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RESEARCH ARTICLE

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ASSESSMENT OF GROUNDWATER CONTAMINATION BY PESTICIDE RESIDUES IN MARKET GARDEN SITES, DEPARTMENT OF MADAOUA-NIGER

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ABSTRACT

In the Department of Madaoua-Niger, the intensification of market gardening and the uncontrolled use of unregistered pesticides in the majority of cases are sources of pollution of water resources that are also used for human consumption, animal watering and household needs. The objective of this study is to quantify pesticide residues in water from market garden in order to show their level of contamination by its residues and the health risks associated with its consumption. Fifteen (15) water samples from market garden drilling were taken at the end of the 2019 dry season and analyzed by the QuEChERS method. Seventeen pesticide residues belonging to five chemical families, namely organochlorines, organophosphates, pyrethroids, carbamates and dinitroanillins were quantified at concentrations ranging from 0.02 to 0.5 µg/l. The results show that the waters of these market garden sites are contaminated by aldrin (0.1-0.3 µg/l), heptachlor (0.05-0.5 µg/l), glyphosate (0.17-0.5 µg/l), deltamethrin (0.12-0.35 µg/l), cypermethrin (0.2-0.46 µg/l), and lambda-cyhalothrin (0.11-0.34 µg/l). Their concentrations increase from 1.10 to 16.66 times their WHO and EU MRLs in all samples. In addition, the concentrations of DDT, α -endosulfan, β -endosulfan, chlorpyrifos methyl, pendimethalin and carbofuran exceed their EU drinking water MRLs by 1 to 5 times in all samples. The sum of the concentrations of all quantified pesticide residues ranges from 2.427 to 3.675 µg / l and is 4.73 to 7.95 times higher than the WHO and EU potability standard of 0.5 µg / l for the total concentrations of active ingredients determined in a water sample. Some pesticides such as DDT, aldrin, dieldrin, endosulfan, and lindane are even banned according to Annex III of the Rotterdam Convention for health or environmental reasons. The search for pesticide residues has revealed the pollution of water from the market garden sites studied.

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INTRODUCTION

The valley lands of the Department of Madaoua, commonly known as the Lower Tarka Valley are among the most exploited areas in Niger for market-gardening crops. Indeed, market gardening is practiced on the same plots two to three times a year and for more than ten years (UNDP, 2009). In these areas, the main water uses are irrigation, domestic needs and animal watering through, in order of importance, the use of boreholes and market garden wells (Mato, 2011; Zabeirou et al., 2018). Water resources for irrigation in this area are very vulnerable to pollution by pesticides, especially herbicides, due to the shallow depth of the water table, which

varies between 6 and 12 m (Mato, 2011). To increase yields, growers use fertilizers and pesticides for which they have little technical knowledge for rational and safe application. Moreover, the intensive application of phytosanitary products in the Department of Madaoua had begun in the 1990s with the intervention of some development projects such as the Lower Tarka Valley Project (PBVT), which considerably supported producers in the acquisition of agricultural inputs (Mato, 2011). A study conducted on farmers' pesticide use practices in the three communes of the Department of Madaoua (Zabeirou et al., 2018), revealed an abusive use of unregistered pesticides on market-gardening crops. This

represents a source of environmental pollution and enormous risks to human and animal health. In addition to drift and spills of residual spray solution or rinse water from sprayers into watercourses, through runoff, persistent pesticide residues in soils can be carried to surface waters and by drainage to groundwater (Gouda *et al.*, 2018). The objective of this study is to determine the presence and concentration of pesticide residues in water samples from market gardening boreholes in the Department of Madaoua, Tahoua-Region, Niger in order to show their level of contamination by its residues and the health risks associated with its consumption.

MATERIALS AND METHODS

Presentation of the study area: The department of Madaoua belongs to the Sahelian zone. It lies between the meridians 5°45' and 6°30' and the parallels 13°40' and 14°20' and covers an area of 4503 km², with an estimated population of 652 865 inhabitants on 30 November 2018 (NIS, 2018a). The department of Madaoua is composed of six (6) communes distributed in the basin of the base valley of the Tarka River. The municipalities concerned by this study are those of Galma, Madaoua and Sabon Guida, pink color in Figure 1.

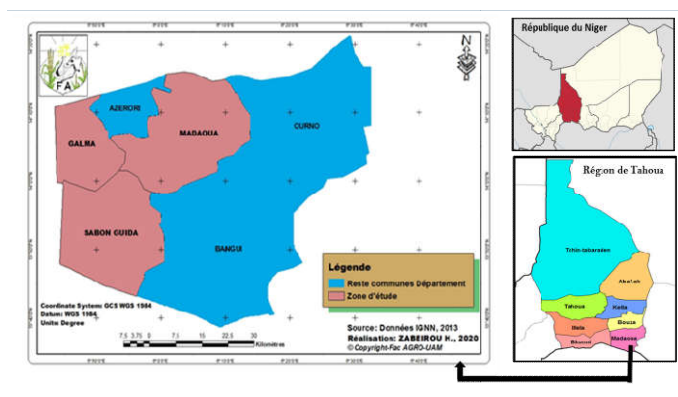


Fig. 1. Location of the study area

From 2013 to 2018, the average recorded precipitation is 632.33 mm and the mean temperature is 29.75°C (NIS, 2018a; NIS, 2018b). The main morphological units are plateaus, slopes, ponds, glacis, low-lying areas or shallows, dune buildings. The soils are predominantly clayey and clay-silt textured (NIS, 2018a). Irrigated agriculture is being developed throughout the area where the potential for irrigable land is estimated at 121 955 ha in 2012 (INS, 2012). On average, 7000 ha per year are sown with market gardening on a total of 69 sites inventoried from 2016 to 2018 (MAG/EL, 2018). The study concerned the market gardening boreholes of three municipalities of the department, namely Galma, Madaoua and Sabon Guida. These are the communes of intervention of the Research and Development for Food Security and Climate Change (RED/SAAC) project, which took charge of the study. The choice of these communes is based on accessibility reasons, the large number of market gardeners, the concentration and diversification of crops and above all the intensive use of pesticides.

Sampling: To determine the concentration levels of pesticide residues, fifteen (15) samples of water from market gardening boreholes were collected including five in the commune of Galma, five in Madaoua and five in Sabon Guida. The figure 2

shows the geographical position of the sampled market gardening boreholes.

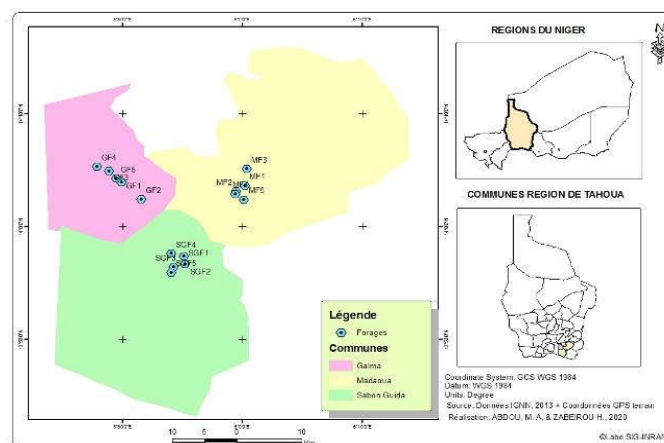


Fig. 2. Geographical position of the sampled market gardening boreholes

Sampling was done using the same technique that was applied in Togo, Senegal and Niger (Gbénonchi, 2008; Diop, 2013; Adamou, 2014). For this purpose, water samples from market gardening boreholes were collected in 1000 ml plastic bottles, previously rinsed with distilled water and sterilized. When sampling, the bottles were first rinsed three times with the borehole water before putting the sample in. Aluminium foil was placed under the cap before sealing to prevent any exchange between the sample and the outside. The bottles were then wrapped with aluminium foil to avoid the effect of illumination and labelled. Finally, they were transported in coolers with ice to the laboratory of the Faculty of Agronomy of the University of Niamey where they were kept in the refrigerator at 4°C before being shipped to the analysis laboratory.

Choice of molecules to search

The pesticide monitoring obtained from the 2018 surveys (Zabeirou and al., 2018) was used as a reference for the choice of active substances to be researched. However, other secondary parameters were also taken into account. These are:

- Physico-chemical properties of pesticides: degradation rate, water solubility, toxicity and persistence.
- Types of pesticides reconditioned since importation. In practice, market gardeners use some pesticides imported from Nigeria or Ghana, countries whose phytosanitary legislation is not identical to the process of pesticide registration by the Sahelian Pesticide Committee (CSP) of which Niger is a member. These pesticides are repackaged in 5 to 25 liter drums without any label. The active ingredient(s) and use instructions are not known. Other pesticides are repackaged in drums with the indication of some active ingredients such as DDT, endosulfan and heptachlor.

In addition to this, the Department of Madaoua has been subject to intensive pesticide application in recent years during mass locust control treatments by the General Direction of Plant Protection-GPG of Niger. Taking all these parameters into account, it was deemed necessary to carry out a broad analysis of residues by chemical family for the ten most commonly used chemical families, namely organochlorines,

organophosphates, pyrethroids, carbamates, avermectins, dinitroanillins, oxadiazonoles, chloroacetanillides, triazoles and Bipyridylum.

Extraction and separation of pesticide residues

The extraction and analysis of pesticide residues in water samples from market garden boreholes was carried out using the QuEChERS method (Anastassiades and al., 2003). Liquid/liquid extraction is the method used to extract pesticide residues from water samples taken. It consists of transferring 500 ml of water sample to a 1l separating funnel to which 60 ml of extractive solvent composed of a hexane/dichloromethane mixture (70/30, v/v) is added. The whole thing is shaken vigorously for 4 minutes, periodically expelling air. The organic phase is allowed to settle for 10 minutes, at the end of which the organic phase is collected in a 250 ml flask with a funnel containing anhydrous sodium sulphate on Whatman® cellulose filter paper. The operation is repeated twice with 40 ml of organic solvent and the extracts collected in the same flask as before. The total combined extract obtained is then concentrated in the rotavapor at 35-40°C to a volume of 2-3 ml.

RESULTS

The analytical results of pesticide residues in the fifteen (15) water samples from the market garden boreholes studied are presented in Table 1. The analysis of Table 1 shows that seventeen (17) pesticide residues belonging to five chemical families were quantified at concentrations ranging from 0.020 to 0.500 µg/l. The families to which these pesticide residues belong are organochlorines (DDT, aldrin, chlorothalonil, endosulfan, heptachlor and lindane), organophosphates (dimethoate, methyl chlorpyrifos, malathion, profenofos and glyphosate), pyrethroids (deltamethrin, cypermethrin, lambda-cyhalothrin), carbamates (Carbofuran) and dinitroanillins (pendimethalin). Organochlorines are in first place with 41.2 %, followed by organophosphates with 29.4 % and pyrethroids are in third position with 17.6 %. Carbamates and dinitroanillins each have 5.9 % of the total. The levels of contamination of the groundwater of these market gardening sites by pesticides are compared to: 1) the WHO potability standards of 0.1 µg/l per individual substance and 0.5 µg/l for total active ingredients (WHO, 1994; WHO, 2004; WHO, 2017); 2) European Directives 75/440/EEC and 98/83/EC which set Maximum Allowable Concentrations - MACs for

Table 1. Concentrations of pesticide residues in water samples from market gardening boreholes in Galma, Madaoua and Sabon Guida (µg/l) in comparison with WHO (1994, 2004, 2017) and EU (1975, 1998) MRLs (µg/l)

	GF1	GF2	GF3	GF4	GF5	MF1	MF2	MF3	MF4	MF5	SGF1	SGF2	SGF3	SGF4	SGF5	Moy	LMR OMS	LMR UE
DDT	0,150	0,154	-	0,022	0,021	-	0,160	0,185	0,158	0,055	0,046	0,150	0,084	0,160	-	0,090	1	0,1
Aldrin	-	0,110	0,160	0,200	0,100	0,300	0,200	0,160	-	0,150	-	0,120	0,170	0,200	0,170	0,136	0,03	0,03
Chlorothalonil	0,020	0,020	-	0,046	0,029	-	0,050	-	0,056	0,064	0,020	0,050	-	0,040	0,030	0,028	0,1	0,1
α-Endosulfan	0,200	0,350	0,105	0,360	0,100	0,320	0,310	0,152	0,410	0,500	0,350	0,200	0,440	0,380	0,180	0,290	2	0,1
β-Endosulfan	-	0,170	-	0,300	0,140	0,120	-	0,350	0,290	0,220	0,250	0,150	0,180	-	0,180	0,157	2	0,1
Heptachlor	0,450	0,490	0,050	-	0,130	0,130	0,170	-	0,500	0,390	0,400	0,180	0,250	-	0,460	0,240	0,03	0,03
Lindane	0,039	0,046	0,026	0,041	0,044	0,035	0,081	0,046	0,022	0,028	0,065	0,055	0,122	0,020	0,028	0,047	2	0,1
Dimethoate	0,162	0,127	0,096	0,170	-	0,160	0,143	0,174	0,180	-	0,150	-	0,200	0,117	0,119	0,120	0,1	0,1
Methyl Chlorpyrifos	0,095	-	0,130	0,090	0,240	0,200	0,350	0,180	0,120	0,079	0,280	-	0,306	0,180	0,114	0,158	5	0,1
Malathion	0,167	-	0,210	0,080	0,150	0,420	0,230	0,470	-	0,140	0,128	0,350	0,280	0,119	-	0,183	0,1	0,1
Profenofos	0,110	0,080	0,210	-	0,130	0,210	0,150	0,090	0,210	-	0,110	0,120	-	0,110	0,140	0,111	0,1	0,1
Glyphosate	0,400	0,220	0,310	0,230	0,450	0,500	0,410	0,320	0,430	0,250	0,480	0,170	0,220	0,310	0,410	0,341	0,1	0,1
Deltamethrin	0,170	0,140	0,130	0,150	0,350	0,200	0,150	0,260	0,290	0,160	0,260	0,120	0,130	0,306	0,250	0,204	0,1	0,1
Cypermethrin	-	0,400	0,260	0,370	0,310	0,320	-	0,420	0,260	0,460	0,270	0,370	0,210	0,200	-	0,257	0,1	0,1
λ-Cyhalothrin	0,220	0,130	0,260	-	0,340	0,280	-	0,140	-	0,330	-	0,110	0,210	0,260	0,200	0,165	0,1	0,1
Pendimethalin	0,160	0,200	0,180	0,150	0,130	0,180	0,120	0,140	0,175	0,150	0,120	0,120	0,160	0,140	0,150	0,152	20	0,1
Carbofuran	0,430	0,200	0,300	0,470	-	0,300	0,130	0,410	0,300	0,490	0,140	0,370	0,290	-	0,200	0,269	7	0,1
Total	2,773	2,837	2,427	2,679	2,664	3,675	2,654	3,497	3,401	3,466	3,069	2,635	3,252	2,542	2,631	-	0,5	0,5

Value in "-": pesticide residue not detected or found below the limit of quantification; GF1 to GF5: Galma samples; MF1 to MF5: Madaoua samples; SGF1 to SGF5: Sabon Guida samples; MRL values in red: default values when a specific MRL is not given; WHO MRLs: Guidelines for Drinking Water Quality, 1994, 2006 and 2017 editions; EU MRLs: European Directives 98/83/EC and 75/440/EEC.

The concentrated extract is transferred to a pillbox with 3 ml flushing of the flask and concentrated to dryness under a stream of pure nitrogen (99.9%). The dry residue is taken up with 1 ml of hexane or methanol. Gas chromatography, coupled with electron capture detector (ECD) or thermoionic detector (NPD) was used to determine organochlorines and organophosphates. The other families of pesticides were analysed by high-performance liquid chromatography using a diode-array detector (HPLC/DAD).

Statistical analysis: Excel version 2016 was used to prepare the data and design the graphs. The maps were designed with Arc Gis, version 10.5.

pesticides in raw water and in the consumer's tap water. According to these European Directives, MRLs are set at 0.10 µg/l for each pesticide (except aldrin, dieldrin, heptachlor and heptachloro-epoxide: 0.03 µg/l) and 0.50 µg/l for the total of the substances measured (EU, 1975; EU, 1998).

The results in Table 1 show that:

- Only one product (chlorothalonil) showed concentrations below the maximum residue limits (0.1 µg/l) established by the WHO and the EU in all samples, representing 5.88 % of all residues quantified. Its concentrations range from 0.020 to 0.064 µg/l. The maximum concentration is obtained

in the commune of Madaoua, while the minimum concentration is recorded in Galma and Sabon Guida. Its average concentration for the study area of 0.028 µg/l is also below the WHO and EU MRLs.

- 35.29% of pesticides have residue levels above WHO and EU potability standards in all samples. The organochlorines are aldrin and heptachlor, an organophosphate (glyphosate) and three pyrethroids including deltamethrin, cypermethrin and lambda-cyhalothrin. The figure 3 shows the exceedance of the pesticide residues quoted in relation to the water potability standards set by the WHO and the European Union.

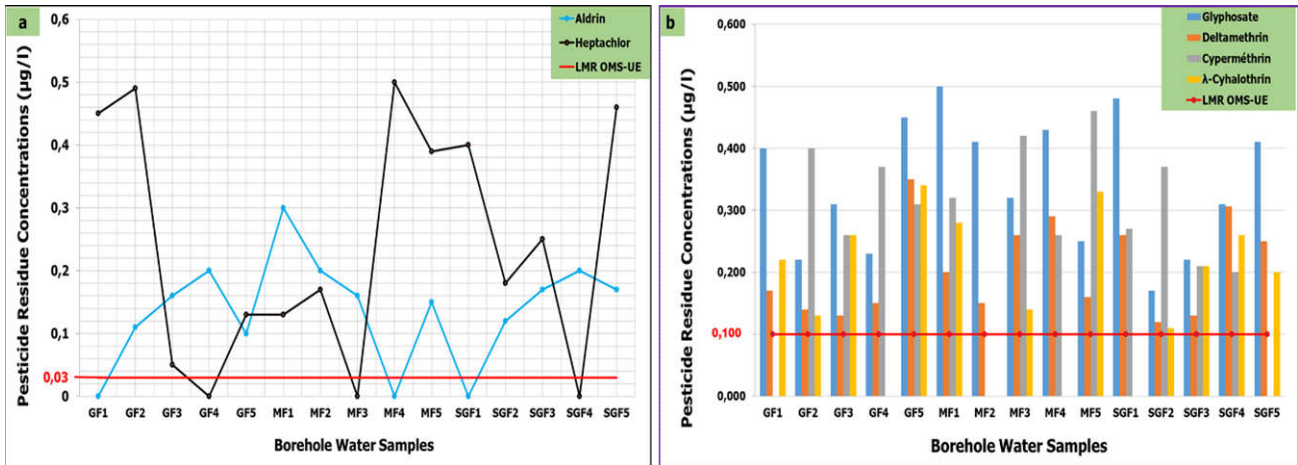


Fig. 3. (a) Residues of organochlorine pesticides (µg/l) with concentrations exceeding the WHO and EU MRLs (0.03 µg/l) in borehole water for market gardening according to sites; (b) Residues of organophosphorus and pyrethroid pesticides (µg/l) with concentrations exceeding the WHO and EU MRLs (0.1 µg/l) in borehole water for market gardening according to sites

- **Aldrin:** the residual values of cypermethrin vary from 0.200 to 0.460 µg/l and were quantified in 80% of the samples. These concentrations exceed the MRLs set for this substance by WHO and the EU by 2 to 4.5 times (0.1 µg / l) in drinking water. The minimum value is obtained in the SGF4 sample from Sabon Guida, while the maximum is found in the MF5 sample from Madaoua. The average concentration of all the drillings analyzed is 0.257 µg/l. This value is 2.57 times the WHO and EU MRLs for cypermethrin in drinking water.
- **Heptachlor:** detected in 80 % of samples, its concentrations fluctuate between 0.050 and 0.500 µg/l. Its residual values are 1.66 to 16.66 times the MRL set according to WHO and EU guidelines for drinking water quality. The average concentration in the boreholes analysed (0.240 µg/l) is 8 times the MRL defined by the WHO and the EU. The minimum (0,050 µg/l) and maximum (0,500 µg/l) values are obtained in Galma (GF3 sample) and Madaoua (MF4 sample) respectively.
- **Glyphosate:** The glyphosate was found in 100 % of the samples at concentrations ranging from 0.170 to 0.500 µg/l. These values are 1.7 to 5 times higher than the MRL for this substance listed in Table 1. The minimum concentration is obtained at Sabon Guida, in the SGF2 sample, while the maximum is found in the MF1 sample from Madaoua. The average concentration at the sites studied is 0.341 µg/l and exceeds its WHO and EU MRL by 3.41 times.
- **Deltamethrin:** It was quantified in 100 % of samples. The concentrations of deltamethrin fluctuate between

0.120 and 0.350 µg/l and exceed the WHO and EU MRLs by 1.2 to 3.5 times (0.1 µg/l) for this substance. The minimum and maximum values are obtained in the Sabon Guida SGF2 and Galma GF5 samples, respectively. The average concentration in the study area is 0.204 µg/let exceeds its MRL in drinking water by 2.04 times.

- **Lambda-cyhalothrin:** its concentrations obtained in 73.33 % of the samples oscillate between 0.110 and 0.340 µg/l, which is 1.1 to 3.4 times higher than the MRL defined by the WHO and the EU. The average concentration in the study area is 0.160 µg/l and is 1.6 times the WHO and EU potability standards for this

substance. The minimum value is quantified at Sabon Guida (sample SGF4) and the maximum at Galma (sample GF5).

- ❖ 35.29 % of quantified pesticides have concentrations below the WHO potability standards. But a large proportion of the samples have values that exceed the MRLs set according to EU directives. This group contains DDT, α-endosulfan, β-endosulfan, chlorpyrifos methyl, pendimethalin and carbofuran.
- **DDT:** Residual concentrations of DDT were measured in 80 % of the groundwater samples and are between 0.021 and 0.185 µg/L. It should be noted that 46.66% of the samples (GF1, GF2, MF2, MF3, MF4, SGF2 and SGF4) have concentrations that increase from 1.5 to 1.85 times the maximum residue limit for DDT set by the European Union which is 0.1 µg/l. The average concentration in the study area is 0.090 µg/l and is below the potability standards for this substance laid down by the WHO and the EU.
- **Alpha and beta-Endosulfan:** determined in 93.93 % of the samples, the concentrations of α-endosulfan ranged from 0.100 to 0.500 µg/l and exceeded the EU MRL (0.1 µg/l) by 1 to 5 times. The average concentration of α-endosulfan in the 15 samples analysed is 0.29 µg/l and is also 2.9 times the MRL set by the EU. The minimum value is obtained at Galma (sample GF5) and the maximum at Madaoua (sample MF5). β-endosulfan was quantified in 73.33% of the samples and all concentrations found are 1.2 to 3.5 times the EU MRL. Its concentrations fluctuate between 0,120 µg/l

(minimum obtained in sample MF1) and 0,350 $\mu\text{g/l}$ (maximum quantified in MF3). The average residue value of β -endosulfan from the sites studied is 0.157 $\mu\text{g/l}$ and exceeds its EU MRL by 1.57 times.

- Chlorpyrifos methyl:** residual values of chlorpyrifos methyl are measured in 86,66 % of the samples and varied between 0,079 and 0,350 $\mu\text{g/l}$. It should be noted that 76.92% of these values exceed the WHO and EU MRL (0.1 $\mu\text{g/l}$) by 1.14 to 3.5 times. The other values are below the international MRLs. The average concentration of 0.158 $\mu\text{g/l}$ in the analysed boreholes multiplies the WHO and EU potability standards for this substance by 1.58 times. The minimum (0,079 $\mu\text{g/l}$) and maximum (0,350 $\mu\text{g/l}$) values are quantified at Madaoua in samples MF5 and MF2 respectively.
 - Pendimethalin:** it was found in 80 % of the samples. Its quantified concentrations range from 0.12 to 0.2 $\mu\text{g/l}$ and surpass its EU MRL by 1.2 to 2 times. The average value of all samples analysed is 0.152 $\mu\text{g/l}$, which is 1.52 times the MRL fixed by the EU. The minimum value is obtained in the samples of Madaoua and Sabon Guida (MAE2, SGF1 and SGF2) while the maximum is recorded only in Galma (GF2).
 - Carbofuran:** detected in 86.66 %, carbofuran concentrations fluctuate between a minimum of 0.13 $\mu\text{g/l}$ and a maximum value of 0.49 $\mu\text{g/l}$, all found in Madaoua. It should be noted that all the values found exceed the MRL of the EU directives by 1.3 to 4.9 times. The mean value, 0.269 $\mu\text{g/l}$ multiplies the EU MRL for this chemical by 2.69 times.
- ❖ Lindane, dimethoate, malathion and profenofos have concentrations, some of which are below WHO and EU standards and some of which are above these international standards.
- Lindane:** It should be noted that 93.33 % (14/15) of the samples have lindane concentrations below the maximum residue limits established by the WHO (2 $\mu\text{g/l}$) and the EU (0.1 $\mu\text{g/l}$). A single sample, SGF3 from Sabon Guida, has a concentration that exceeds the EU MRL (0.1 $\mu\text{g/l}$) by 1.22 times. Its concentrations vary between 0.020 and 1.22 $\mu\text{g/l}$, with an average of 0.046 $\mu\text{g/l}$ from the boreholes analysed, which is also below WHO and EU standards.
 - Dimethoate:** 91.66 % of the values found (11/12 samples) exceed 1.17 to 2 times its maximum residue limits defined by the WHO and the EU (0.1 $\mu\text{g/l}$). Only one value of 0.096 $\mu\text{g/l}$ recorded at Galma (GF3) is below these standards. The average concentration at the investigated sites is 0.12 $\mu\text{g/l}$ and is 1.2 times the WHO and EU MRL.
 - Malathion:** it was quantified in 80 % of the samples at concentrations ranging from a minimum of 0.080 $\mu\text{g/l}$ (found in GF4) to a maximum of 0.470 $\mu\text{g/l}$ (quantified in MF3). It should be mentioned that 91.66% of these values are above the maximum residue limits set by the WHO and the EU (0.1 $\mu\text{g/l}$) by 1.19 to 4.7. The average concentration of all samples was 0.183 $\mu\text{g/l}$ and exceeded its MRLs by 1.83 times.
 - Profenofos:** it was found in 80 % of the samples and 83.33% of the values (10/12) exceed WHO and EU MRLs by 1.1 to 2.1. Values below the MRLs (0.080 and 0.090 $\mu\text{g/l}$) were detected in Galma (GF2) and Madaoua (MF3) respectively and the maximum

concentration (0.21 $\mu\text{g/l}$) was recorded in Madaoua (MF4). The average concentration is above the WHO and EU MRLs by 1.11 times.

The sum of concentrations of the various pesticide residues quantified in sampled water from market garden boreholes range from 2.427 to 3.675 $\mu\text{g/l}$. This cumulated multiplies from 4.854 to 7.35 times the potability standard set by the World Health Organization (WHO) and the European Union (EU), which is 0.5 $\mu\text{g/l}$ for the total of active ingredients quantified in a water sample (see Fig. 4).

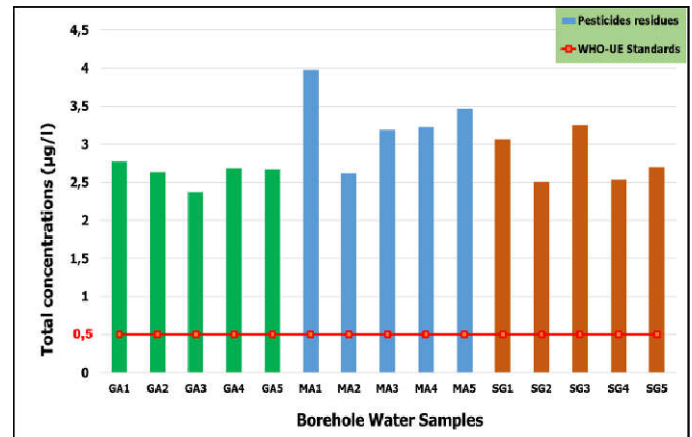


Fig. 4: Total of the concentrations of different quantified pesticide residues in borehole water in Madaoua compared to WHO and EU MRLs ($\mu\text{g/l}$)

For the municipality of Galma, this total fluctuates between 2.427 and 2.837 $\mu\text{g/l}$, which exceeds the international standards of the WHO and the EU by 4.854 to 5.674 times. In the commune of Madaoua, the sum of the concentrations of all the measured residues is between 2.654 and 3.675 $\mu\text{g/l}$, which is 5.308 to 7.35 times higher than the limit of 0.5 $\mu\text{g/l}$ specified by the WHO and the EU. For the municipality of Sabon Guida, the cumulated pesticide residue values measured vary from 2,542 to 3,252 $\mu\text{g/l}$. This sum is 5.084 to 6.504 times higher than the potability standard (0.5 $\mu\text{g/L}$) defined by the WHO and the E.U. for total dosed active ingredients. The water from market gardening boreholes in the commune of Madaoua has recorded the highest cumulative concentration of pesticide residues than those in the communes of Sabon Guida and Galma, with a ranking of sites in the order Madaoua > Sabon Guida > Galma.

DISCUSSIONS

Bad phytosanitary practices likely to pollute the water table are developed by most market garden producers in these sites as elsewhere in the countries of the West African sub-region. This mainly involves the use of highly toxic pesticides and restricted for use by the Sahelian Pesticides Committee (CSP, 2019) such as DDT, lindane, aldrin, etc. at very high doses (1.5 to 2 times the recommended doses) and in repetitive ways (13 to 26 treatments depending on the crop). The soils of the Madaoua Valley are a source of water resource pollution. Indeed, twenty-seven pesticide residues belonging to 8 chemical families were quantified in soils from the same sites at average concentrations ranging from 3.6 to 678 $\mu\text{g/Kg}$ (Zabeirou and al., 2020). The leaching of crop soils by runoff and infiltration are other factors that accentuate the pollution of the water table in market gardening sites (Zabeirou and al., 2018; Gbénonchi, 2008; Diop, 2013; Saley, 2012; Kanda, 2013; Ado, 2014), such as those in the Department of Madoua.

The pesticide residue concentrations obtained in water from market garden boreholes in the Department of Madaoua are similar to several results of studies reported in the literature. The residual level of pesticides detected in groundwater in our study area was more compared to the available data from African countries where phytosanitary practices are quite similar to those prevailing in Niger such as Benin, Burkina Faso, Mali, Senegal, Tanzania and Togo.

A similar study conducted in the Dallol Maouri-Region of Dosso, Niger quantified DDT in market garden wells at a concentration of 0.02 µg/l (Adamou, 2014). The values found in our work increase this concentration from 1.05 to 9.25 times. The average DDT residue concentration in our study area also exceeds this concentration by 4.33 times. DDT has been quantified in the Niayes-Senegal zone at a mean concentration of 0.64 µg/L in the market gardening wells (Diop, 2013). This concentration is 3.45 to 30.47 times higher than the concentrations found in our work. In Togo (Gbénonchi, 2008), DDT residues were measured in the waters of the Anié River at a concentration of 0.11 µg/l, the Mono River at 0.15 µg/l and in the Adéta wells at 0.03 µg/l. It should be noted that the concentration of DDT in water in 58.33% of samples from our study area is 1.36 to 1.68 times the concentration found in the Anié River and 1.53 to 6.16 times the concentration measured in Adéta wells in 83.33% of cases. On the other way, the concentration of the Mono River is close to the concentrations quantified in this work in the majority of cases (60 %). In Kenya, the mean residual concentration of DDT in Lake Nakuru water is 1.09 µg/l (Mavura and Wangila, 2004). This value exceeds the concentrations found in our study by 5.89 to 51.9 times. Aldrin was quantified at a mean concentration of 1.7 µg/L in market gardening wells in the Niayes-Senegal area (Diop, 2013) and at 4.54 µg/L in the waters of Lake Nakuru-Kenya (Mavura and Wangila, 2004). Residual aldrin values obtained in Niayes-Senegal and Kenya exceeded the concentrations found in this investigation by 5.66 to 17 times and 15.13 to 45.4 times, respectively.

In the water of the Mono River in Togo (Gbénonchi, 2008), aldrin was determined at a concentration of 0.07 µg/l. A study of domestic well water in the Korokoro -Mali area (Maiga, 2017) also revealed the presence of aldrin at the concentration of 0.2 µg/l. These data on aldrin residues in water from these studies corroborate with the results obtained through this analysis. In market gardening wells in the Niayes-Senegal zone, alpha-endosulfan and beta-endosulfan were quantified at mean concentrations of 1.26 µg/l and 1.84 µg/l, respectively (Diop, 2013). The concentrations of alpha-endosulfan exceed the concentrations quantified through this analysis by 2.52 to 12.6 times and those of beta-endosulfan also surpass the results of this investigation by 5.25 to 15.33 times. Another study carried out in the Thiaroye-Niayes-Senegal area revealed a concentration of alpha-endosulfan of 2.35 µg/l (Saliou and al., 2012). This concentration is 4.7 to 23.5 times the concentration detected in the fifteen water samples analyzed. In Togo, in the waters of the Anié River, the Mono River and wells in Adéta (Gbénonchi, 2008), the concentrations of alpha-endosulfan measured are 0.29 µg/l, 0.32 µg/l and 0.05 µg/l, respectively. The concentrations found in this study are close to the first two concentrations and are 2 to 10 times higher than the residual alpha-endosulfan concentration found in the wells in Adéta. Beta-endosulfan was also quantified at 0.25 µg/l, 0.40 µg/l and 0.02 µg/l respectively in the waters of the Anié River, the Mono River and wells in Adéta in Togo

(Gbénonchi, 2008). The values obtained in the waters of the Anié and Mono Rivers are close to the concentrations in the samples studied, unlike the well concentration in Adéta, which is much lower. Also in Togo, in the water of the Klobateme market gardening area (Gbénonchi and al., 2014), alpha-endosulfan and beta-endosulfan were quantified at 0.007 µg/l and 0.003 µg/l, respectively. These concentrations are very slightly below values found in this study. Analysis of domestic well water in the Korokoro -Mali area (Maiga, 2017) revealed the presence of endosulfan at a concentration of 1.8 µg/l. This concentration is 5.31 to 14.75 times higher than the concentrations quantified in the investigated sites.

In Senegal, heptachlor was quantified in market garden wells in the Niayes area at a mean concentration of 3.43 µg/l (Diop, 2013). This concentration is 6.86 to 68.6 times higher than the residual values detected in the water from market gardening wells in our study area. In the water of the market gardening area of Klobateme-Togo, heptachlor was quantified at 0.012 µg/l (Gbénonchi and al., 2014), which is slightly lower than those detected in this study. In the waters of the Anié River, the Mono River and wells in Adéta in Togo (Gbénonchi, 2008), heptachlor was also found at concentrations of 0.24 µg/l, 0.11 µg/l and 0.33 µg/l, respectively. These concentrations are close to the values found in this study. In Kenya, the mean residual heptachlor concentration in Lake Nakuru waters is 3.85 µg/l (Mavura and Wangila, 2004). This value significantly exceeds the concentrations found in this study. In the market gardening wells of the Dallol Maouri, Dosso Region, Niger, lindane was quantified at a concentration of 0.053 µg/l (Adamou, 2014), a concentration very close to the values found in the samples of this analysis. In the Niayes area (Senegal), lindane was also measured in market gardening wells at a mean concentration of 0.22 µg/l (Diop, 2013).

This is 1.8 to 11 times higher than the concentrations found in the waters of our study area. In Kenya, the mean residual concentration of lindane in Lake Nakuru waters is 1.33 µg/l (Mavura and Wangila, 2004). This value is 10.90 to 66.5 times higher than the concentrations found in this study. A study carried out in the Thiaroye-Niayes area (Senegal) revealed a dimethoate concentration of 1.9 µg/l (Saliou and al., 2012). This concentration multiplies the residual concentrations detected in water from market garden boreholes in our study area by 9.5 to 19.79 times. In the Dallol Maouri-Region of Dosso, Niger (Adamou, 2014), Chlorpyrifos methyl was detected in market gardening wells at a concentration of 0.052 µg/l, a value that is 1.51 to 6.73 times lower than the concentrations found in water from market gardening boreholes in the Department of Madaoua.

Glyphosate was quantified in water in the horticultural zone of Azaguié, south of Côte d'Ivoire (Soro and al., 2019) at a concentration of 0.43 µg/l. This value is very close to the concentrations found in this investigation. The concentrations of deltamethrin found in the samples studied are 1.13 to 3.30 times higher than the one obtained in the water of market garden wells in the Dallol Maouri-Region of Dosso, Niger, which is 0.106 µg/l (Adamou, 2014). The residual concentrations quantified in this study also exceed 18.8 to 21.32 times the deltamethrin concentration found in the Thiaroye-Niayes area, Senegal, which amounts to 0.01 µg/l (Saliou and al., 2012). They are also 12.78 to 14.50 times higher than the residual value of 0.0147 µg/l of deltamethrin

found at Komplan 2 in the commune of Dano in Burkina Faso (Bayili, 2014). The lambda-cyhalothrin concentration of 1.49 µg/l detected in the water at the Komplan 2 site in the commune of Dano in Burkina Faso (Bayili, 2014) multiplies the concentrations of water samples from our study area by 4.38 to 13.54 times. Results of analysis of pesticide residues in the waters of Lake Nakuru in Kenya (Mavura and Wangila, 2004) showed an average residual concentration of carbofuran of 2.301 µg/l. This value is 7.05 to 11.50 times higher than the concentrations found in this study. In contrast, the carbofuran concentration of 0.055 µg/l quantified in the market garden wells of Dallol Maouri, Dosso Region, Niger (Adamou, 2014) is considerably below the concentrations detected in this study. Much of the water pollution caused by pesticides is related to the intrinsic chemical and physical characteristics of the active ingredients. For example, some pesticides have a very high persistence in soil and water, as notified by the Stockholm Convention. These include DDT, lindane, aldrin, dieldrin, heptachlor... Their degradation occurs over time, according to a more or less long and complex cycle. The degraded products can then interact with other pesticides, with heavy metals present in the water, or even with natural elements. These substances can then recombine into new polluting molecules, or even recombine the initial pollutant. This could explain some of the new spikes in the presence of organochlorines, many years after the end of their use. Among the quantified pesticides, some are banned according to Annex III of the Rotterdam Convention, such as DDT, aldrin, dieldrin, alpha-endosulfan, beta-endosulfan, heptachlor, lindane, and carbofuran (FAO, 2015). They are persistent (therefore dangerous for the environment), suspected of being carcinogenic, mutagenic, toxic for reproduction and are classified as priority hazardous by the WHO (WHO, 2009).

Conclusion: The analysis of pesticide residues in water samples from market garden sites in the 3 communes shows that the water table is polluted. Residues of seventeen (17) pesticides belonging to five chemical families were quantified at concentrations ranging from 0.02 to 0.50 µg/l. The study showed that 35.29% of the pesticides had residue levels above the WHO and EU potability standards in all samples. These are aldrin, heptachlor, glyphosate, deltamethrin, cypermethrin and lambda-cyhalothrin. Their residue levels increase from 1.10 to 16.66 times the potability standards established by both the WHO and the EU. It also appears that 35.29% of the other pesticides have residue concentrations that exceed the MRLs set by the European Union by 1 to 5 times in all samples. These are DDT, α -endosulfan, β -endosulfan, chlorpyrifos methyl, pendimethalin and carbofuran. It should be noted that only one pesticide, chlorothalonil (5.88% of all quantified residues) has concentrations below the maximum residue limits (0.1 µg/l) established by the WHO and the EU in all samples. Cumulative concentrations of the various pesticide residues quantified in samples of water from market gardening boreholes range from 2.427 to 3.675 µg/l. This total increases from 4.854 to 7.35 times the potability standard set by the World Health Organization (WHO) and the European Union (EU), which is 0.5 µg/l for the sum of the active ingredients quantified in a given water sample.

The current state of pesticide pollution of the water resources of the market gardening sites in Madaoua constitutes a serious danger to public health because if the water tables are contaminated, agriculture will produce contaminated food and this will have a negative effect on our food and our health. In

order to reduce the environmental pollution and health risks to humans and animals associated with the use of water from these market gardening boreholes, it is more than necessary to disseminate good pesticide management practices in rural areas. To do this, it is first necessary to draw growers' attention to the risks associated with the misuse of pesticides on vegetable crops through an awareness and training program. Then, it is important to apply the legislation on the use of pesticides by making available to producers the list of pesticides and the pesticides approved by the Sahelian Pesticides Committee, and to raise awareness and train all actors in the chain on the proper management of pesticides. Finally, there is a need to support research and the transfer of alternative methods of using synthetic pesticides in plant protection.

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