.94 $\mu\text{g}\cdot\text{kg}^{-1}$), chlortoluron (78.58%; 8.53 $\mu\text{g}\cdot\text{kg}^{-1}$), prometryn (85.71%; 6.21 $\mu\text{g}\cdot\text{kg}^{-1}$) and linuron (64.29%; 7.94 $\mu\text{g}\cdot\text{kg}^{-1}$) (**Table 1**). In addition, the pesticide molecules of chlorpropham (0.00%; 0.00 $\mu\text{g}\cdot\text{kg}^{-1}$), lambda-cyhalothrin, cypermethrin, glyphosate, and 2,4 D with the detection frequency and median concentration of 42.86% and <0.039 $\mu\text{g}\cdot\text{kg}^{-1}$ respectively are the lowest found in the agricultural soils of the BUW. Moreover, in the agricultural soils of the BDW, the molecules of chlortoluron (84.62%; 10.12 $\mu\text{g}\cdot\text{kg}^{-1}$), metazachlor (61.54%; 10.31 $\mu\text{g}\cdot\text{kg}^{-1}$), Vinclozilin (69.23%; 8.71 $\mu\text{g}\cdot\text{kg}^{-1}$), methabenzthiazuron (69.23%; 8.32 $\mu\text{g}\cdot\text{kg}^{-1}$) and methoxuron (76.92%; 5.70 $\mu\text{g}\cdot\text{kg}^{-1}$) are successively the most detected. However, the detection and concentration frequencies of the molecules, which are the least detected and quantified in the agricultural soils of the BDW, concern the molecules of chlorpropham, diuron, lambda-cyhalothrin, cypermethrin and fenuron with the respective values of (0.00%; 0.00 $\mu\text{g}\cdot\text{kg}^{-1}$), (7.69%; <0.022 $\mu\text{g}\cdot\text{kg}^{-1}$), (46.15%; <0.039 $\mu\text{g}\cdot\text{kg}^{-1}$), (46.15%; <0.039 $\mu\text{g}\cdot\text{kg}^{-1}$) and (7.69%; <0.022 $\mu\text{g}\cdot\text{kg}^{-1}$) respectively. The U Mann-Whitney comparison test carried out on all the pesticide values found in agricultural soils shows that significant differences only exist between the values of the active molecules of simazine and chlorfenvinphos ($p > 0.05$) in the agricultural soils of the BW agricultural areas.

3.1.4. Influences of Soil Differentiation of BW Agricultural Areas on Their Total and Pesticide Availability

The results of the Principal Component Analysis (PCA) based on the physico-chemical parameters recorded in the different soils of the agricultural zones of the Béré watershed (BW) are showed by **Figure 6**. The first two axes expressing 54.3% of the total inertia with 41.3% for axis 1 and 13% for axis 2 have been retained for the expression of the PCA results (**Figure 6(A)**). The correlation circle shows that axis 1 is negatively correlated to the proportions of total porosity (PT), the cation exchange capacity (CEC), the proportions of clays (A), the concentrations of calcium ions (Ca^{2+}), and magnesium ions (Mg^{2+}), the contents of organic matter (MO) and total nitrogen (N), the proportions of silts (L), fine silts (LF) and coarse silts (LG) and the hydrogen potential (pH) (**Figure 6(B)**). On the other hand, the proportions of sands (S) and coarse sands (SG) are positively correlated to this axis. Axis 2 is expressed positively by temperatures (T), potassium ion concentrations (K^+), and the carbon: nitrogen ratio (C:N) and negatively by the proportions of fine sand (SF) and sodium ion concentrations (Na^+). The soils of the Béré upstream watershed (BUW) agricultural zone are relatively different from those of the Béré downstream watershed (BDW) agricultural zone (**Figure 6(C)**). Indeed, the agricultural soils of the BUW are more characterized by higher proportions of sand (S) and coarse sand (SG). On the other hand, total porosity (PT), cation exchange capacity (CEC), clays (A), organic matter (MO), silts (L), fine silts (LF), coarse silts (LG), total nitrogen (N) and potassium ions (K^+) are more important in the soils of the BDW agricultural area.

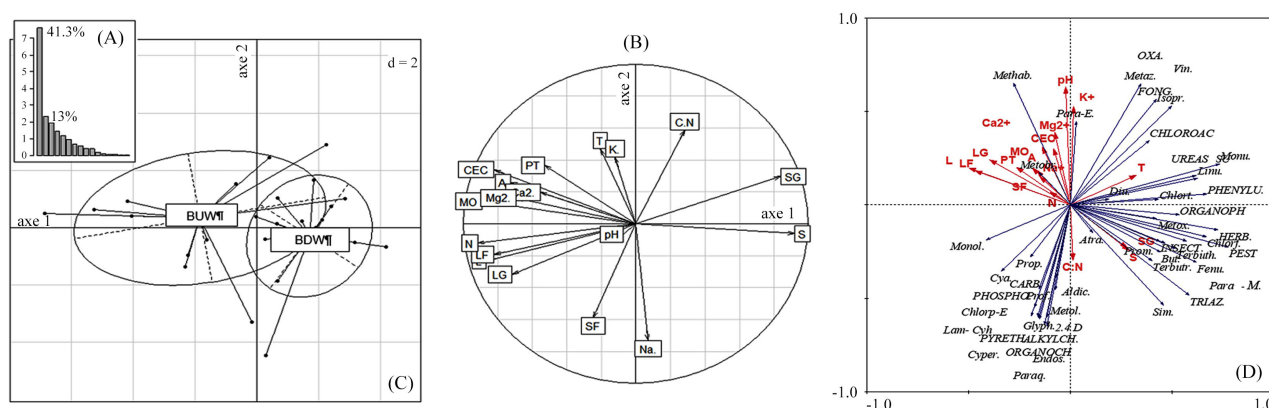


Figure 6. Results of the Principal Component Analysis (PCA) and Redundancy Analysis: Histogram of the eigenvalues of the axes (A), Correspondence Factor Map (B), Correlation Circle (C), and Redundancy Analysis of the physicochemical properties of the agricultural soils of pesticide molecules (D) of the agricultural soils of the Béré watershed (BW). A: Clay, L: Silt, LF: Fine Silt, LG: Coarse silt, SF: Fine sand, S: Sand, SG: Coarse sand, PT: Total Porosity, T: Temperature, MO: Organic material, pH: Hydrogen Potential, Ca^{2+} : Calcium ions, Mg^{2+} : Magnesium ions, K^{+} : Potassium ions, Na^{+} : Sodium Ions, CEC: Cationic Exchange Capacity, N: Total Nitrogen, C:N: Carbon: nitrogen ratio; Para-M.: Parathion-methyl, Chlorf.: Chlofinvinphos, Para-E: Parathion-ethyl, Prof.: Profenofos, Paraq.: Paraquat, Endos.: Endosulfan, 2,4 D: 2,4 Dichlorophenyl, Glyph.: Glyphosate, Adic.: Aldicab, Chlorp.: Chloprofam, Metox.: Metoxuron, Metab.: Methabenthiazuron, Monol.: Monoluron, Chlort.: Chlortoluron, Isopr.: Isoproturon, Metobr.: Metobromuron, Linu.: Linuron, Fenu.: Fenuron, But.: Buturon, Diu.: Diuron, Metol.: Metolachlore, Metaz.: Méthazaclor, Sim.: Simazine, Cya.: Cyanazine, Atra.: Atrazine, Prop.: Propazine, Terbut.: Terbutylazine, Prom.: Prometryn, Terbutr.: Terbutrin, Vin.: Vinclozilin, Cyper.: Cyperméthrin, Lam-Cya.: Lamda-cyhalothrin; ORGANOPH.: Organophosphates, ORGANOCH.: Organochlorines, ALKYCLCH.: Alkylchlorophenoxy, PHOSPHO.: Phosphonoglycines, CARB.: Carbamates, UREAS SUB.: Urea substitute, PHENYLU.: Phenylureas, CHLOROAC.: Chloroacetamides, TRIAZ.: Triazines, OXA.: Oxazoles, PYRETH.: Pyrethroids, HERB.: Herbicides, INSECT.: Insecticides, FONG.: Fungicides et PEST: Total pesticides; BUW: Béré upstream watershed, BDW: Béré downstream watershed.

The canonical redundancy analysis carried out on the basis of all the active pesticide molecules, total nitrogen, and the physicochemical parameters of the BW agricultural soils provides a synthetic visualization of the information by summarising in the foreground (axes I and II) 52.9% of the cumulative variance of the relations (**Figure 6(D)**). The Monte-Carlo permutation test indicates that the result of this analysis is significant ($p < 0.05$). The first axis of The Redundancy Analysis (RDA) accounts for 30.1% of the total inertia; it is strongly positively correlated to temperature (T), coarse sand (SG), and sand (S) and negatively correlated to total nitrogen (N), fine sand (SF), silt (L), fine silt (LF) and total porosity (PT) his axis opposes the stations richer in nitrogen, silt and porous with a higher monlinuron active ingredient and the stations less rich in nitrogen, less porous, and with low but very abundant sand temperatures which turn out to be the most favourable to the chemical families of phenylureas (monuron, buturon and Diuron), urea substitutes (linuron, chortoluron and metoxuron), organophosphates (parathion-methyl and chlorfenvinfos), triazines (prometryn, terbuthylazine, fenuron, terbutryn and simazine) and generally total pesticides found including herbicides and insecticides. Axis 2 express 22.8% of the variability; it is highly correlated with potassium ions (K^{+}), pH, magnesium ions (Mg^{2+}), calcium ions (Ca^{2+}), cation exchange capacity (CEC), clay (A), organic matter (MO) and sodium ions (Na^{+}) on the positive side, while on the negative

side it is correlated with the C:N ratio. Thus, the stations which are positively correlated to the second axis show the strongest contributions to the abundance of the active molecules metobromuron, methabenzthiazuron, ethyl parathion, metazachlor, isoproturon, the chemical family of oxazoles (vinclozolin) including the biological family of fungicides. On the other hand, the stations that are negatively correlated to axis 2 influence the abundance of active ingredients of atrazine, aldicarb, metolachlor, 2,4 D amine salt, glyphosate, endosulfan, paraquat, cypermethrin, lambda-cylothrins, chlorpyrifos-ethyl, cyanazine, propazine, profenofos as well as generally the chemical families of carbamates, phosphoglycines, pyrethroids, alkylchlorophenoxys and organochlorines.

3.2. Discussion

The Béré watershed (BW) is an agro hydrosystem that includes large areas of farms with cropping systems that remain as expansive as they are intensive. The importance of the proportion of farming areas in the BW (45%) can be explained mainly by the fact that the economy of the country's rural population, and particularly of this area, is based mainly on agricultural activities. Thus, the improvement in the prices of the region's main agricultural products such as cotton and cashew nuts in recent years would be the driving factors behind the expansion of the area under cultivation by farmers and producers in the region. The aim is to maximize their production and increase their income. Moreover, the predominance of annual croppings (32.65%) and perennial croppings (21.47%) respectively in the Béré upstream watershed (BUW) and the Béré downstream watershed (BDW) would be related to the increasing occupation of agricultural land in the south of the BW and its surroundings by the growing cashew and cocoa orchards, which would lead to the migration of producers to the northern part of the BW to conquer new land suitable for annual cultivation of cotton, maize, rainfed rice, market gardening, etc. This would also lead to the development of new croppings (e.g. cotton, maize, rainfed rice, etc.). Moreover, this land pressure observed in the BUW is also explained by the development of the agricultural sector since 1998 in the country through the distribution of the cotton basin to several farming structures. This situation had favored the displacement of farmers and producers towards the incursion of new operators proposing innovations in management and offering more advantageous conditions as shown by the work of [48]. In addition, the studies of [1] had shown that in addition to the expansion of cultivation areas, an increasing evolution of semi-intensive and intensive cropping systems had been observed in the early 2000s in the country to the detriment of the traditional ones. Indeed, despite all the training, information, advice, credit and knowledge related to agriculture, processing and marketing, agricultural extension was also accompanied by the supply of large quantities of agricultural inputs such as fertilisers and phytosanitary products to farmers and producers [49]. As a result, given the high consumption of agrochemicals involved in growing cotton including most annual croppings compared to perennial croppings such as cashew nuts [2] and [11],

one would think that the agricultural area of the BUW would concentrate a high rate of agrochemical use, unlike the BDW. Thus, the spatial repair of intensive cropping systems in the BUW following unsuitable agricultural practices would present risks of soil contamination as well as consequences on the quality of water resources through the risks of water erosion and sedimentation of contaminated soil materials outside the agricultural area during the rainy events, these had been highlighting by the works of [3] [7] [21] [22] [50]. It is moreover this situation that prompted the initiative characterization of the physicochemical parameters of soils in the agricultural areas of the BW in order to learn more about their contributions to the retention and/or transfer of pollution to water resources. This study carried out on the 0 - 20 cm horizons of the agricultural soils of the BW shows that these are generally of a moderately desaturated ferrallitic type [33]. These soils have characteristics similar to those of tropical soils found in West Africa which are composed of quartz, kaolinite, and very rich in iron and aluminum sesquioxides (Fe_2O_3 and Al_2O_3) with an ochre (goethite) or red (hematite) coloring [11]. As a result, the BW's agricultural soils as a whole present generally have acid pH values (5 - 7.29) and high temperatures (17.30°C - 29.89°C). However, soils in the BUW agricultural zone are relatively different from those in the BDW agricultural zone based on the results of the Principal Component Analysis (PCA) of the data. According to the soil quality guide values recommended by [51] [52], the silty-sandy texture with a high proportion of sand (76%) that the agricultural soils of the BUW would be a limiting factor for cultivation due to the acidity of the soils, contrary to that of the BDW having a sandy clayey-silt texture that could offer an overall good fertility ability. This situation would lead farmers and producers in the BUW agricultural zone to use large quantities of mineral fertilizers in order to ensure their production. In addition, the high sand content of the agricultural soils in the BUW should influence the rapid nitrogen mineralization in this agricultural area (Ratio C:N = 12.42). According to studies by [53], mineralization rates are higher in sandy soils because of their coarse texture which allows sufficient aeration. However, soils in the agricultural area of the BUW remain less rich in nitrogen ($0.84 \text{ g}\cdot\text{kg}^{-1}$). Could this situation be related to the influence of the acidity observed in the agricultural soils of the area (pH = 6.05)? In addition, studies by [54] had shown that acidity inhibits nitrification and limits nitrogen mineralization in the soil. Thus, the low nitrogen content observed in these soils would be linked to the rapid and massive assimilation of annual croppings observed in the agricultural zone of the BUW as well as to leaching and water erosion following significant rainfall events of the available nitrogen following the rapid mineralization by the activities of soil micro-organisms under the influence of temperature of the quantities of fertilizers applied which are ineffective in an acid environment [55] [11]. This would increase the contamination of nearby water resources [7]. In addition, the capacity through the clays (30%), silt (15%), total porosity (34.7%), cation exchange capacity ($10 \text{ cmol}\cdot\text{kg}^{-1}$), organic matter ($26.60 \text{ g}\cdot\text{kg}^{-1}$), total nitrogen ($1.2 \text{ g}\cdot\text{kg}^{-1}$) and C ratio: N ratio (12.61) of BDW's agricultural soils

are very considerable. Indeed, it can be deduced that the degradation of organic matter would be slow in the soils of the agricultural zone of the BDW given its high C:N ratio. Moreover, nitrogen in organic form from organic matter would further enrich the soils of the agricultural zone of the BDW as noted by [56] studies. Also, the nitrogen richness of the agricultural soils of the BDW could be explained by the fact that soil depletion in this area would be very slow through the weak exploitation of perennial croppings given the importance of their biomass, their deep and permanent rooting, their permanent soil cover and their abundant organic restitution [11]. About pesticides, the concentrations of total pesticides are higher in the soils of the agricultural area of the BUW (193.80 $\mu\text{g}\cdot\text{kg}^{-1}$) in contrast to those of the BDW which have low levels (94.81 $\mu\text{g}\cdot\text{kg}^{-1}$). The total pesticide concentrations observed in the BUW far exceed not only those observed in the soils of some African countries but also those of the BUW (94.81 $\mu\text{g}\cdot\text{kg}^{-1}$) [13] [14], but also remain superior to the reference threshold of 100 $\mu\text{g}\cdot\text{kg}^{-1}$ marking the limit between the contaminated and non-contaminated soils, according to the Canadian Soil Protection Guidelines [57]. Furthermore, it was found that, of all the detection frequencies and concentrations of the registered biological families of pesticides, herbicides were the most found in the agricultural soils of BW including 100% detection and a herbicide concentration of 134.035 $\mu\text{g}\cdot\text{kg}^{-1}$ in the BUW front of insecticides and fungicides. This situation could be explained by the increased use of herbicides, which are all the more obsolete, for weeding agricultural plots, especially annual croppings (maize, cotton, rainfed rice and market garden produce, etc.) in the BUW to the detriment of manual or motorized techniques. In addition, the chemical families of triazines (100%; 79.37 $\mu\text{g}\cdot\text{kg}^{-1}$) and urea substitutes (100%; 44.02 $\mu\text{g}\cdot\text{kg}^{-1}$) were the most detected herbicides in the soils of the BUW and BDW agricultural zones respectively. Indeed, the results obtained in BUW's tropical agricultural soils corroborate with those of [57] which had shown that in tropical soils anionic compounds and pesticide molecules with weak base behavior, such as those of triazines, would be more fixed and therefore predominant in the solid phase of the soil. This is due to the increase in ionized molecules, the importance of ionic bonds and exchange mechanisms, especially of anionic pesticides under the influence of the acid pH, and the richness of tropical agricultural soils in the area in metallic oxides and hydroxides, which generally have positive electrical charges that can adsorb more anions than in temperate soils [10] [11]. In revenge, the importance of active materials of acidic pesticides such as urea substitutes in the tropical agricultural soils of the BDW could also be explained by the fact that in an acid environment the proportion of non-ionized molecules of these chemical substances, hydrophilic polar interactions, hydrogen bonds, and therefore exchange mechanisms with water molecules in the liquid phase of the soil increase with the organic matter which is also important there. Thus, regardless of the agricultural area of BW, a total of 34 active pesticide molecules were found in agricultural soils, almost half of which (45%) were no longer registered in Côte d'Ivoire [58]. Some molecules were forbidden from use in Euro-

pean countries for more than a decade, such as aldicarb, atrazine, chlorfenvinphos, endosulfan, linuron, parathion-methyl, chlortoluron, methabenzthiazuron, monolinuron, simazine, and paraquat have been found in BW's agricultural soils. This demonstrates the clandestine infiltration of large quantities of obsolete (fraudulent, obsolete, or prohibit) pesticide products into the country and farmers' lack of knowledge about pesticide use. The detection frequency and concentration pairs of the active ingredients of simazine (92.86%; $13.17 \mu\text{g}\cdot\text{kg}^{-1}$), of the triazine family, were the most found in BUW agricultural soils and the active molecule of chlortoluron (84.62%; $10.12 \mu\text{g}\cdot\text{kg}^{-1}$) of the urea substitute family not registered in Côte d'Ivoire were more notable in BDW agricultural soils, even though they are prohibited. Moreover, the analysis of the influence of physicochemical parameters of agricultural soils on pesticides through The Redundance Analysis (*RDA*) showed the existence of strong positive correlations between sand, coarse sand, and the abundance of simazine and chlortoluron molecules respectively in acidic agricultural soils of BUW and BDW. Indeed, [59] and [60] had shown that the simazine molecule was generally more persistent ($\text{DT}_{50} = 60$ days) in sandy soils under the influence of acid pH, low humidity, and moderate temperatures in the area; which justifies its abundance specifically in the agricultural soils of BUW. However, despite its average permanence of 45 days in the soil, the active chlortoluron molecule is also strongly fixed by the clay-humic complex of soils with high clay and organic matter content [10]; which could also justify the importance of its concentration in the agricultural soils of the BDW. In addition, the Groundwater Ubiquity Score (GUS) indices of simazine (3.35) and chlortoluron (2.82) indicate that they have a low susceptibility to degradation and are therefore sensitive to leaching and lateral movement through soils into the water, could also explain their importance in the different soils of the BW agricultural areas, including their bioaccumulation in soil organisms [61]. Thus, the vulnerable agricultural soils of the BW, like the tropical soils of the West African ferrallitic type, are heavily contaminated by pesticides, especially the active molecules with a weak base, due to the increased use of pesticides, to the detriment of manual or motorized techniques used by producers in the different agricultural zones during the wet season. Therefore, the BW's water resources present worrying risks of contamination during rainy events that deserve to be assessed and monitored.

4. Conclusion

This study made it possible to assess the contribution of the spatial organization of cropping systems and the physiochemical characteristics of the surface layers of soils in agricultural zones of tropical hydrosystems to the spatial availability of nitrogen and pesticides in wet season soils such as the Béré watershed (BW) in Côte d'Ivoire. This study shows that the BW has large areas of farms divided into two large agricultural areas, the Béré upstream watershed (BUW) dominated by annual croppings and the Béré downstream watershed (BDW) by perennial croppings. The expansion of these croppings would lead to an intensification of

the use of inputs and plant protection products, contaminating the surface layers of the soils of the BW agricultural plots and thus influencing the fate of nitrogen and pesticides. Indeed, important concentrations of nitrogen and a number of 34 active molecules of pesticides are found in the agricultural soils of the BW whose herbicides were the most significant, specifically those of the chemical families triazines and urea substitute with respectively the highest concentrations of the active ingredients of simazine and chlortoluron. Most of these pesticides were obsolete due to the lack of clandestine infiltration of products and the lack of knowledge of producers. In addition, it is noted that given that the agricultural soils of BW are of a moderately desaturated ferrallitic type whose characteristics correspond to those of tropical soils found in West Africa with acid pH, very rich in iron and aluminum sesquioxides, and having a high sand content, these are favorable to the retention of pesticides found in these soils, especially the active ingredients with a weak base but to the leaching of nitrogen in the wet season. This situation was more observed in the agricultural soils of the upstream part of the BW where the detections and concentrations of pesticides were the highest and those of nitrogen lower in contrast to the soils of its downstream part. In relation to the properties of pesticides, these also condition the availability of pesticide molecules in the soil. Therefore, BW's water resources present worrying risks of contamination during rainy events that deserve to be assessed and monitored. Mitigation measures should therefore be implemented to preserve the quality of the environment.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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