Occurrences, distribution and risk assessment of polar pesticides in Niger River valley and its tributary the Mekrou River (Niger Republic)

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Abstract

The increase in food needs due to high population growth in Niger has led to the intensification of urban agriculture and the increased use of pesticides. The objective of this study is primarily to assess the polar pesticide contamination (mainly herbi-cides) of the Niger River and its tributary, the Mekrou River, in Niger, using both grab sampling and POCIS (Polar Organic Chemical Integrative Samplers), and then to evaluate the risk to the aquatic environment. Two water sampling campaigns were carried out during the wet and dry seasons. The polar pesticides were analyzed by liquid chromatography coupled with tandem mass spectrometry, which allowed the identification of compounds with concentrations in the grab samples above the WHO guide values and the EU directive: diuron with 2221 ng/L (EU quality guideline: 200 ng/L), atrazine with 742 ng/L (EU quality guideline: 600 ng/L) and acetochlor with 238 ng/L (EU quality guideline: 100 ng/L). The risk assess-ment study indicated that diuron and atrazine present a high risk for the aquatic environment during the wet season. The main source of water contamination is the intensive use of pesticides in urban agriculture near the city of Niamey, and the intensive cotton farming in the Benin. Moreover, the surveys (30 producers interviewed) showed that 70% of the pesticides used are not approved by the Interstate Committee for Drought Control in the Sahel (CILSS) and some are prohibited in Niger. The inventory of pesticides sold in the zone showed that active ingredients used by producers are 48% insecticides, 45% herbicides, and 7% fungicides.

Keywords Agriculture · Niger River Valley · Mekrou River · Pesticides · POCIS · Risk assessment

Introduction

In Niger, agriculture constitutes the third largest source of income, following uranium mining and livestock farming. Due to the high annual population growth rate (3.9%) in Niger, agricultural activity is in full development and is mainly practiced in the southern part of the country; along the Niger River and its tributaries (Guengant and Banoin 2003). The Mekrou River is a temporary tributary of the right bank of the Niger River that originates in Benin in the plain to the west of the Atakora Mountains (Le Barbe et al. 1993; Vernet 1994). This river is heavily involved in cotton production, which began in 1965. The growth of agricultural activities has led to the use of several pesticides in the Niger River watershed to protect crops.

In a broader perspective, agricultural activities in Africa occupy an important place in human nutrition and contribute to the national gross domestic product of many countries. The growing demand for agricultural products, associated with yield improvements, involves the systematic use of pesticides to control crop pests (Ahouangninou et al. 2011; Andres and Lebailly 2011; Illyassou et al. 2015; Kanda et al. 2013), which consist mainly of tropical insects and parasites (Gahukar 1989). For African countries in the Sahelian zone that are part of the Interstate Committee for Drought Control

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in the Sahel (CILSS), the use of these pesticides is regulated by the Sahelian Pesticides Commitee (CSP). According to the CSP, the chemicals used in the Sahelian countries are constituted of the following: 47% insecticides, 42% herbicides, and 11% fungicides.

Several studies have shown high concentrations of non-polar pesticides such as dichloro-diphenyl-trichloroethane (DDT), endosulfane, pyrethroids, dieldrine, paraquat, and organophosphate pesticides in water, sediment, soil, food, air, and aquatic organisms in countries connected with the Niger River Basin (Agbohessi et al. 2011, 2012; Zabeirou et al. 2018; Le Bars et al. 2020). A few studies, focused on the polar pesticide contamination such as glyphosate, paraquat, diuron, and atrazine, have been done in Niger, Benin, Guinea, Mali, Burkina Faso, and Cameroon, again connected with the Niger River Basin (Crampon et al. 2014; Adechian et al. 2015; Traoré and Haggblade 2017; Lehmann et al. 2018; Branchet et al. 2018). There is no published literature on the water contamination by polar pesticides (herbicides) along the Niger River and on the Mekrou River, in the Niger section, although herbicides are extensively used in rice cultivation to control weeds and are applied in double cropping during the year. The other studies focus on the surveys carried out on the management and use of pesticides by producers and risk assessments. The literature (Ahouangninou et al. 2011; Son et al. 2017; Tarnagda et al. 2017; Lehmann et al. 2017, 2018; Gouda et al. 2018; Le Bars et al. 2020) highlights that the producers used non-homologated pesticides without any adequate protective measures, with a potential environmental exposure and probable cancer for children and adults.

On the Mekrou River, a temporary tributary of the right bank of the Niger River, studies have only involved part of Benin, and the work has shown alarming concentrations of non-polar pesticides such as endosulfan (746 μg/L), DDT (100 μg/L), dieldrin (48 μg/L), and heptachlor in some water samples of the W Park and the river, as well as endosulfan and lindane in fish and sediment (Yehouenou et al. 2006; Agbohessi et al. 2011, 2012, 2015; Ahouangninou et al. 2011, 2012; Adechian et al. 2015). The W Park is a large transboundary biosphere reserve straddling Benin, Burkina, and Niger, was listed as a Unesco World Heritage Site since 1996, and has been protected since 2007 by the Ramsar Convention.

The use of pesticides allows a good crop yield, but several works have highlighted environmental and health risks caused by them, including reproductive function expectations, neurological disorders, and cancerous pathologies (Multigner 2005; Ahouangninou et al. 2011; Mamane 2015; Gouda et al. 2018; Le Bars et al. 2020). The use of non-homologated pesticides for agricultural purposes could be a source of environmental and health problems in the Niger River watershed in Niger. Most of these pesticides were not homologated by the Sahelian Pesticides Committee (Zabeirou et al. 2018). According to the WHO, there were, in 2008, approximately one million severe pesticide poisonings worldwide with some 200,000 deaths (WHO, 2006 and WHO, 2008).

Along the Niger River valley, the work done concerns the risk of exposure to residues of pesticides products near the city of Niamey and shown that the the exposure is higher for the children than the adults for all the residues detected, regardless of the product (Massalatchi et al. 2018). This exposure was also detected in farmers above acceptable levels for all of the active substances; varying from 0.0013 mg/kg bw/day to 0.4125 mg/kg bw/day (Massalatchi et al. 2017; Zabeirou et al. 2018). Additionally, an increased risk of respiratory ailments was found for the people living in agricultural areas, compared to the people in pastoral areas (Mamane et al. 2014, 2016).

In the Niger River Valley, pesticides are used by farmers to protect their crops from pests and are mainly exported from neighboring countries. To evaluate the pesticide contamination in the study area, some grab and passive sampling was performed. The passive sampling technique is commonly applied to quantify pesticides in different bodies of water (surface water, lakes, marine water, etc.) (Ahrens et al. 2015). This technique has advantages in terms of the preconcentration of compounds in water and increases the probability of detecting and quantifying compounds present at very low concentrations in water and hence improving the diagnosis of contamination (Di Carro et al. 2014). The passive sampling using Polar Organic Chemical Integrative Samplers (POCIS) has been widely used to investigate polar pesticides in surface water (Mazzella et al. 2014; Lissalde et al. 2014; Poulier et al. 2014; Desgranges 2015).

The objective of this study was to determine the occurrence and distribution of polar pesticides in the Niger River Valley and its tributary, the Mekrou River, by combining a survey of farmers and water analysis using grab and passive samples. There are no studies performed concerning the polar pesticide (mainly herbicides) in the Niger River Valley and its tributaries. This was the first time that the passive sampling technique was used to assess the polar pesticide contamination in the Niger River Valley and its tributaries. This study proposes to assess the risks in the three trophic levels (algae, aquatic invertebrates and fish), relative to the contamination levels detected, for each sampling site, in order to highlight the impact of these pesticides on the aquatic environment.

Materials and methods

Presentation of the study area

The study area is located in the Niger River watershed, in Niger, from the border with Mali in the North to the border with Benin and Nigeria in the South, and crosses the region of Tillabéry, over 420 km, and that of Dosso, over 130 km (Fig. 1). Its hydrological regime is highly variable over time and depends on the amount of rainfall in Upper Guinea and Northern Côte d'Ivoire, constituting the Guinean flood in December–January and the local flood between August and September, fed by its tributaries. It is the main watercourse in Niger and its irrigable area is estimated at 142,500 ha (SOGREAH/BRGM 1981). Several rice fields are located along the Niger River in both regions, covering an area of about 8500 ha and more than 2000 beneficiaries are involved (Ehrnrooth et al. 2011). Several hydro-agricultural developments were carried out by the State of Niger over an area of 13,000 ha; the management of which was entrusted to the National Office of hydro-agricultural developments and then transferred to farmers' organizations grouped into agricultural cooperatives with the objective of growing twice as much rice per year through the support of the officein the framework of advice and provision of services (Baron et al. 2010).

Niger's climate is Sahelian, characterized by two seasons: a 9-month dry season (October to June) and a 3-month wet season (July to September). Niger's agro-climatic zones are made up of the Sahelo-Sudanian zone, the Sahelian zone, the Sahelo-Saharan zone, and the Saharan zone. The Niger River is located in the Sahelian zone with a rainfall of between 350 and 600 mm per year, where agriculture is predominantly rainfed and irrigated. The Mekrou River is located in the most watered part of Niger and crosses the W Park, at the common border between Niger, Benin, and Burkina. It is covered by the Sahelo-Sudanese zone, which receives 600 to 800 mm of rainfall per year with conditions that are very favorable for rainfed and irrigated agriculture. The latter receives about 80% of its water from Benin, which is one of the country's main cotton producing areas. The cultivable area of the zone is small so there is no agricultural activity in W Park, as it is a protected zone (Fig. 1).

Methodology for the survey of agricultural practices and pesticide use

Information on farming practices and pesticides used by farmers was collected using questionnaires. The

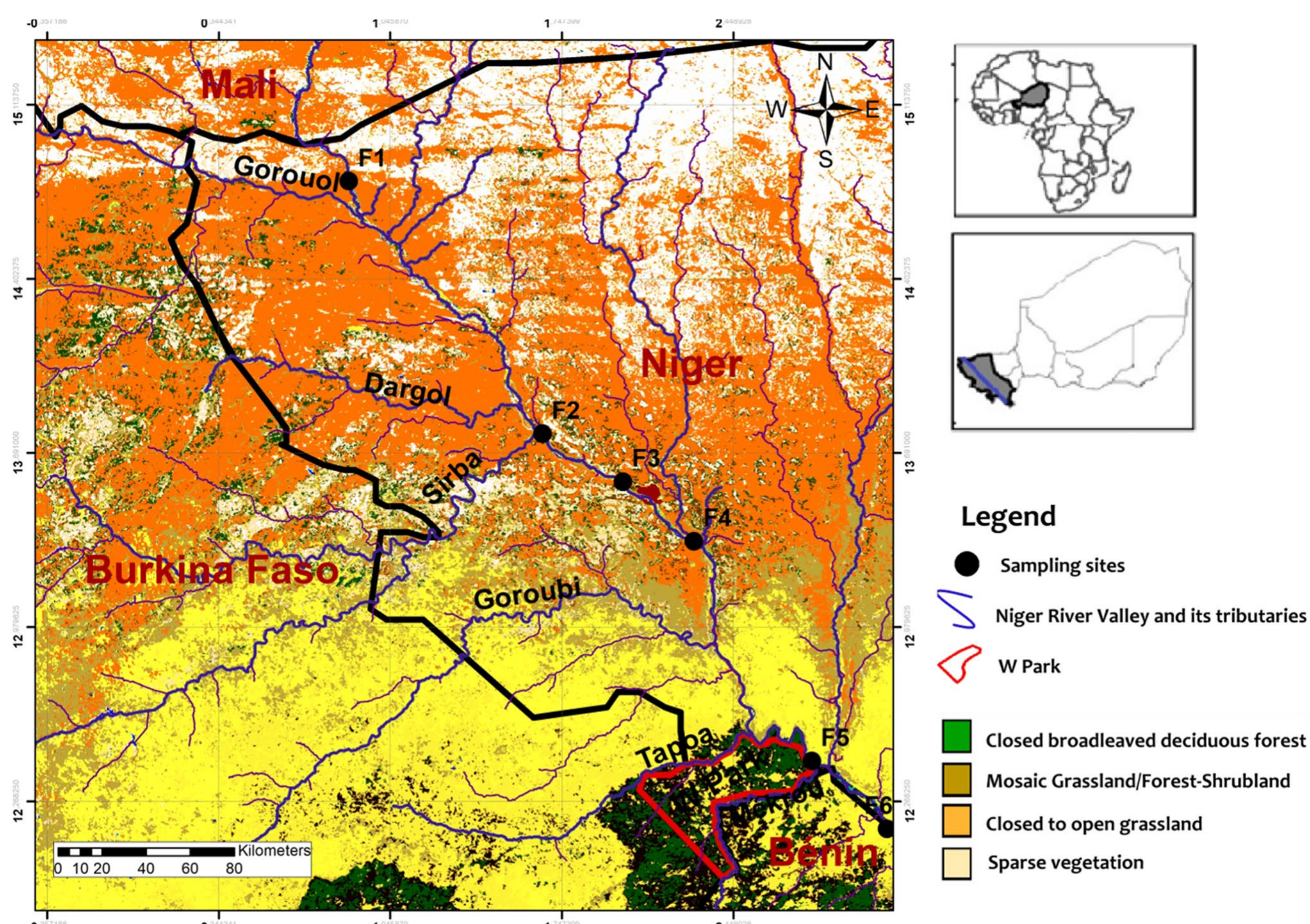

Fig. 1 Location of the study area and sampling sites

representative sample of the surveyed farmer population is composed of 30 producers, mostly men, on the Liboré and Saga hydro-agricultural development sites for rice production and the market garden sites located downstream from the city of Niamey along the Niger River, corresponding to sampling site F4. Urban agriculture is the main activity which is practiced along the Niger River by about 600 market gardeners at the Gamkalle site, and about 1800 allottees in the surrounding villages use the two irrigated perimeters for rice cultivation. These agricultural activities are performed for two harvests per year.

The questionnaire included general data on the farmer, such as level of education, age, and agricultural training received; data on the characteristics of the farm, such as the area cultivated for market gardening or irrigation, agricultural practices, and the origin of water used; and the type, frequency, and technique of chemical fertilizer and pesticide use. The last part of the questionnaire is related to the integration of producers in professional networks and their knowledge of the environmental issues related to the use of pesticides, as well as their opinion on the prospects for improving their activity.

The objectives of the survey were first explained to the members of the cooperative and to the producers present on the studied sites in order to have their involvement; the survey was carried out with the perfect collaboration of the producers with a response rate of 100%. The survey involved twenty producers from the irrigated sites and ten from the market gardening sites.

Materials and method of pesticides analysis

Choice of sampling sites

The preliminary study of the investigated area according to its size, and the types of agricultural activities carried out along the Niger River in Niger and near its tributaries, made it possible to select six sampling sites, five of which are on the Niger River (F1, F2, F3, F4, F6) and one at its confluence with the Mekrou River (F5), so as to investigate the pesticides used and cover the entire watershed (Fig. 1). Site F1 is located at the entrance of the Niger River from Mali, where there is no intense agricultural activity on the Niger side and no input from its tributaries into the main river. Site F2 is located at the confluence of the Niger River with its right bank tributary, the Sirba, where there are agricultural plots for market gardening, and upstream from the pumping stations for the water supply of the city of Niamey. Site F3 is located upstream of the city of Niamey and before the large market gardening sites, and site F4 is positioned downstream of Niamey with several human activities and after the market gardening sites and the irrigated areas of Saga and Liboré. Site F5 is located at the confluence of the Mekrou River with the Niger River and allows the evaluation of pesticide contamination from this river; and finally, site F6 is located in Gaya, which is a Sahelo-Sudanese area and at the exit of the Niger River from Niger territory, to evaluate pesticide inputs from the Niger side.

Sampling method

The grab sampling and passive sampling campaigns were carried out during both the wet season, between August and September, and the dry season, between April and May. They took place at the six sampling sites (F1, F2, F3, F4, F5, F6), selected in order to better evaluate the contamination in the same hydrological context of the Niger River. At each site, in situ measurements were made to collect the pH and conductivity in order to obtain a physico-chemical fingerprint and to compare water sample compositions (Table S1). Three POCIS were deployed at each site (triplicate) for a period of 15 to 20 days. They were placed in a cage, attached to an empty canister that floats and immersed vertically in the river water. Upon removal, the POCIS are rinsed with Milli Q water, wrapped in aluminum foil, then put in a plastic bag, and stored in a cooler before being transported to the laboratory for extraction.

Water samples are collected manually in 1-L glass bottles (grab sampling) previously rinsed with the water to be sampled, on the days of deployment and withdrawal of POCIS. They are also kept in a cooler during transport prior to extraction.

Materials

The sampling materials used consisted of a MP512-03 pH meter and a DDS-307 conductivity meter for in situ measurements of physical parameters and 1-L and 500-mL glass bottles. Filtration was performed to eliminate suspended matter, using a Nalgene filtration unit (for GL45 flask), a hand pump and GF/F disposable filters (0.7 μm pore size) purchased from Whatman (Maidstone, UK). The Oasis HLB cartridges (60 μm, 6 cm^3, 500 mg) obtained from Corporation (Milford, USA) were conditioned at the IMT Mines Alès with 5 mL of acetonitrile under vacuum, followed by 5 mL of methanol (MeOH) and 5 mL of ultrapure water (Ibrahim et al. 2013b), and transported to Niger in a cooler at 4 °C. POCIS were purchased from Expos Meter AB Company (Tavelsjö, Sweden) with the pharmaceutical receiving phase composed of approximately 230 mg of the solid adsorbent *N*-vinylpyrrolidone-divinylbenzene (Oasis HLB). The POCIS sampling area was 41 cm^2. The 3 mL polypropylene cartridges used to recover the POCIS receiving phases were purchased from Supelco (Bellefonte, USA) (Branchet et al. 2018).

For both types of sampling, a membrane pump was used during the extraction step (Oasis HLB cartridge and POCIS receiving phase).

Extraction of water grab samples and POCIS

On the site, the collected water grab sample (1L) was divided into two 500-mL flasks and vacuum-filtered with a 0.7 µm pore size GF/F filter. Each water grab sample was spiked with 50 µL of atrazine-d5 (1 ng/µL acetone) for recovery value estimation during the solid phase extraction on Oasis HLB®. Then, the filtered water samples have been loaded on the Oasis HLB®. These cartridges were stored in a refrigerator in Niamey before being transported to the laboratory at IMT Mines Alès for extraction and analysis. Before elution, the catridges were dried under vacuum for 1 h. The elution step was performed on a Visiprep solid phase extraction (SPE) purchased from Supelco (Bellefonte, USA). Analytes were recovered by eluting the cartridges with 8 mL of acetonitrile at a flow rate of 1 mL/min (Mhadhbi et al. 2019).

For POCIS, the receiving phase was transferred into an empty solid-phase extraction tube (SPE) packed with two polyethylene frits with 20 µm porosity. The sorbents were spiked with 50 µL of atrazine-d5 (1 ng/µL acetone) and then eluted with 8 mL of acetonitrile.

Both for Oasis HLB® cartridges and POCIS receiving phase elution, the extracts were concentrated under a gentle stream of nitrogen to obtain a final extract of 1.5 mL, which were spiked with 150 µL of the internal standard simazine-d5 (1 ng/µL acetonitrile) before being analyzed by tandem mass spectrometryin order to assess the coefficient of analysis variation (Ibrahim et al. 2013b).

Tandem mass spectrometry analysis of polar pesticides (herbicides)

The analysis of the extracts was performed at IMT Mines Alès by tandem mass spectrometry using an Alliance HPLC system (Waters Series 2695). This system is equipped with a quaternary pump, a degasser and a sample changer. Analytical separation was performed with a Kinetex C18 analytical column (100 mm × 4.6 I.D. × 260 Å; Phenomenex) (Branchet et al. 2018; Mhadhbi et al. 2019). The volume injected was 25 µL. Milli-Q water and acetonitrile, both including 0.05% formic acid, were used as the mobile phase, at a constant flow rate of 0.4 mL/min. The linear gradient started at 60% and reached 100% in 10 min to allow the elution of acetonitrile, followed by stabilization before returning to initial conditions for 2 min. The system was coupled to a triple quadrupole mass spectrometer (Micromass Quattro micro MT, Waters) equipped with an electrospray ionization (ESI) source, used as a detection device. The spectrometer operated in positive ESI mode under the following conditions: capillary voltage (3.5 kV), source temperature (120 °C), desolvation temperature (300 °C), drying (600 L/h), and nebulization gas (N_2) flow (30 L/h). Argon was used as collision gas. For each compound, acquisition was performed in the multiple reaction-monitoring modes (MRM).

The analytical results were recovered from one transition, one for the quantification of the target substances and the other for confirmation (Table S2). Moreover, the twenty-eight target compounds were identified according to their retention time.

Concentrations of pesticides in the water during POCIS deployment

The use of passive sampling (POCIS) is recommended in the European Commission's guidance document (EC Guidance Document No. 19) and in the Directive 2013/39/EU (EU 2013) for priority substances as a complementary method for monitoring surface water contamination. POCIS was used in this study to assess its effectiveness in environmental monitoring along the Niger River.

Determination of pesticide concentrations in POCIS.

Contaminant accumulation by passive samplers generally follows first-order kinetics with an initial integration phase followed by curvilinear and equilibrium partitioning phases (Branchet et al. 2018; Mhadhbi et al. 2019). In the linear region of POCIS retention, the amount of a chemical accumulated in the sampler (M) is described by Eq. (1):

$$\mathrm{M} = \mathrm{C}w \times \mathrm{Rs} \times \mathrm{t} \tag{1}$$

where Rs is the sampling rate (L/day), $\mathrm{C}w$ is the time-weighted concentration of the compound in water (ng/L), and t is the exposure time (days).

The time-weighted average concentrations (TWAC) in water were calculated with Eq. (2) proposed by Miège et al. 2003:

$$\mathrm{C}water = \mathrm{C}pocis \times \mathrm{M}pocis / \mathrm{Rs} \times \mathrm{t} \tag{2}$$

where

C_{water} time-weighted average concentration of pesticide (over the sampling period) in the ambient water (µg/L)

C_{pocis} concentration in POCIS (µg/g)

M_{pocis} mass of the absorbing phase in the POCIS (g)

R_s sampling rate (L/day)

T duration of POCIS deployment (days)

The sampling rates (*Rs*) are involved in the estimation of the TWA concentration from the quantities of pesticides accumulated in the POCIS into a concentration by nanograms per liter. The sampling rates (Rs) were determined in a previous work by Ibrahim et al. (2012, 2013b) under laboratory conditions for each compound by dividing the slope of the linear regression curve by the average aqueous concentration of selected compounds over a 15-day period. Some of the sample rates were not determined at IMT Mines Alès and were therefore retrieved from the literature (Ahrens et al. 2015; Desgranges 2015; Greenwood et al. 2007; Poulier et al. 2014; Branchet et al. 2018). Given that they depend on environmental conditions such as flow, temperature, pH, organic matter, and biofouling (Charlestra et al. 2012; Yabuki et al. 2016), they allow the calculation of semi-quantitative concentrations of pesticides in water and the comparison of the relative levels of contamination between sites (Ibrahim et al. 2013b). From a practical point of view, it is not possible to determine in situ Rs for the Mekrou and Niger Rivers.

The average Rs of the compounds used in this study is 0.215 L/day (Table 1 gives the sampling rates for each analyzed compound) and the lowest values are for DIA (0.068 L/day) and DEA (0.133 L/day).

Quality assurance/control

The linearity, LOQs and LODs, precision and accuracy of the analytical methods were carefully validated. Instrumental LODs were calculated as $3 \times Sy/b$ and LOQs as $10 \times Sy/b$, where Sy is the standard deviation of the response and b is the slope of the calibration curves.

The LODs and LOQs obtained by tandem mass spectrometry (instrumental LOD and LOQ expressed in µg/L) are listed in Table S2. The LODs and LOQs of all selected pesticides were determined from the calibration curves for each analytical campaign in which $R^2 > 0.98$. The calibration curves have been established for all the 28 targeted compounds for a range of concentration values from 3 to 45 µg/L in the elution mixture used for tandem mass spectrometry.

Moreover, the detection limit and the quantification limit in water sample have been calculated according to the global analytical procedure (including all the steps of the analytical procedure) and are mentioned Table 1.

The mean recovery rate in the natural water spiked (100 ng/L) was recovered with the 28 targeted compounds. Its value is 82% (Table S2) with the highest recovery for linuron (102%) and the lowest for DPCU (5%). For flazasulfuron, hydroxyl-terbuthylazine, and hydroxyl-simazine, the recovery rates were not calculated (Table 1).

A certificated reference material (WaR™ Pollution Nitrogen Pesticides, Lot No. P246-674) purchased from ERA Waters Company (Golden, USA) was used to determine pesticide recoveries in water samples (120 ng/l). This reference material was a water solution composed of 24 pesticides including the 6 pesticides selected in our study (alachlor, atrazine, DEA, DIA, metolachlor, and simazine). The pesticide concentrations in the reference material ranged from 3.37 to 16.80 µg/L. The recovery values and coefficients of variation were $108 \pm 4\%$ (atrazine), $78 \pm 4\%$ (alachlor), $61 \pm 3\%$ (DEA), $58 \pm 3\%$ (DIA), $110 \pm 2\%$ (metolachlor), and 79 ± 2 (simazine) after solid-phase extraction (Oasis HLB) and tandem mass spectrometry analysis ($n = 9$) of the water sample of the reference material using our laboratory method.

The average extraction recoveries with atrazine-d5 were $98 \pm 11\%$ and $90 \pm 12\%$ for the grab and passive samples respectively ($n = 33$ samples). The average variation coefficient variation with the internal standard simazine-d5 was $17 \pm 6\%$ for all tandem mass spectrometry injections ($n = 120$ injections).

Statistical analysis of data

For all analysis, triplicate analytical measurements were performed and data were tabulated as mean ± standard deviation. Statistical treatments of the data were performed using STATISTICA analysis software and statistical significance was set at $p < 0.05$.

Risk assessment

The risk assessment was based on the calculation of the risk quotient (RQ), according to the OECD and European guidelines for diuron and atrazine. The effect of herbicides and other chemicals on inhibition of photosynthesis and algal growth rate has been addressed by Tang and Escher (2014). Atrazine can reduce and change the behavior of fish (Graymore et al. 2001) and can act as a chemical barrier to the migration of fish populations (Araújo et al. 2018). The RQ was calculated on three representative trophic levels: fish, algae, and invertebrates, using three representative species, *Oncorhynchus mykiss*, *Raphidocelis subcapitata*, and *Daphnia magna*, respectively (Viegas 2021; Branchet et al. 2018; Wernke 2014; Jansen and Harmsen 2011). *Daphnia magna* species is one of the most commonly used species in ecotoxicological risk assessment and has been widely used as invertebrate model in aquatic toxicology and environmental monitoring. These organisms are among the most used in aquatic ecotoxicology tests (ISO 10706 2000; OECD 309 1998) and data on the non-observed effect concentration (NOEC) calculated using standardized approaches is available for each pollutant (https://sitem.herts.ac.uk/aeru/ppdb/en/index.htm). From NOEC data, the predicted non-effect concentration (PNEC) was calculated according to the

Table 1 Inventory of active substances used in agriculture along the Niger River in Niamey

Active substances	Active ingredient family	Target pests	Crop type
Herbicides			
Acetochlor[b,c]	Chloroacetanilide	Mono and dicotyledonous weeds	Cotton, corn, peanuts
Atrazine[b,c]	Chlorotriazine	Annual weeds	Cereal crops
Dichloride paraquat[b]	Bypirydilium	Mono and dicotyledonous weeds	Vegetable and cereal crops
Glyphosate[a]	Organophosphorus	Mono and dicotyledonous weeds	Vegetable and fruit crops
Propanil[a]	Anilide	Annual and perennial weeds	Rice
Butachlor	Chloroacetanilide	Annual and perennial weeds	Rice and vegetables
Bensulfirion-methyl	Pyrimidinylsulfonylurea	Annual and perennial weeds	Rice
Haloxyfop-R methyl[a]	Organophosphorus	Monocotyledonous weeds	All crops
Pendimethalin	Dinitroaniline	Annual weeds	Vegetable crops
Oxadiazon	Oxadiazolone	Annual and perennial weeds	Rice
Propanil[a]	Anilide	Annual and perennial weeds	Rice
Propanil + 2.4-D	Phenoxyacetic acid	Annual and perennial weeds	Rice
Pyrazosulfuron-éthyl[a]	Pyrazole	Mono and dicot weeds	Rice
Fungicides			
Carbenzadime[c] + mancozeb	Carbamate + Dithiocarbamate	Anthracnose, alternaria, mildew, powdery mildew	Rice, sugar cane
Chlorothalonil[a]	Organochlorine	Anthracnose, alternaria, mildew	Vegetable crops
Insecticides			
Abamectin[a]	Avermectin	Sucking pests, caterpillars, leaf miners	Vegetable crops
Acetamiprid[a] + indoxacarbe[a]	Neonicotinoïd + Oxidiazine	Sucking pests, caterpillars	Vegetable and green bean crops
Acetamiprid[a] + lambda-cyhalothrin	Neonicotinoid + pyrethroid	Sucking bugs, caterpillars,	Vegetable crops
Carbofuran[b]	Carbamate	Nematodes, caterpillars, sucking bites, termites	Vegetable crops
Chlorpyrifos	Organophosphorus	Sucking bites, termites, aphids, white flies, caterpillars	Vegetable and cereal crops, cowpea, rice, maize, sorghum,
Dichlorvos	Organophosphorus	Broad spectrum of insects	All crops
Emamectin benzoate[a]	Avermectin	Caterpillar	Vegetable crops
Cyperméthrin[a] + diméthoate	Pyrethroid and organophosphorus	Sucking bugs	Vegetable crops
Deltamethrin[a]	Pyrethroid	Caterpillar, aphids, flies, trips, sucking bites	Vegetable crops and rice
Fipronil[b]	Phenypyrazole	Sucking bites, caterpillars, beetles	Vegetable crops
Imidacloprid[a,c]	Neonicotinoid	Sucking pests, bugs, caterpillars, termites, beetles	Vegetable crops
Lambda-cyhalothrin + dimethoate[a]	Pyrethroid + organophosphorus	Sucking bugs, aphids, caterpillars, grasshoppers, beetles	Vegetable crops and rice

Additional Sources for information (DPV 2003): suplly center, rice cooperatives, POs and authorized distributors

[a]Pesticides approved by the Sahelian Pesticides Committee (CSP)

[b]Product banned in Niger and by the CSP

[c]Product analyzed at IMT Mines Alès

formula PNEC = NOEC / 1000; the value 1000 corresponds to the safety factor applied to take into account the inherent uncertainty of the toxicity data obtained in the laboratory.

The risk quotient value RQ was calculated using the formula RQ = MEC / PNEC with MEC corresponding to the measured environmental concentration of the grab samples (µg/L). The MEC used are the maximum values in each campaign, representing the worst-case scenario. The RQ obtained were compared to the recommended acceptable concentrations and the risk was classed as low, medium, or high.

The two pesticides presenting the highest concentrations were chosen for risk assessment.

Results and discussion

Results of the survey on agricultural practices and phytosanitary products

In Niger, there is no database on pesticide management, particularly export and consumption, and the porous nature of the borders facilitates the sale of fraudulent and toxic products. The results of the surveys carried out in March 2021 showed that 95% of the producers are illiterate men and 60% reported having received training in the use of pesticides. The area cultivated under irrigation in the surveyed zone represents about 390 ha and the area of market gardening sites is about 10 ha. The main crops inventoried in the market gardening site are tomatoes, cabbage, peppers, carrots, zucchini, parsley, celery, and lettuce, which are grown mainly during the dry season.

Pesticides are used in these crop areas by all producers, depending on the time of year and type of crop, to improve yields by controlling pests such as caterpillars, termites, grasshoppers, crickets, locusts, worms, and weeds. Seventy percent of the pesticides used are not approved by the Inter-State Committee for Drought Control in the Sahel (CILSS) and some are banned in Niger. Unfortunately, these products are sold in ¼-liter bottles in the markets of Liboré and Saga, corresponding to the site of F4, near Niamey, the capital of Niger. Sixty percent of producers claim to have received guidance on the dangers of certain pesticides on human health, such as in the case of Daksh product which stings the eyes and nose. Some products have reduced their effectiveness in recent years and are used three times with an interval of three days; thus, doses are twice higher than those recommended on the labels, with the consequence of weakening the leaves, as was seen in melon plants. Seventy-five percent of the trained producers pointed out a lack of recycling of the training received, forty percent (40%) of the respondents reported a total lack of training, and less than 10% expressed satisfaction. The results of the survey made it possible to draw up an inventory of pesticides on sale in the zone and showed that producers use several types of commercial products with 48% of active ingredients for insecticides, 45% for herbicides, and 7% for fungicides. The producers do not have appropriate storage facilities for pesticides and in sites F4, near Niamey and F5 at the confluence between the Mekrou and Niger Rivers; empty packaging is also found discarded in the wilderness.

The survey revealed that the majority of producers, including those who have already been trained, are not aware of the doses to be applied, the frequency of treatment, and the effects on health or the environment. They fail to follow procedures, and some do not use personal protection equipment during treatment (Le Bars et al. 2020; Massalatchi et al. 2017). Several studies in African countries have shown that the use of inappropriate materials for pesticide dosing by mostly illiterate producers is a factor that can increase their exposure (Lehmann et al. 2017 and 2018; Gouda et al. 2018; Le Bars et al. 2020).

Table 1 provides a non-exhaustive list of active ingredients inventoried at sites F4 and F5 in the study area according to pesticide type, pest type, and crop type. Of the twenty-eight polar compounds analyzed at IMT Mines Alès, 28% are homologated in Niger and are included in the list of pesticides registered by the Sahelian Pesticides Committee (CSP INSAH 2015; PPAAO 2016). Of all active ingredients found in the study area, 15% were analyzed at IMT Mines Alès by tandem mass spectrometry, corresponding to 27% of herbicides. These herbicides are used extensively in rice cultivation to control weeds and are applied in double cropping during the year (wet and dry seasons). Some active ingredients are homologated in Niger, others are non-homologated in Niger and by the CSP, and some were analyzed at ITM Mines Alès as mentioned in Table 1.

Analysis of the results of grab samples and passive sampling (POCIS)

Frequency of detection and quantification of herbicides and fungicides in the Niger River

Twenty-eight target compounds, consisting of twenty-three pesticides (acetochlor, alachlor, atrazine, azoxystrobine, chlortoluron, dimethomorph, diuron, epoxiconazole, imidachloprid, isoproturon, linuron, metalaxyl, metholachlor, oxydiaxyl, Penconazole, prochloraze, propyzamide, prosulfocarb, pyrimethanil, simazine, tebuconazole, terbuthylazine, tetraconazole) and five degradation products (DCPMU, DCPU, DEA, DET, DIA), were analyzed (Table 2).

For all the sampling campaigns, twelve pesticides, including ten herbicides composed of acetochlor, alachlor, diuron and its metabolites (DCPMU and DCPU), atrazine and its metabolites (DEA and DIA) and simazine, and two fungicide compounds metalaxyl and tebuconazole, were detected, representing 38% of the compounds analyzed, and 32% were quantified (Figs. 2 and 3). For the grab samples, the fungicide tebuconazole was never detected and the fungicide metalaxyl was detected but not quantified. Due to a low recovery values for DCPMU, this compound was never detected or quantified in grab samples. DCPU was not detected and quantified in POCIS even if the sampling rate is around 0.333 L/day (obtained in lab conditions). The herbicide tebuconazole was only detected and quantified at low concentrations in POCIS. Alachlor was detected but not quantified in any of the samples.

Table 2 Limit of detection (LOD) and quantification (LOQ) on water samples and POCIS samples for the twenty-eight targeted pesticides

Active Substances	Chemical Family	Water LOD (ng/L)	Water LOQ (ng/L)	POCISLOD (ng/L)	POCISLOQ (ng/L)	Sampling rate Rs (L/day)	Reference
Herbicides							
Acetochlor	Chloroacetamide	5	16.7	0.4	1.4	0.223	Ibrahim et al. 2013a
Alachlor	Chloroacetamide	11.4	37.9	0.8	2.7	0.256	Ibrahim et al. 2013a
Atrazine	Triazine	7.2	23.9	0.5	1.7	0.254	Ibrahim et al. 2013a
Chlortoluron	Urea	14.1	47.1	0.5	1.7	0.252	Ibrahim et al. 2013a
DCPMU	Urea	6.8	22.7	0.5	1.7	0.285	Ibrahim et al. 2013a
DCPU	Urea	11.3	37.6	0.9	3.2	0.333	Ibrahim et al. 2013b
DEA	Triazine	19	18.1	0.3	1.1	0.133	Ibrahim et al. 2013b
DET	Triazine	8.5	28.3	0.4	1.2	0.254	Ibrahim et al. 2013b
DIA	Triazine	12.4	41.3	1.9	6.4	0.068	Ibrahim et al. 2013a
Diuron	Phenylurea	6.5	21.6	0.4	1.3	0.257	Ibrahim et al. 2013a
Isoproturon	Urea	15..3	50.9	1.1	3.6	0.237	Ibrahim et al. 2013a
Linuron	Urea	5.9	19.8	1.4	4.8	0.141	Ibrahim et al. 2013a
Metolachlor	chloroacetanilide	4.2	14.0	1.3	4.2	0.268	Ibrahim et al. 2013b
Oxadixyl	Phenylamide	7.9	26.5	0.5	1.5	0.263	Ibrahim et al. 2013a
Propyzamide	Benzamide	12.3	40.9	1.2	3.9	0.195	Ibrahim et al. 2013a
Prosulfocarbe	Thiocarbamate	7.9	26.5	2.9	9.6	0.071	Ibrahim et al. 2013a
Simazine	Triazine	3.9	12.9	0.5	1.8	0.218	Ibrahim et al. 2013a
Terbutylazine	Triazine	3.6	21.9	1.2	4.2	0.163	Ibrahim et al. 2013a
Fungicides							
Azoxystrobine	Strobilurin	5.2	17.5	0.4	1.5	0.154	Ibrahim et al. 2013a
Dimethomorphe	Morpholine	13.2	43.8	0.9	3.1	0.395	Poulier et al. 2015
Epoxiconazole	Triazole	9.2	30.7	0.4	1.3	0.28	Ahrens et al. 2015
Metalaxyl	Phenylamide	6.7	22.4	0.9	3.0	0.264	Ibrahim et al. 2013a
Penconazole	Triazole	7.6	25.4	0.5	1.8	0.279	Ibrahim et al. 2013a
Prochloraz	Azole	13.3	44.3	3.1	10.3	0.08	Desgranges 2015
Pyrimethanil	Anilinopyrimidine	13	43.2	0.2	0.6	0.231	Ibrahim et al. 2013a
Tebuconazole	Triazole	7.7	25.8	1.0	3.3	0.24	Greenwood et al. 2007
Tetraconazole	Triazole	5.9	19.8	Undetermined	Undetermined	Unavailable	
Insecticides							
Imidacloprid	Neonicitinoïd	9.7	32.4	0.4	1.2	0.29	Poulier et al. 2015

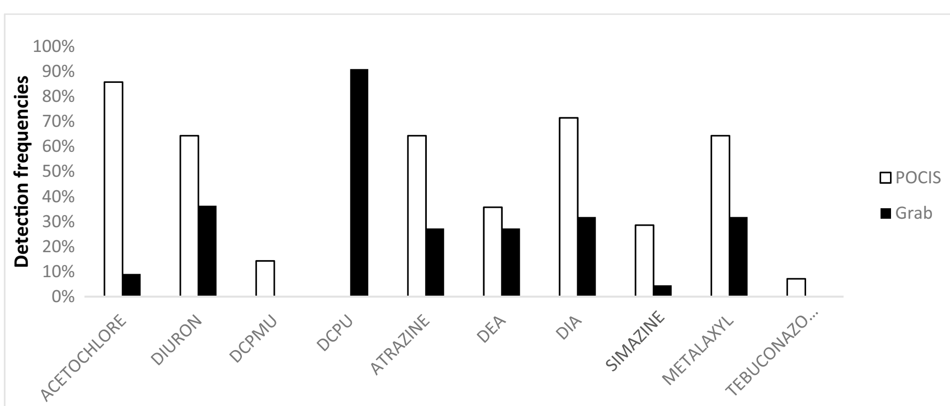

Fig. 2 Detection frequency of herbicides and fungicides for the two sampling campaigns

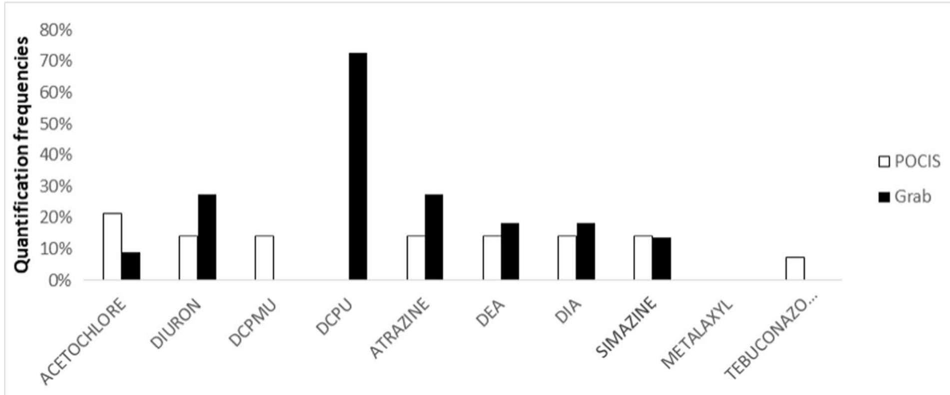

Fig. 3 Quantification frequency of herbicides and fungicides for the two sampling campaigns

The detection and quantification frequencies depend on the types of pesticides and the sampling periods. According to the results of the two sampling campaigns, the POCIS show the highest detection frequencies with 86% for acetochlor, 71% for DIA, and 64% for diuron, atrazine, and metalaxyl (Fig. 2). The highest percentage of quantification frequencies (Fig. 3) is observed for POCIS sampled during the wet season campaign between June and September 2019 and the lowest percentages for both sampling types are between April and May. The results are presented in the supplementary data (Table S3).

During the wet season from the two sampling campaigns, the pesticides with the highest quantification frequencies in the grab and passive samplings were diuron with 60%, atrazine with 40%, and acetochlor with over 20%.

Contamination of the Niger River and the Mekrou River by herbicides and fungicides

The highest concentrations, with quantification frequencies greater than 20%, were found for the grab sampling. The main pesticides encountered were as follows: diuron (2221 ± 147 ng/L) and atrazine (742 ± 143 ng/L) with its degradation products, followed by acetochlor (238 ± 22 ng/L). The two main pesticides (diuron and atrazine) were measured for the site F5 located at the confluence of the Mekrou River and the Niger River in samples collected during the month of August. The highest concentration of acetochlor was measured for the site F4 during September, downstream of the Niger River, after the city of Niamey. Pesticide concentrations in the water sampled at site F5 decreased over 3 weeks (August 09–30) and ranged from 3352 ± 178 to 1090 ± 46 ng/L for diuron and from 938 ± 44 to 546 ± 34 ng/L for atrazine (Table S4). Atrazine metabolites showed stable concentrations and few variations during the 3 weeks (100 ± 7 ng/L for DEA and 39 ± 3 ng/L for DIA). During the same wet season campaign, the other sampling sites, F1, F2, F3, F4, and F6, showed low concentrations of diuron with a detection limit of 19 ng/L for atrazine. For the other dry season, spot sampling campaigns show very low concentrations for all the compounds analyzed. The only acetochlor concentration observed during the wet season was not observed during the dry season campaign (between April/May). The presence of acetochlor at this site could be related to a one-time contamination.

For POCIS, the highest concentrations are highlighted site F5 located at the confluence of the Mekrou River and the Niger River and sampled during the month of August. The two main pesticides are diuron with an average concentration of 316 ng/L and atrazine with 217 ng/L. The POCIS for sites F1, F2, F4, and F6 of the two campaigns gave results below the detection limit and were therefore not usable (Table S4).

Summary of results obtained

According to Directive 2008/105/EC, the concentration of acetochlor, obtained by grab sampling, found for site F4 (238 ± 22 ng/L) is more than two times higher than the value of the environmental limit (100 ng/L), that of diuron for site F5 (2221 ± 147 ng/L) is eleven times higher than the norm (200 ng/L), and that of atrazine (742 ± 143 ng/L) is also higher than the norm (600 ng/L) (Table 3). In all CILSS countries, there is a lack of knowledge of the fate and behavior of pesticides in small streams in agricultural watersheds, particularly due to the great variability of the slope inputs and the complexity of the phenomena involved such as the agricultural pratiques and the rainfall event characteristics such as flooding (Rabiet et al. 2008). The intensive use of pesticides along the Niger River and its tributaries is the anthropogenic factor behind the high contamination of diuron, atrazine, and acetochlor.

The high concentrations of atrazine and diuron measured in the waters of the Boumba site (F5) merit special attention, given the large quantities of pesticides used in intensive cotton farming, which is vulnerable to insect and other pest attacks. The source of the Mekrou River is 80% located in Benin, where cotton cultivation is practiced at high altitudes and some of the pesticides used can easily run off into the

Table 3 Herbicide and fungicide average concentrations of sites F4 and F5 during the wet season in ng/L

Sampling month		August/September			
Sampling type		Grab sampling			Passive sampling
Pesticides	Actives substances	F4	F5		F5
Herbicides	Acetochlor*	238	<LD		<LD
	Diuron*	<LD	2221		277
	DCPMU	<LD	<LD		122
	DCPU	48	49		<LD
	Atrazine*	18	742		160
	DEA	<LD	97		23
	DIA	<LD	33		<LD
	Simazine*	7	38		<LD
Fungicides	Metalaxyl*	<LD	<LD		<LD
	Tebuconazole*	<LD	<LD		<LD
DCPMU	N-(3,4 dichlorophenyl)-N-(methyl)-urea			Metabolites of diuron	
DCPU	N-(3,4 dichlorophényl)- urea				
DEA	Atrazine-desethyl			Metabolites of atrazine	
DIA	Atrazine deisopropyl				

*Parent chemicals

Niger River. These transfers of pollutants from the application site at the level of the Mekrou River to the Niger River via the W Park, located on the borders of Niger, Benin, and Burkina Faso, constitute a threat and can generate significant disruptions to the ecosystems. In the Beninese and Burkinabe parts, studies have highlighted the impact of pesticides such as endosulfan, DDT, dieldrine, heptachore, lindane, pyrethroïds, and carbamates used by riparian populations on ecosystems (Soclo 2003; Ahouangninou et al. 2011; Son et al. 2017).

Although there is no data on the intensive use of pesticides in crops in southern Burkina on the Mekrou River, the high concentrations of pesticides found in Benin and Niger in this study show a potential for exposure to environmental and health impacts in this area. The potential impacts of pesticide use can result in decreased soil fertility and release of pollutants, water pollution by nitrate, ammonium NH_4^+, and heavy metals (Pb, Zn, and Mn), and other toxic compounds, as well as risks to human health, including acute poisoning, decreased fertility, and even death (Lawani et al. 2017). Table 3 below shows the concentrations observed for sites F4 and F5 during the wet season. The concentrations obtained by grab sampling are significantly higher than the LOQ (ng/L water) except for DIA at site F4 and DCPU at site F5. Moreover, for site F5, the measured concentrations are higher than for site F4, with F5 located at the confluence of the Mekrou and Niger Rivers. For POCIS, the calculated average concentrations are lower than those obtained by grab sampling. This is surprising due to their potential capacity to accumulate polar pesticides during the time of exposure (*Rs* range from 0.218 to 0.333 L/day except for DIA with a *Rs* of 0.068 L/day). The environmental conditions during POCIS exposure could explain these weak results, in particular during the wet season where the suspended matter concentration is very high and thus could disturb the accumulation efficiency (Table 3). The average concentration results of sites F4 ($n=6$ values) and F5 for grab samples ($n=12$ values) and for POCIS ($n=6$ values) are given in Table 3. The concentration results for all sampling sites for both seasons are presented in the supplementary data (Table S4).

Summary of main results and origin of pesticide contamination

For the two sampling campaigns and the two types of sampling carried out per site, the highest concentrations were observed for diuron and atrazine, followed by acetochlor. These concentrations are only observed for sites F4 and F5 sampled during the wet season campaign. Diuron and atrazine are frequently quantified in streams (Herrero-Hernández et al. 2017; Mac Loughlin et al. 2017; Ryberg and Gilliom 2015; Branchet et al. 2018).

The decrease in diuron and atrazine concentrations observed between the first and second grab sampling over a period of 3 weeks may be related to the first effect of leaching of pesticides generated by heavy rains, and concentrations would have been diluted with the increase in river flow for sites F4 on the Niger River and site F5 on the Mekrou River (Palma et al. 2004). Sampling was conducted after the first rains in June and July upstream of the Niger River in Guinea, Mali, and Burkina, where it originates. During this same period, the Niger recorded a few days of rainfall between

July and August, after a long dry season from October to June. These first rains at the beginning of the wet season may be the cause of the drainage of pollutants from the crops in the form of runoff, especially from the cotton crop in Benin on the Mekrou River and the vegetable crops in Niamey on the Niger River, thus explaining the variation of concentrations over a period of 3 weeks. This process shows that there is an influence of rainfall and runoff on the concentration of pesticides in the Niger and Mekrou Rivers (Fig. 4).

For site F4, the water sampling during September, at the end of the wet season, showed very low concentrations of diuron and atrazine. This suggests that the pesticides were diluted in the August water stream, and hence, that there is a seasonal variation in pesticide concentrations.

The presence of diuron and atrazine with highly variable concentrations at site F5, at the confluence of the Mekrou River and the Niger River, suggests a diffuse contamination of these molecules. The samples with the highest concentrations, during the first sampling, may be related to punctual contamination.

Figure 4 shows the relationship between the concentration of the diuron and atrazine analyzed in some grab samples, the distribution of the average annual rainfall in Niger at stations near Niamey, and the water level in the Niger River in 2019.

The graph shows that the high concentrations of diuron and atrazine appear during the intermediary time between the low water period and the arrival of the first rains in the Niger and Mekrou Rivers. During the periods of the year when the water level and flow are very high, the concentrations of pesticides are diluted and become low.

Site F4 has a high concentration of acetochlor and is located downstream from the city of Niamey, where market gardening is practiced on the sites of Gamkalley and Saga with two irrigated perimeters of Saga and Liboré for rice cultivation. Surveys conducted showed that farmers use different types of pesticides, depending on the crop, to control pests, diseases, and weeds, and acetochlor is mainly used in vegetable crops. The origin of this contamination seems to be mainly related to urban agriculture and irrigated crops.

Pesticide contamination comes from the upstream part of the Mekrou River at the Beninese border. Benin is the leading producer of cotton in Africa, and the Mekrou River is mostly affected by this production. This growth in cotton production is accompanied by the fraudulent use of pesticides of varying origin and quality to protect the crop (Agbohessi et al. 2011). The origin of this contamination therefore seems to be linked to intensive cotton farming.

In both types of agriculture, some of the applied pesticides can be adsorbed by soil particles and then transported to the Niger River or the Mekrou River by runoff (Chen et al. 2017; Fairbairn et al. 2016; Jorgenson et al. 2013; Mast et al. 2007; Smernik and Kookana 2015). The persistence of these pesticides in the environment is related to their susceptibility to degradation and their adsorption to suspended solids. This allows for frequent encounters with pesticides that do not rapidly break down in the water column.

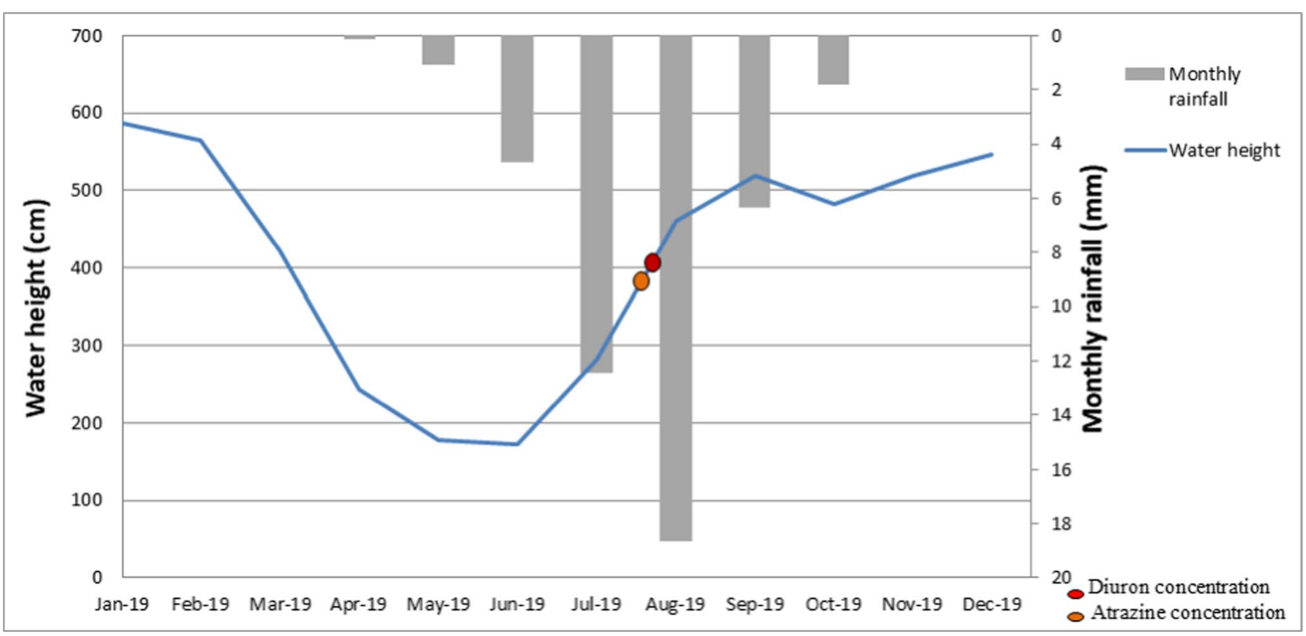

Fig. 4 Average concentration of diuron and atrazine in the grab samples in relation to water depth and rainfall

Among the pesticides found in high concentrations in the study area, acetochlor and atrazine are not homologated by the Sahelian Pesticide Committee (SPC) and are not allowed to be used in Niger due to their high toxicity and dangerousness. Their presence can be explained by their effectiveness in crop protection.

In addition to the use of certain non homologated and banned pesticides, certain poor practices by farmers, particularly during the preparation, handling, spreading, and storage of pesticides, can also contribute to environmental contamination.

The low concentrations recorded at site F2 (Table S4) show that the Sirba River, which originates in Burkina Faso, does not contribute to pesticide contamination in the Niger River. The results of the analysis of the samples from sites F1 and F6 do not show any compounds with concentrations higher than the WHO and EU water quality standards. This shows that the water of the Niger River coming from Mali is not contaminated as well as its outlet to Nigeria. The absence of contamination upstream of the city of Niamey and its presence downstream and after the market gardening sites suggest that there is a link between the intensive use of non-homologated pesticides and poor practices in the cultivation system.

Potential risk assessment for ecosystems contamination

The risk assessment (RQ) was determined using the calculated predicted non-effect concentration (PNEC) values for algae, crustacean *Daphnia magna* and fish, taking into account the highest observed water concentrations measured by grab sampling at all sampling sites on the Niger river valley and its tributary the Mekrou River. The results are presented in Table 4.

According to the results, it can be seen that the high-risk quotients are only observed for sites F1, F4, and F5 for samples taken during the wet season. Sites F1 and F4 present low risks for diuron for the algae, which has low concentrations compared to site F5.

Site F5 has high-risk quotients for all three trophic levels during the wet season, especially in August. Risks are very high for all three model species for diuron with an RQ as high as 1215.30 for algae. Pereira et al. (2015) denote that diuron has an anti-androgenic effect for Nile tilapia that impairs its reproductive function, and Coquillé et al. (2015) showed significant effects for the microalgae *Tetraselmis suecica*, notably on a 125% (± 2.3%) increase in doubling time and 25% (± 1.8%) increase in fluorescence relative to the presence of reactive oxygen species (ROS, by flow cytometry), and a 25% (± 1.8%) decrease in photosynthetic yield and 38% (± 1.9%) decrease in relative lipid content.

For atrazine, the risk is very high for algae and crustacean *Daphnia magna* and medium to low for fish. It affects the behavior of zooplankton and modifies community biodiversity. Marie et al. (2000) showed that the responses of algae vary considerably depending on the concentrations used, the duration, and the species of algae tested. Torres

Table 4 Risk quotient (RQ) calculated for atrazine and diuron from water concentrations observed after grab sampling, based on three selected trophic levels

Sites	Algae				Crustacean *Daphnia magna*				Fish			
	August/September		April/May		August/September		April/May		August/September		April/May	
	Atrazine	Diuron	Atrazine	Diuron	Atrazine	Diuron	Atrazine	Diuron	Atrazine	Diuron	Atrazine	Diuron
F1	0.13	**7.07**			0.03	0.20			0.00	0.05		
F2			0	0			0	0			0	0
F4	0.31	**2.15**	0	0	0.07	0.06	0	0	0.01	0.01	0	0
F5	**25.01**	**1215.30**			**5.90**	**34.18**			**0.74**	**8.00**		
F6			0	0			0	0			0	0

RQ > 1 (high risk)

RQ entre 0.5 et 1 (medium risk)

RQ < 0.5 (low risk)

No data

and O'Flaherty (1976) highlight a decrease in chlorophyll content (41 to 67%) after 7 days of exposure to 1 g/L of atrazine for the green algae *Chloralla vulgaris* and *Stigeoclonium* and for in the blue-green algae *Oscillatoria lutea.* WHO 1990, indicates that atrazine bioaccumulation capacity in fish remains low.

The presence of diuron and atrazine, particularly at sites F4 and F5, constitutes a major risk for the aquatic environment. No risk was identified during the dry season and only diuron presents high risks for the three trophic levels.

Conclusion

The present study confirms the pesticide contamination of the Niger River and the Mekrou River by diuron, atrazine, and acetochlor. The high pesticide concentrations observed in the study area are highlighted during the wet season mainly at sampling site F5, at the confluence between the Niger River and the Mekrou River, and at site F4 located along the Niger River, downstream of the market gardening sites and irrigated perimeters, near the city of Niamey. These sites are the most exposed to pesticide contamination in the Niger River area. The results of the survey revealed that the majority of producers use several types of commercial products with 48% of active ingredients for insecticides, 45% for herbicides, and 7% for fungicides and they are not aware of the doses to be applied.

The origin of this contamination seems to be linked to the increased use of pesticides in urban agriculture on the one hand, and in intensive cotton farming in Benin on the other. The pesticide concentrations measured could be influenced by the variation in rainfall, the increase in river flow, and the availability of non-homologated pesticides in Niger. They are higher during the first rains at the beginning of the wet season and diluted with the increase of the flow. The concentrations of diuron (obtained by grab sampling) at more than eleven times the environmental quality standard, atrazine and acetochlor at more than two times the standard, constitute a worrying situation on the quality of the waters of the Niger River and the Mekrou River. Sampling with POCIS provided information on the presence of polar pesticides (high detection frequency of herbicides and fungicides) but the quantification of their concentrations indicates lower accumulation efficiency than expected according to sampling rates obtained in lab conditions. Nevertheless, passive sampling could be an appropriate method for environmental monitoring of pesticide contaminants, in space and time, along the Niger and Mekrou Rivers, due to the lack of specialized laboratories for the analysis of organic pollutants, adequate sampling equipment, and the remoteness of some sites. The risk quotient determination highlighted a high risk for phytoplankton (algae: *Raphidocelis subcapitata species*), zooplankton (*Daphnia magna*), and fish (*Oncorhynchus mykiss*) for diuron. That of atrazine is also very high for algae and aquatic invertebrates and medium to low for fish.

Given the results of this exploratory work on pesticide contamination and the high risks for site F5, it is necessary to consider additional sampling along the Mekrou River in the direction of Benin and to set up environmental monitoring of the waters of the Niger River to gain a good understanding of the variation of contaminants over time and space.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s11356-022-23526-3.

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Author contribution The authors confirm contribution to the paper "Occurrences, distribution and risk assessment of polar pesticides in Niger River valley and its tributary the Mekrou River (Niger Republic)". Oumar El Farouk Maman Illatou contributed to the sampling, sample preparation, survey of agricultural practices and pesticide use, analysis and results interpretation, and writing of the final manuscript. Catherine Gonzalez, Sylvie Spinelli, Murielle Avezac, and Marine Bertrand contribute to the program of the sampling and sample preparation and analysis and interpretation of results and manuscript preparation. Marc Vinches contributes to the preparation of sampling, interpretation of results, and manuscript preparation.

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Data availability All data generated or analyzed during this study are included in this published article. They are openly available.

Declarations

Ethical approval Not applicable.

Consent to participate Not applicable.

Consent for publication I Mahamadou, responsible of the farmers, give my consent to publish our information on the agricultural practices and pesticides used during the survey work done by Oumar El Farouk Maman Illatou. I have discussed in detail with him and give my approval for publishing all of the results of the survey done.

My name will not be published on his article.

Competing interests The authors declare no competing interests.

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