



(RESEARCH ARTICLE)



Seasonal contamination level of the waters from the Déganobo lake system by fourteen herbicides residues and their ecological and health implications

Kouadio Fabrice Arthur KONAN ^{1,2} and Marcel Konan YAO ^{2,*}

¹ PhD school of Sciences, Technology and Sustainable Agriculture, 01 BPV 34 Abidjan, Cote d'Ivoire.

² Reaction and constitution of Matter Laboratory, UFR SSMT, Félix Houphouët-Boigny University, 22 BP 582 Abidjan 22, Cote d'Ivoire.

GSC Advanced Research and Reviews, 2023, 17(02), 167–180

Publication history: Received on 09 October 2023; revised on 16 November 2023; accepted on 19 November 2023

Article DOI: <https://doi.org/10.30574/gscarr.2023.17.2.0442>

Abstract

The aim of this study was to assess the seasonal contamination level of the waters from the Déganobo lake system by 9 triazine herbicides and 5 substituted urea herbicides and, their ecological and risks implications. It was conducted during one year (from August 2021 to July 2022). The waters samples, collected monthly, were analysed according M.A. 403-Pest 3.1 standard with some modifications. The ecological and health risks were assessed by using the Directive 2013/39/EU, the MDDP water quality guidelines, the SEQ-Eau V2 water quality guidelines and, the Quotient Risk. Simazine was the herbicide residue the most important, whereas atrazine, chlorotuluron and, terbutryn were the least important in all season. Diuron, fenuron, monuron and, Terbutylatrazine were not detected in these waters in all seasons. The hydroclimate, as well the temperature, transparency and, dissolved oxygen of these waters, were influenced significantly the seasonal dynamic of the herbicide residues detected in these waters. All the water quality guidelines used in this study and the quotient risk were highlighted the relative high pollution of these waters with likely severe health risks for its biota and for human in all season, because of its high seasonal concentrations in simazine.

Keywords: Côte d'Ivoire; Herbicides; Pesticide pollution; San-Pédro city; Water pollution.

1. Introduction

Environmental pollution by pesticides is a global concern. According to WHO [1], 1000 pesticides are currently used worldwide in agriculture. The quantity of pesticide used almost doubled between 1990 and 2018, from 2.3 to 4.1 million tonnes in accordance with FAO data [2]. 85 to 90% of these pesticides do not reach their targets, thus representing a significant source of chemical pollution [3]. Indeed, several recent studies have shown the presence of pesticide residues and their metabolites at relatively high concentrations in soils, waters and, foods, as well as in the atmosphere [4]. Many of these pesticides, particularly the oldest, can persist for many years in soils and waters. They are likely to impact human health and lead to ecological scourges. So, many pesticides with very high persistence in the environment have been banned by many conventions and organisms, such the Stockholm Convention [5] and the Sahelian Pesticide Committee [6]. However, unregistered pesticides continue to be used. This is especially the case in developing countries, particularly in sub-Saharan Africa. WHO surveys have shown that African countries import less than 10% of the pesticides used in the world, but they account for half of accidental poisonings and more than 75% of fatal cases [7].

According De et al. [8], cited by Sharma et al. [9], herbicides are the most pesticides uses around the world, 47.5% of the total pesticides. They heavy use in cropping system eventually made them ubiquitous, with adverse effects on environment, particularly on nontarget organisms and human health [10, 11]. Triazine herbicides and substituted urea herbicides are among the most uses. Their severe adverse for aquatic biota are reported by many studies [10,12].

* Corresponding author: Marcel Konan YAO

The fate of pesticide residues in aquatic ecosystems depend on their hydrolysis, biodegradation and, photolysis according to their origins and their nature. These reactions are influenced by many physical and biogeochemical parameters of these ecosystems (temperature, transparency, organic matter content, dissolved oxygen content, etc.), as well as by the hydroclimate where they are located [13,14].

In Côte d'Ivoire, many recent studies were highlighted the presence of the residues of triazine herbicides and substituted urea herbicides in surface waters [15-19]. However, very few of them have linked their presence in these waters with hydroclimate and, some of their physic and biogeochemical parameters. So, it is an important to conduct studies on this research line to contribute to the knowledge of the contamination of the surface waters from Côte d'Ivoire by the residues of these herbicides. It is in this context, this study was carried out in the Déganobo lake system. This lake system has its watershed dominated by agricultural activities with a heavy use of herbicides. Its waters have never been subject to pesticide pollution studies. The main objective was to assess of the seasonal contamination level of its waters by fourteen herbicides from triazine herbicides and substituted urea herbicides. The secondary objectives were to assess the impact of hydroclimate (ambient temperature and rainfalls) and some of its physical and chemical characteristics on its seasonal contamination level by these pesticide residues in the one hand and; to assess their seasonal ecological and health risks implications, on the other.

2. Material and methods

2.1. Briefly presentation of the study area

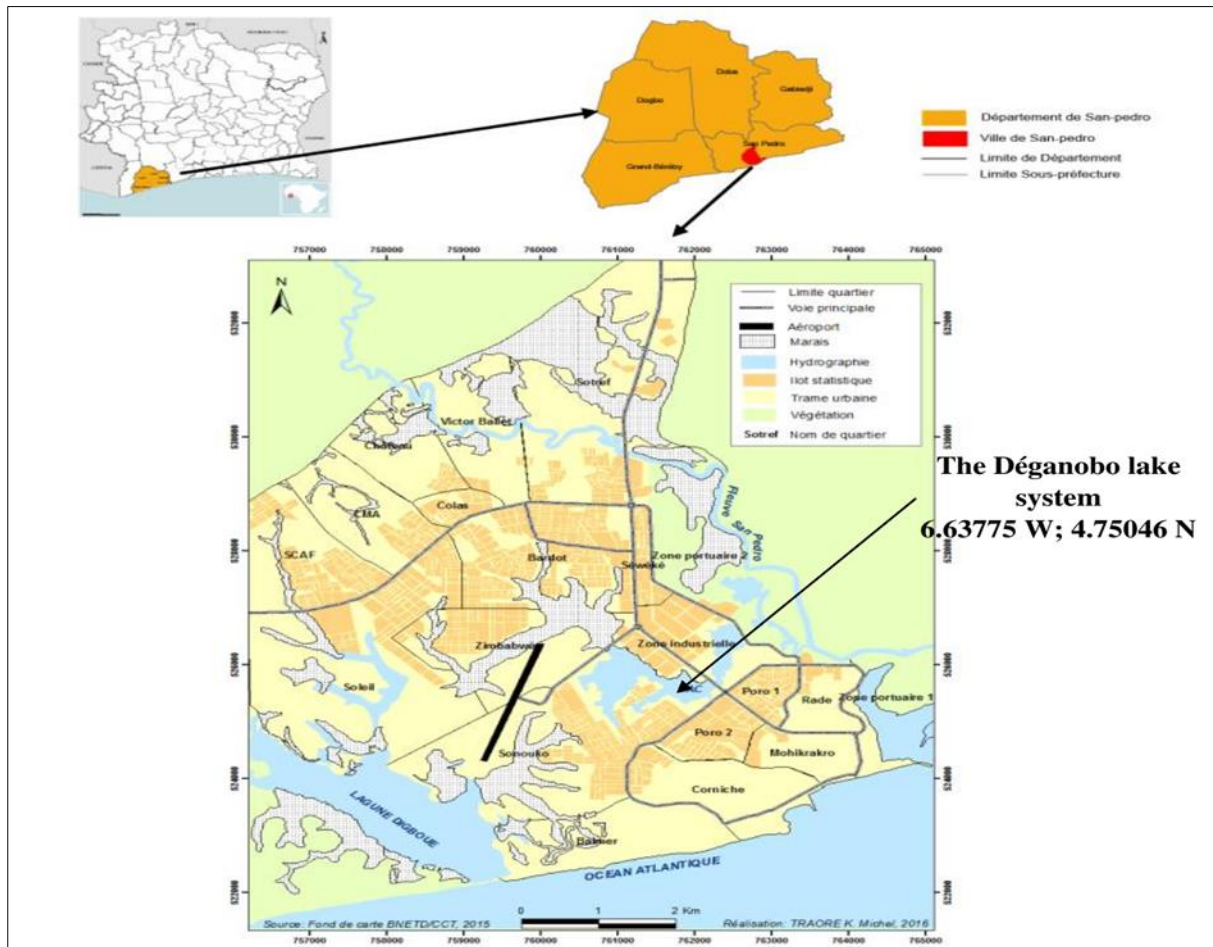


Figure 1 Geolocation of the Déganobo lake system (Map source: Traoré [22] cited by Konan and Yao [20]).

As mentioned by Konan and Yao [20], the Déganobo lake system is located to 6.63775W, 4.75046N (Figure 1). Its water seasons linked on a subequatorial climate to which San-Pédro Department is subject are following: a Great Dry Season (GDS) from December to March; a Great Rainy Season (GRS) from April to July; a Small Dry Season (SDS) from August

to September, marked by the manifestation of the great upwelling season in the ivoirian coastline and, a Small Rainy Season (SRS) from October to November.

This lake system consist of two lake connected by a tunnel: Lac Ouest with current open water surface area of 49.05 ha (the greatest) and, Lac Est with current open water surface area of 29.87 (the smallest) [21].

The hydrography of this lake system consist of the San-Pédro River and the Digboué Lagoon, linked between them by a lot of wetlands [20, 23, 24]. It has a great remarkable biodiversity [20, 23]. This aquatic ecosystem is the receptacle of wastes of all kind without pretreatment [20, 23, 25], especially those from agricultural residues [20].

2.2. Experimental techniques

2.2.1. Sample collection and, their conservation in situ and in laboratory

This study was conducted in the same period as that of Konan and Yao [20], namely from August 2021 to July 2022. The collection of the water samples was carried out on the same sampling site as theirs. The water column samples were collected using a 1 L capacity Niskin bottle in eight sampling sites (Figure 2).

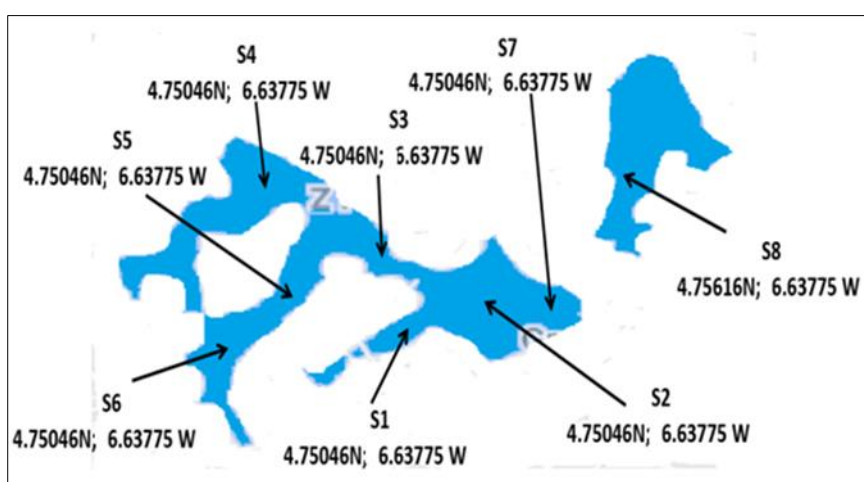


Figure 2 Geolocation of sample sites used in this study (Konan and Yao, 2023)

Immediately collected, the water samples were transferred twice in clean and dry 1 L inactinic borosilicate glass bottles. They were subsequently acidified with a 0.1 N H_2SO_4 solution to bring their pH below 2 in order to inhibit the action of microorganisms. Well before sealing the inactinic borosilicate glass bottles, aluminium foil was placed over the neck to prevent any contact between the sample and the plastic cap, as recommended by MA. 403-Pest 3.1 standard [26]. All these glass bottles were kept in situ in a light-tight cooler containing an important quantity of ice so that the interior temperature was around 4° C, as recommending by NF EN ISO 5667-3 standard [27]. During this this period, a monthly sampling was doing in these eight sample sites, for a total collection of 192 water samples.

Once arrived at the laboratory, the water samples were stored in the refrigerator.

2.2.2. Analysis of herbicide residues in the water samples

Target herbicides residues

14 herbicide residues were searched in the water samples, given their important use in the watershed of this aquatic ecosystem, namely:

- 9 from the triazine herbicides (atrazine (ATZ), cyanazine (CNZ), desethylatrazine (DEA), deisopropylatrazine (DIA), metribuzin (MTZ), propazine (PPZ), terbutryn (TBT), terbuthylazine (TBTL) and, simazine (SIZ)) and;
- 5 from the substituted urea herbicides (buturon (BTR), chlortoluron (CTL), diuron (DRN), fenuron (FEN) and, monuron (MNR)).

Protocol implemented

The determination of the concentration of these herbicide residues in the water samples was done according to the MA. 403-Pest 3.1 standard [26] with some modifications.

Like any assay methods of pesticide based on solid-phase extraction (SPE), this standard aims to extract pesticides using an SPE C-18 cartridge (1g), followed by their elution with an ethyl acetate solution. The eluate is recovered with pure isooctane under an argon atmosphere. The purified extract is analysed by GC-MS.

- Sample preparation

The water samples were homogenized by vigorous stirring, then filtered with a Whatmann paper filter with a diameter of 0.47 μm in order to eliminate suspended matter.

- Solid-phase extraction and purification

The SPE C-18 cartridge (1 g) (LabBox brand) was first cleaned-up with 6 mL of pure ethyl acetate, maintaining a vacuum such that the elution rate was 5 mL/min. It was subsequently conditioned by 3 successive portions of 6 mL of methanol followed by 2 successive portions of 6 mL of pure water, always maintaining the elution rate at 5 mL/min. To 150 mL of the water sample collected in a graduated cylinder and, 1 mL of a sodium sulfate solution and 15 μL of the extraction solution (obtained with all the target herbicides in pure isooctane with each of them having a concentration of 300 ng/L in solution) were added. The sample was passed through the SPE C-18 column (1 g) always maintaining the elution rate at 5 mL/min. The column was subsequently washed with 6 mL of pure water, then completely dried under an argon jet for 90 min. The pesticides retained in column C-18 (1 g) were eluted with 2.5 mL of the elution solution (90% ethyl acetate solution). The eluate was collected in a centrifugation tube precalibrated with 150 μL of isooctane. 150 μL of pure isooctane was then added. The eluate, approximately 15 mL, was quickly concentrated to approximately 135 μL under an argon jet in a water bath at approximately 35° C. A blank consisting of 150 mL of pure water and the control solutions (500 ng/L concentration for each herbicide) were treated in the same conditions.

- Analytical procedure

The purified extract, the blank and the control solutions were taken up in 15 μL of the standard injection solution (obtained with all the target herbicides in pure isooctane with a concentration of 100 ng/L for the some and 600 ng/L for others). They were transferred into conical glass vials for GC-MS assay. Previously, the standard solutions for the assay and the control were prepared by adding 250 μL of the calibration solution (obtained with all the target pesticides in pure isooctane at various concentrations (between 0.01 and 3500 ng/L), 50 μL of the extraction standard solution, 50 mL of the injection standard solution and, 150 μL of pure isooctane.

The analyses of purified extracts were doing by GC-MS using the spectrometer GC-MS QP 2010 Shimadzu (Japan). During the assay process, the different components of the purified extracts were decomposed by gas chromatography in an Rxi-5ms capillary column (RESTEK, Bellefonte, Pennsylvania) of size (30 m long x 25 mm inner diameter x 0.25 μm film thickness). The helium carrier gas had a purity of 99.999% and its flow rate was 1mL/min. the injection volume was 1 μL . The programming of thermal decomposition was as follows: a start of thermal decomposition at 70°C for 2 min, followed by a progressive increase due to 20°C/min up to 320°C and the maintenance of this temperature for 5 minutes. As for the temperature of the vaporization injector and that of the ion source, they were all maintained at 250°C. The injector operation was programmed as follows: in “splitless” mode for 2 min then in “split” mode following the 50:1 ratio. The mass spectrometer, equipped with a quadrupole mass filter (Optdesign™ Shimadzu, Japan), made it possible to detect mass intervals, identify and confirm compounds using retention times. It was operated in “electronic impact source (EI)” mode for detection. The electronic energy was 70 eV and the line transfer temperature was maintained at 250°C. The choice of fragmentation products for each substance was based on the strongest signal. The programming of the different stages of the analyses and the processing of the results was done with the GCMSsolution software, including a large database of mass fragments (m/z). The concentrations are calculated by comparing the peak areas of the sample products to the areas obtained with standard solutions of known concentrations.

- Quality control analysis

The experiments were carried out in triplicate to assess the precision of the method. All the reagents used were analytical purity, especially those of the target herbicide residues certified Dr Erhenstorfer Laboratories (GmbH Germany))

The precision of the protocol implemented in this study was done on the basis of the determination coefficient (R^2) of the different calibration curves, the RSD of the precision of this method and, the RSD of the precision of the method intermediates. So, this protocol is precise if:

- R^2 of the different calibration curves are greater than 0.98, as recommended by the International Organization Standard [28];
- The RSD of the precision of this method is less than 10% and, those of the precision of the intermediate methods are less than 15%, as suggested by Rahman et al. [29].

The limit of detection (LOD) and that of quantification (LOQ) were obtained according to the methods of US-EPA [30] and PAM [31]. The LOD was obtained as the lowest concentration of a target pesticide that provided a chromatographic peak three times higher than the mean baseline noise at the same retention time. As for LOQ, it was determined to be equivalent to 10 times the noise peak at the same retention time [32].

2.2.3. Assessment of ecological and sanitary risks

The assessment of the seasonal ecological and health risks was done using the Directive 2013/39/UE [33] by taking into account their seasonal and annual mean concentrations in ATZ, SIZ and, TBT. It has been the same using the SEQ V2 water quality guidelines [34] relatively to their seasonal and annual mean concentrations in all the target herbicide residues. The MDDP water quality guidelines [35] was also used for this purpose in reference to their seasonal and annual mean concentration in ATZ, CNZ and, SIZ.

The Quotient Risk (QR) was used to assess the ecotoxicity risks of ATZ, CTL, SIZ and, TBT for the biota of this lake system. This index is defined as follows:

$$QR = \frac{MEC}{PNEC}$$

with:

MEC, the Measurement Environmental Concentration ;

PNEC, the Probable No Effect Concentration.

So, for $0.01 \leq QR < 0.1$, the ecotoxicity risks of the herbicide residue for aquatic biota are low; for $0.1 \leq QR < 1$, they are medium and; for $QR \geq 1$, they are high [36].

The different PNEC used in this study is: 0.6 for ATZ, 0.1 for CTL, 1 for SIZ and, 1.69 for TBT [37].

2.2.4. Source of physical and chemical and hydroclimate data used

The monthly data of the ambient temperature and those of rainfall on the study period were provided by historique-meteo [38, 39].

2.3. Statistical analysis

In addition to standard statistical techniques (m (mean), s (standard deviation), VC (variation coefficient), Min (minimum mean value) and, Max (maximum mean value)), Normalized Principal Component Analysis (NPCA), one-way ANOVA and, the Student t-test were used.

NPCA was used to assess the seasonal effects of the hydroclimate and of some physical and chemical parameters of these waters in the seasonal dynamics of some herbicide residues within them.

The purpose of using one-way ANOVA was to check whether there is a significant difference between the seasonal concentration in these herbicide residues of these waters. If this was the case then three post hoc tests were used to determine the seasonal means which differ, but also the homogeneous subgroups which do not differ from each other. They were the Fisher LSD test, the Tukey HSD test and, the Dunnett test. To ensure the significant difference between two seasonal mean and/or homogeneous subgroups of seasonal means not different in a parameter, the Fisher LSD and the Tukey HSD test were simultaneously carried out. If there was a difference between the results obtained, then the Dunnett test was carried out in the column(s) where the results diverge. The results of one-way ANOVA and the post hoc tests were considered statistically significant for $p < 0.05$.

The student t-test was used in the different limits defines by the different water quality guidelines used and the QR index for a statistical confirmation or none of the level of ecological and health risks obtained. The student t-test was statistical significant for $p < 0.05$.

3. Results

3.1. Precisions of the protocol implemented

R^2 of the different calibration curves of the target herbicides obtained in this study were between 0.9907 and 0.9978. These calibration curves were therefore efficient in this study, given the condition of 0.98 for the determination coefficient for good linearity according to International Organization Standard [28]. These very good correlations reflect the high probability of linearity between the concentration of the herbicide residue and the size of the peak after analysis according to Durak et al. [40]. The recovery rate of the control solutions for the target herbicides was between 85 and 120%. The RSD of the precision of this method was 1 to 8.158% (< 10%) and, those of the precision of the intermediate methods was 1 to 12.846% (< 15%). So, the protocol implemented for the quantification of target herbicide residues in this study is satisfactory and reproducible. The LOD values and those of LOQ of the different target herbicides are given in the table 1.

Table 1 LOD and LOQ of target herbicides obtained with the implemented protocol

Herbicide family	Target herbicides	LOD (ng/L)	LOQ (ng/L)
Triazines	ATZ	0.02	0.5
	CNZ	0.05	0.5
	DEA	0.03	0.4
	DIA	0.03	0.4
	MTZ	0.02	0.5
	PPZ	0.03	0.4
	TBT	0.03	0.4
	TBTL	0.03	0.5
	SIZ	0.02	0.4
substituted ureas	BTR	0.18	1.5
	CTL	0.13	1.0
	DRN	0.28	2.5
	FEN	0.02	0.9
	MNR	0.06	0.9

3.2. Seasonal dynamic of the target herbicides residues

Of all the target triazine herbicides in these waters, only TBTL was undetected in these waters. SIZ was the most important and, TBT and ATZ were the lowest in these waters in all seasons over this period. The highest seasonal mean concentration of DIA, DEA, SIZ, PPZ and, CNZ of these waters were all obtained in GDS and; the weakest were all in SDS, with the exception of those in DEA and DIA determined in SRS. Their highest seasonal mean concentrations in TBT were determined in GDS and GRS and, their lowest a in SDS. As for their seasonal mean concentration in ATZ, it was relatively high in GRS and low in SDS. For their seasonal mean concentration in MTZ, it was relatively high in SDS and relatively low in SRS. The intra-seasonal variations of their concentration in these herbicides residues were low, except those of their mean concentration in TBT very high in SRS (Table 2).

Table 2 Seasonal and annual mean concentrations in target triazine herbicide residues of the waters from the Déganobo lake system on the study period

Seasons		DIA	DEA	SIZ	ATZ	PPZ	CNZ	TBT	TBTL	MTZ
SDS	m±s	0.407±0.107	0.578±0.013	23.323±0.673	0.011±0.003	0.706±0.007	0.624±0.034	0.012±0.004	< LOD	0.216±0.010
	VC (%)	26.372	2.327	2.885	28.748	1.003	5.498	32.275		4.815
	Min-Max	0.130-0.890	0.280-0.740	19.860-27.390	0.010-0.020	0.480-0.830	0.360-0.870	0.010-0.020		0.140-0.290
SRS	m±s	0.289±0.053	0.524±0.009	24.364±0.201	0.026±0.010	0.774±0.040	0.673±0.004	0.018±0.015	< LOD	0.138±0.009
	VC (%)	18.397	1.805	0.825	39.881	5.150	0.532	86.661		6.450
	Min-Max	0.090-0.640	0.260-0.740	14.220-36.870	0.010-0.080	0.550-1.110	0.370-0.930	0.010-0.050		0.060-0.190
GDS	m±s	0.563±0.028	0.621±0.015	29,912±0.025	0.044±0.005	0.904±0.001	0.841±0.006	0.037±0.002	< LOD	0.196±0.001
	VC (%)	*5.037	2.464	0.082	10.377	0.148	0.727	4.476		0.520
	Min-Max	0.320-0.690	0.490-0.720	27.890-38.850	0.010-0.070	0.760-1.050	0.740-0.950	0.020-0.060		0.170-0.230
GRS	m±s	0.549±0.056	0.605±0.054	29.299±3.965	0.045±0.001	0.883±0.008	0.822±0.071	0.037±0.002	< LOD	0.197±0.019
	VC (%)	10.133%	9.006	13.532	3.082	0.918	8.667	4.476		9.720
	Min-Max	0.300-1.030	0.350-1.030	16.720-47.790	0.010-0.011	0.440-1.250	0.440-1.300	0.020-0.060		0.140-0.250
Annual	m±s	0.452±0.066	0.582±0.048	26.725±3.046	0.031±0.011	0.817±0.069	0.740±0.070	0.026±0.002	< LOD	0.187±0.014
	VC (%)	16.649	8.169	11.399	35.555	8.394	9.425	12.911		7.731
	Min-Max	0.130-1.030	0.480-1.030	14.220-47.790	0.010-0.011	0.440-1.250	0.360-1.300	0.010-0.060		0.060-0.290

Their inter-seasonal variations were quite marked overall, as also highlighted by one-way ANOVA. One-way ANOVA showed also an overall significant difference between the different seasonal mean concentrations of all triazine herbicide residues detected in these waters ($p < 0.05$). The post hoc tests used in this study were shown:

- non-statistically significant differences between their concentrations in ATZ, CNZ, DIA, PPZ, SIZ and, TBT obtained in GDS and those determined respectively in GRS ($p > 0.05$);
- non-statistically significant differences between their mean concentrations in CNZ, PPZ, SIZ and, TBT obtained in SDS from those determined in SRS ($p > 0.05$);
- a non-statistically significant difference was observed between all their mean concentrations in DEA ($p > 0.05$), except between that obtained in SRS and that determined in SDS ($p < 0.05$);
- As for their mean concentration in MTZ obtained in SRS, it was statistically different from those obtained in SDS, GDS and, GRS ($p < 0.05$).

The seasonal and annual values of the DEA/ATZ ratio were all greater than 0.5. This ratio decrease from SDS (57.813) to GRS (13.445).

CTL was only detected in these waters in SDS, unlike BTR which was detected in these waters in all seasons. Their highest seasonal mean concentration in BTR was obtained in GDS and, the lowest in SDS. The intra-seasonal and the inter-seasonal variations in their concentration in BTR were all low (Table 3). This fact is confirmed by one-way ANOVA for the inter-seasonal variations of their concentration in BTR. One-way ANOVA also revealed an overall significant difference between their seasonal concentrations in BTR over the study period ($p < 0.05$). The post-hoc tests used in this study highlighted that only their concentration in BTR obtained in SDS is statistically different from those obtained in the other three seasons ($p < 0.05$).

Table 3 Seasonal and annual mean concentrations in BTR and CTL of the waters from the Déganobo lake system over the study period

		Seasons				Annual
		SDS	SRS	GDS	GRS	
BTR	m±s	1.114±0.062	1.502±0.021	1.681±0.052	1.641±0.213	1.484±0.184
	CV (%)	5.523	1.427	3.083	12.969	12.388
	Min-Max	0.180-2.230	1.350-1.820	1.310-1.880	1.310-1.880	0.180-2.230
CTL	m±s	0,020±-	< LOD	< LOD	< LOD	0,020±-
	CV (%)	-				-
	Min-Max	-				-

3.3. Impact of some hydroclimate and some physical and chemical parameters of these water on some target herbicide residues

The three first factors of NPCA give at 100% (F1 (49,130%), F2 (33,316%) and, F3 (17,554%)) the information about 27 variables involved in this study. Ambient temperature, as well COD and the concentrations in ATZ, CNZ, PPZ and, SIZ of these waters, have the high positive correlations with F1; while CTL has a high negative correlation with this factor. Their temperature and their concentration in DEA and MTZ have the high negative correlations with F2; in opposite of the mean depth of this lake system, which has a high negative correlation with this factor (Table 4). As concerned to the individuals, GDS has a high negative correlation with F1, while GDS have a high positive correlation with this factor. SRS have a high positive correlation with F2 (Table 5).

So, according to these NPCA results, the low rainfall series would contribute to the relative important presence in these waters of the residues of ATZ, CNZ, PPZ and, SIZ in GDS; in opposite of the maximum of the ambient temperature. It will not be the case for CTL. The slight increase in the mean depth of this aquatic ecosystem, due to rainfall, would contribute to the slight decline of their mean concentration in, in opposite to their temperature in SRS.

Table 4 Coordinate factorials of the variables based on the correlations obtained with NPCA in this study

Variables	Factors		
	F1	F2	F3
pH	0.244451	0.566830	0.786733
Redox potential	-0.183269	-0.455422	-0.871208
Salinity	0.585777	-0.197761	0.785975
Conductivity	-0.781464	-0.595765	0.185415
Water temperature	-0.495602	-0.846601	-0.194023
Depht	0.079579	0.974498	-0.209812
Ambient temperature	0.877760	0.016813	0.478805
Rainfalls	0.045613	0.555866	-0.830019
COD	0.994306	0.037020	0.099931
DIA	0.629652	-0.771319	-0.092763
DEA	0.511226	-0.857799	0.053194
SIZ	0.919941	-0.366264	-0.139853
ATZ	0.963813	-0.096734	-0.248410
PPZ	0.970666	-0.196075	-0.139148
CNZ	0.939574	-0.309320	-0.146704
TBT	0.920457	-0.324811	-0.217385
MTZ	-0.149466	-0.987541	0.049220
BTR	-0.620720	-0.742798	0.250914
CTL	-0.872612	-0.435268	0.221562

Table 5 Coordinate factorials of the individuals based on the correaltions (a) and their contribution for the construction of the factors (b) obtained with NPCA in this study.

Individuals	Factors			Factors		
	F1	F2	F3	F1	F2	F3
SDS	-3.99910	-1.64268	0.60695	0.839095	0.141577	0.019328
SRS	-0.51326	3.75013	0.01802	0.018387	0.981590	0.000023
GDS	3.14136	-0.99139	1.86027	0.689521	0.068675	0.241804
GRS	1.37101	-1.11606	-2.48524	0.202078	0.133911	0.664011
	a			b		

3.3.1. Comparison of the mean annual concentration in some herbicide residues of these waters with that of other ivoiran surface waters

The table 6 highlights that all the annual mean concentrations in ATZ, CNZ, DIA, DEA and, TBT of these waters obtained in the study period are less important than those determined in the waters from the Lake Adaou [15], the Mé River [16], the Aghien Lagoon and, the Potou Lagoon [18]; except to their annual mean concentration in SIZ related to that of the waters from the Potou Laggon [18] (Table 6).

Table 6 Comparison of the annual mean concentration in some herbicide residues detected in the waters from the Déganobo lake system over the study period with those determined in others ivoirien surface waters

Herbicide residues	Annual means obtained in this study (µg/L)	Mé River (µg/L) [16]	Lake Adaou (µg/L) [15]	Aghien Lagoon (µg/L) [18]	Potou Lagoon (µg/L) [18]
				5.76±5.47	
CNZ	0.740±0.070		2.56±-	15.03±23.67	271.17±465.12
DIA	0.452±0.066		207.81±289.74	4.84±7,46	16.84±20.72
DEA	0.582±0.048		57.26±80.89	40.35±37.12	161.08±194.13
SIZ	26.725±3.046		3.65±5.11	142.74±433.54	5.56±10.23
TBT	0.026±0.002	0.19±0,26	6.57±		

3.4. Ecological and health risks

According to the Directive 2013/39/EU [33], only SIZ was heavy polluted these waters in all season (inferior limit of the admissible maximum concentration of 4.0 µg/L), as confirmed by the Student t-test ($p < 0.05$). For the SEQ-Eau V2 water quality guidelines [34], these waters were not ability for ecological activities and for all anthropogenic uses linked to the human health over all the study period, because of all their seasonal mean concentration in SIZ (reference value for very poor quality > 2 µg/L) and, of all their seasonal mean concentration in BTR, except in SDS (reference value for poor quality between 1.4 and 2.0 µg/L). These results were again confirmed by the student t-test ($p < 0.05$). The MDDEP water quality guidelines [35] was highlighted the severe ecological and health risks of these waters in all season, due to their seasonal mean concentration in SIZ (high chronic adverse (the inferior limit of the reference value of 10 µg/L)), as confirmed again by the Student test ($p < 0.05$). As for QR, it was highlighted the severe ecotoxicity of SIZ for the biota of this aquatic ecosystem (all the QR values for SIZ were between 23.184 and 29.912) [36]. This result was also confirmed by the Student t-test ($p < 0.05$).

4. Discussion

SIZ appears to be the herbicide the most used in the watershed of this lake system. This could be explained by its sustainable for the selective elimination of broad-leaved herbs and grass in vegetable crops and legumes (tomatoes, cabbage, lettuce, corn, beans, spinach, okra, pepper, eggplant, etc.) [41] in the wetlands nearby to this aquatic ecosystem. Its high persistence in soils and waters compared to those of other target herbicides in this study would contribute to its high presence in these waters [42,43]. The high presence of this herbicide residue in ivoirien surface water were again mentioned by Ahoussi et al. [16], Siriki et al. [17] and, Traoré et al. [18]. The relative high presence of ATZ in these waters in all seasons would illustrate their pesticide pollution mainly of agricultural origin [44]. Furthermore, the DEA/ATZ ratio of these waters, all greater than 0.5 over the study period, would highlight that the long historical discharge and the long residence time of these target herbicide residues in the watershed of this lake system [45]. The localization of this lake system in the center of San-Pédro city, the lot of wetlands around this lake system and, its flow toward the San-Pédro River [20, 23], would explain its low concentrations in some target herbicide residues in comparison to those obtained by Ahoussi et al. [16] in the waters from the Mé river, Atto et Mondé [15] in the waters from the Lake Adaou, Traoré et al. [18] in the waters from the Aghien Lagoon and the Potou Lagoon.

The relatively high temperature of these waters over the study period would have been conducive to the activation of microbial degradation of target herbicide residues [13, 14]. Due to its hypereutrophication, these waters are anoxic during the day and supersaturated with oxygen at night [46]. The aerobic microbial degradation of these pesticide residues would therefore be slowed down in these waters during the day, but significant at night; opposite to the microbial anaerobic one [14]. However, the very high turbidity of these waters would have disadvantaged their degradation by photolysis in these waters, in particular those of SIZ [42, 43] and, MTZ [47] over the study period.

In GDS, the heavy use of the target herbicides in the watershed of this aquatic ecosystem would lead to the relatively high presence of their residues in its waters; especially those of DIA, DEA, SIZ, PPZ, CNZ, TBT and, CTL. This fact would be highlighted by the NPCA for ATZ, ADC, CNZ, DIA, and PPZ, whose importance in these waters was in contradiction with their relatively high temperature. However, the relative important temperature of these water seems to favour the degradation of CTL in them, as highlighted by the NPCA in this study. The concentrations in the target herbicides

residues of these waters would have been higher by their relative important inputs from the low inputs of meteorite waters in this season. However, this process would be obscured by the high biological activities in this season, favoured by the relative high temperature of these waters [13, 14]. In GRS, the very significant leaching of the watershed of this aquatic ecosystem by meteorite waters would contribute to this situation, but to a lesser degree because of the dilution effects, due to the rise in water, as well as their renewal. These processes would be shown by the slight drops of the concentrations in the target herbicide residues of these waters in this season relative to those determined in GDS. This could explain the non-significant difference between their concentrations in ATZ, CNZ, DIA, PPZ, SIZ and, TBT obtained in GDS and those determined in GRS, as highlighted by the tests post-hoc implemented in this study. The renewal of these waters induced by the meteorite waters in GRS combined with the drop in their level in SDS, following their partial flow towards the wetlands around and the San-Pédro River, would have contributed to a clear drop in their concentrations in these herbicide residues in SDS. The meteorite waters inputs in SRS would generally have very slightly enriched these waters in all target herbicide residues, consequences of the effects of the importance of meteorite waters inputs in GRS and their low use on the watershed of this ecosystem in this season. The rainfall in SRS seem to not impact significantly their concentration in DIA, in opposite of their concentration in MTZ between these consecutive seasons, as shown by the tests post-hoc implemented in this study. The renewal of the waters from this lake system by the meteorite waters inputs, increasing from SDS to GRS, would reduce a residence time of these target herbicide residues in these water, as highlighted by the decrease of the ration DEA/ATZ from SDS to GRS [45].

The relatively high presence of SIZ in these waters would make them highly polluted according the Directive 2013/39/EU [33]. So, they were unsuitable for all biological activities and for all anthropogenic uses linked to human health over the entire study period, as highlighted by the SEQ-Eau V2 water quality guidelines [34]. This would be again shown by its seasonal values of its QR, highlighted its severe ecotoxicity for the biota of this lake system in this period [36]. This fact would be likely to lead to chronic risks for its biota according to the MDDEP water quality guidelines [35]. This herbicide residue is likely to have effects on the endocrine system and neurotoxicity in aquatic and terrestrial mammals, although it is likely to be non-genotoxic and non-carcinogenic according to US EPA [48]. Its toxicity could be moderate for its aquatic invertebrates and fish [49]. The ecotoxicity risk of SIZ for its flora would have been significant by the inhibition of photosynthesis, consequently for the aquatic fauna that depends on it [40].

5. Conclusion

This study was highlighted the relative important contamination of the waters from the Déganobo system lake by herbicide residues. This situation is due to the heavily use of pesticides, particularly synthetic herbicides on its watershed. The consequences are its relative important degradation with severe risks for its biota, as well for human health. Another studies must be carried out to assess the real level of its chemical pollution, namely by other kind of synthetic pesticides, polycyclic aromatic hydrocarbons and, trace metals. Also, the competent authorities must raise awareness among the populations living in its watershed about the consequences of the intensive use of the synthetic herbicides on its ecological state, strengthen the fight against dangerous pesticides and, promote the use of natural pesticides.

Compliance with ethical standards

Disclosure of conflict of interest

Authors have declared that no competing interests exist

Authors' Contributions

- Kouadio Fabrice Arthur KONAN managed the literature research, designed the study, wrote the protocol and the first draft.
- Marcel Konan YAO, designed this study, managed the analyses of the study and, performed the statistical analysis.

References

- [1] WHO. Pesticide residues in food [Internet]; 2022 [cited 2022 Sep 15]. Available from <https://www.who.int/en/news-room/fact-sheets/detail/pesticide-residues-in-food>, accessed Sep 21.
- [2] Deguine J-P, Aubertot J-N, Flor RJ, Lescourret F, Wyckhuys KAG, Ratnadass A. Integrated pest management: good intentions, hard realities. *A review. Agronomy for Sustainable Development*. 2021; 41(38): 1-35.

- [3] Hamdache S. Photochemistry and fate of pesticides used in agricultural greenhouses in Liban : Mixing, photosensitization and carried effects [Ph.D. dissertation]. Clermont Auverge, Clermont Auverge : University of Clermont Auverge ; 2018.
- [4] Bajolet A, Beauval V, Lebreton D, Mathieu B, Miller M. Training guide : Agroecology to get rid of pesticide. Reduce the use and risks of pesticides and veterinary products through viable alternative practices. Lyon: AVSF-AFD; 2020.
- [5] Stockhom. Convention. Stockholm convention of 22 May 2001 on Persistent organic pollutants (POP convention), text and annex. Stockhom; 2001.
- [6] Sahelian Pesticides Committee, 2014. Global list of pesticides authorized by the Sahelian Pesticides Committee. Version December 2021. Sahel Institute ed. Bamako: Secrétariat permanent du CSP INSAH ; 2014.
- [7] Compaore H, Ilboudo S, Nati ADB, Dama-Balima MM. 14. Farmer practices for pesticide management in rice-growing in wetlands. Health and environmental risks (Dano, Burkina Faso). In Sultan B., Bossa A.Y., Salack S, Sanon M, eds. RD Climate risks and agriculture in west Africa. Marseille: IRD ; 2020. p. 189-204.
- [8] De A, Bose R, Kumar A, Mozumdar S. Worldwide pesticide use. In De A, Bose R, Kumar A, Mozumdar S, eds. Springer Targeted delivery of pesticides using biodegradable polymeric nanoparticles. Berlin: Springer; 2014. p. 5–6
- [9] Sharma A, Kumar V, Shahzad B, Tanveer M, Sidhu GPS, Handa N, Kohli SK, Yadav P, Bali AS, Parihar RD, Dar OI, Singh K, Jasrotia S, Bakshi P, Ramakrishnan M, Kumar S, Bhardwaj R, Thukral AK. Worldwide pesticide usage and its impacts on ecosystem. SN Applied Sciences. 2019; 1:1446.
- [10] Nwinyimagu AJ, Eyo JE, Nwonumara GN. Distribution and ecological risk assessment of herbicide residues in water, sediment and fish from Anyim River, Ebonyi State, Nigeria. Environmental Toxicology and Pharmacology. 2023; 100:104131.
- [11] Ozaslan C, Gürsoy S, Di Tommaso A. Band herbicide application combined with inter-row cultivation as a sustainable weed management strategy for reducing herbicide use: A meta-analysis. Crop Protection. 2024; 175: 106474.
- [12] Lei Q, Zhong J, Chen S-F, Wu S, Huang Y, Guo P, Mishra S, Bhatt K, Chen S. Microbial degradation as a powerful weapon in the removal of sulfonylurea herbicides. Environmental Research. 2023; 235: 116570.
- [13] Chang J, Fang W, Chen L, Zhang P, Zhang G., Zhang H., Liang J, Wang Q., Ma W., 2022. Toxicological effects, environmental behaviors and remediation technologies of herbicide atrazine in soil and sediment: A comprehensive review. Chemosphere. 307(Part 3): 136006.
- [14] Wang Z, Ouyang W, Tysklind M, Lin C, Wang B. Seasonal variations in atrazine degradation in a typical semi enclosed bay of the northwest Pacific Ocean. Environmental Pollution. 2021; 283: 117072.
- [15] Atto Y, Mondé S. Assessment of the contamination level of the Lake Adaou (East of Côte d'Ivoire) by phytosanitary products. Environmental dynamics. 2020 ; 45 : 56-60.
- [16] Ahoussi KE, Séka AMP, Traoré A. Characterization of a hydrological environment influenced by the use of pesticides in agriculture in Côte d'Ivoire : Case of the Mé River watershed. Journal of Applied Biosciences. 2021; 161: 16652 – 62.
- [17] Siriki K, Yao KM, Gnonsoro UP, Trokourey A. Transboundary river water pesticide pollution in historical agriculture areas in West Africa: a case study in the Comoe, Bia, and Tanoé rivers (Cote d'Ivoire). Arabian Journal of Geosciences. 2021 ; 14 : 2068.
- [18] Traoré A, Ahoussi KE, Aka N, Traoré A, Soro N. Level of contamination by pesticides in the waters from the Aghien and Potou lagoons (South-east of Côte d'Ivoire). International Journal of Pure Applied and Bioscience. 2015; 3(4): 312-22.
- [19] Yao KS, Kouamé KV, Yao KM, Atsé BC, Trokourey A, Tidou AS. Contamination, distribution and assessment of ecological risks by pesticides in the sediments from the Ebrié Lagoon, Côte d'Ivoire. Afrique Science. 2018; 14(6) : 400 – 12.
- [20] Konan KFA, Yao MK. Occurrence, Ecological and Health Risks of Organic Pollution of the Waters from a Tropical Lake System. International Journal of Environment and Climate Change. 2023; 13(11): 2509-21.
- [21] PRICI. Environmental and social impact study relating to the project to develop the primary collectors of the San-Pédro city. Final report. Abidjan : MCLAU ; 2016.

- [22] Traoré KM. Analysis of the vulnerabilities of the coastal town of San-Pédro (South-east of Côte d'Ivoire) [Ph.D. dissertation]. Cocody, Abidjan : Université Felix Houphouët-Boigny ; 2016.
- [23] AIP. The minister of water and forest reflects on development plan for the Lake San-Pédro [Internet]. AIP ; 2022 [cited 2022 sep 15]. Available from <https://www.aip.ci/cote-divoire-aip-le-ministre-des-eaux-et-forets-reflechit-sur-un-plan-damenagement-du-lac-de-san-pedro/>.
- [24] Doumbia MY, Tchakam MG, Terric Jouaillec M. DINIYO in San-Pédro city from the port city to the coastal metropolis. Context document. San-Pédro International Urban Project Management Workshop 2021. San-Pédro : AFD ; 2021.
- [25] Koko ATN, Tuo P, Anoh KP. Environmental management and population health in the San-Pédro city [Internet]. Regardsuds ; 2018(1) [cited 2023 Nov 2]. Available from <https://regardsuds.org/gestion-de-lenvironnement-et-sante-de-la-population-dans-la-ville-de-san-pedro-sud-ouest-de-la-cote-divoire/>.
- [26] CEAEQ. MA. 403-Pest 3.1-Determination of organophosphate, triazine, carbamate and substituted area pesticides in water : extraction with C-18 ; assay by gas chromatography coupled with a mss spectrometer. Québec : MDDEP ; 2011.
- [27] NF EN ISO 5667-3. Water quality-Sampling-Part 3 : Storage and handling of water samples. Paris: AFNOR; 2013.
- [28] International Organization for Standardization. General requirements for the competence of testing and calibration laboratories with later amendments ISO/IEC 17025. Genève: ISO; 2005.
- [29] Rahman M, Hoque MdS, Bhowmik S, Ferdousi S, Kabiraz MP, Brake MLv. Monitoring of pesticide residues from fish feed, fish and vegetables in Bangladesh by GC-MS using the QuEChERS method. Heliyon. 2021; e06390.
- [30] US-EPA. Method for the determination of organic compounds in drinking water, Method 525.1, revision 2.2 [Internet]. USA: Federal Register 56:30272; 1991 [cited 2023 Oct 30]. Available from https://www.epa.gov/sites/production/files/2015-09/documents/method_525-1_rev-2-2_1991.pdf
- [31] PAM (Pesticide Analytical Manual) [Internet]. U.S. Food and Drug Administration, U.S. Department of Health and Human Service, Washington, DC, USA; 1994. Available from <https://www.fda.gov/food/laboratory-methods-food/pesticide-analytical-manual-volume-i-pam-3rdedition>
- [32] Abbassy MA, Khalifa MA, Nassar AMK, Nour El-Deen EE, Salim YM. Analysis of organochlorine pesticides residues in fish from Edko Lake (North of Egypt) using eco-friendly method and their health implications for humans. Toxicology Research. 2021; 37: 495–503.
- [33] Directive 2013/39/EU. Directive 2013/39/EU of the European Parliament and of the Council of 12th August 2013, amending Directives 2000/60/EC and 2008/105/EC with regard to priority substances in the field of water policy, Official Journal of European Union L 226/1. 2013: 12-17.
- [34] MEDD et Agence de l'eau. Water Quality Analysis (SEQ-Eaux), assessment grids. 2nd eds. Paris : MEDD et Agence de l'eau ; 2003.
- [35] MDDEP. Surface water quality criteria. EDS Directorate for monitoring the state of the environment. Québec : MDDEP ; 2009.
- [36] European Commission, 2003. Technical guidance document on risk assessment part II.
- [37] INERIS. Summary of regulatory values for chemical substances, in force in water, foodstuffs and in the air in France as of June 30, 2020. Technical report n°-20-200358-2190502-v 2.0 19/10/2020. Verneuil en Halatte : INERIS ; 2020.
- [38] Historique-meteo [Internet]; 2021 [Cited 2023 Feb 23]. Available from <https://www.historique-meteo.net/afrique/cote-d-ivoire/san-pedro/> /2021.
- [39] Historique-meteo [Internet]; 2022 [Cited 2023 Feb 23]. Available from <https://www.historique-meteo.net/afrique/cote-d-ivoire/san-pedro/> / 2022.
- [40] Durak J, Rokoszak T, Skiba A, Furman P, Styszko K. Environmental risk assessment of priority biocidal substances on Polish surface water sample. Environmental Science and Pollution Research. 2021; 28: 1254–66.
- [41] Suárez F, Guzmán E, Muñoz JF, Bachmann J, Alister COC, Kogan M. Simazine transport in undisturbed soils from a vineyard at the Casablanca valley, Chile. Journal of Environmental Management. 2013; 117: 32-41.

- [42] Lojo-López M, Andrades JA, Egea-Corbacho A, Coello MD, Quiroga JM. Degradation of simazine by photolysis of hydrogen peroxide Fenton and photo-Fenton under darkness, sunlight and UV light. *Journal of Water Process Engineering*. 2021; 42: 102115.
- [43] Xu J, Olvera-Vargas H, Teo FYH, Lefebvre O. A comparison of visible-light photocatalysts for solar photoelectrocatalysis coupled to solar photoelectro-Fenton: Application to the degradation of the pesticide simazine. *Chemosphere*. 2021; 276: 130138.
- [44] Bancon-Montigny C, Gonzalez C, Delpoux S, Avenzac M, Spinelli S, Mhadhbi T, Mejri K, Hlaili AS, Pringault O. Seasonal changes of chemical contamination in coastal waters during sediment resuspension. *Chemosphere*. 2019; 235: 651-61.
- [45] Triassi M, Montuori P, Provisiero DP, Rosa D, Duca FD, Sarnacchiaro P, Díez S. Occurrence and spatial-temporal distribution of atrazine and its metabolites in the aquatic environment of the Volturno River estuary, southern Italy. *Science of The Total Environment*. 2022; 803: 149972.
- [46] Adolph M-L, Dreßler M, Troelstra V, Wrozyzna C, Haberzett T. Eutrophication and contamination dynamics of Schweriner See, NE Germany, during the past 670years – A multi-proxy approach on lacustrine surface sediments and sediment cores. *Science of The Total Environment*. 2023; 877: 162745.
- [47] Wahla AQ, Anwar S, Mueller JA, Arslan M, Iqbal S. Immobilization of metribuzin degrading bacterial consortium MB3R on biochar enhances bioremediation of potato vegetated soil and restores bacterial community structure. *Journal of Hazardous Materials*. 2020; 390: 121493.
- [48] US-EPA. Simazine: Revised Preliminary HED Chapter of the Reregistration Eligibility Decision Document (RED); Revised for Error Correction. Office of Prevention, Pesticides and Toxic Substances. Washington: EPA; 2005.
- [49] Stara A, Machova J, Velisek J. Effect of chronic exposure to simazine on oxidative stress and antioxidant response in common carp (*Cyprinus carpio* L.) *Environmental Toxicology and Pharmacology*. 2012; 33(2): 334-343.