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Level of Contamination of Fishponds Water in Pesticide Residues and Metallic Trace Elements (Pb, Cd, As, Hg): Case of Fishponds of ZEPREGUHE (Daloa, Côte d'Ivoire)

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Abstract

Fishponds waters intended to satisfy the nutritional needs of the populations in terms of supply of fish resources are strongly and unfortunately exposed to the mobility and dispersion of metallic trace elements (TMEs) or to the persistence in the environment and in the form of pesticide residues from human activities. The objective of this work is to evaluate, on the one hand, the levels of identified pesticide residues and, on the other hand, those of researched TMEs (lead, cadmium, mercury and arsenic) in the waters of ponds used for fish farming in Zépréguhé, a locality located 9 km from the town of Daloa in the centre-west of Côte d'Ivoire. The dosage of the samples carried out by means of a gas chromatograph coupled to a mass spectrometer (GC/MS) made it possible to detect nine (9) pesticide molecules, including eight (8) organochlorines and a single molecule from the pyrethroid family, obtained from the detection limit of 0.006 µg/L and the quantification limit of 0.018 µg/L. The maximum average concentration was obtained with α-endosulfan for a content reaching 0.8038 µg/L and well above the maximum admissible concentration of 0.1 µg/L. The TMEs were quantified using an atomic absorption spectrophotometer (AAS). Arsenic is the most abundant metal with an average concentration of 9.497 µg/L. With the exception of lead, these measured levels are above the acceptable limit values for freshwater. This study showed that human activities such as the use of fertilisers and plant protection products in plantations, sand extraction and road traffic have a negative impact on the quality of the water in ponds used for fish breeding.

Keywords

Fishpond Water, Metallic Trace Elements, Pesticide Residues, Maximum Residue Levels

1. Introduction

Aquatic ecosystems are more and more endangered by the pollution generated by anthropogenic activities such as urbanisation, industrialisation, agriculture, etc. The substances resulting from these activities are capable of contaminating the environment in the short or medium term and are responsible for differents biotopes alteration.

In particular, water, which is an excellent solvent, becomes a major vector of anthropogenic contaminants to the receiving environments following the transfer. These contaminants reach particularly vulnerable aquatic systems from the pintural and diffuse sources (drainage water, waste water, radioactive and agricultural effluents) [1] [2] [3]. Among the many compounds emitted by human activities, trace metals (TMEs) and pesticide residues are major sources of contamination.

In fact, TMEs are not only naturally present in the environment through erosion or rock alteration [4] but also derive from numerous anthropogenic activities. Some of these said to be essential elements, such as iron and zinc, are essential for the growth and well-being of living organisms, including humans [5]. A very low concentration of these elements could even bring about phenomenone of lack. However, present in great quantities, these could lead to the risk of toxicity. Other TMEs, such as mercury, lead or cadmium, are not so essential because they are not indispensable to metabolic activities and even provoke established toxicity in very low quantities [6].

The contamination of aquatic ecosystems by TMEs remains a serious environmental problem so much of the ubiquitous nature of their presence in the biosphere also by their toxicity and potential bioaccumulation in many aquatic species [7].

Pesticides, also called phytosanitary products to play a predominant role in the quantitative and qualitative improvement of agricultural productivity. They involve many chemical families with diverse behaviors in their actions and also their environmental future. According to the destruction the pesticides aim at insecticides, herbicides, fungicides and other groups. The increasing use and even uncontrolled used of these substances lead to negative consequences on the environment due to their persistent nature.

The presence of TMEs and pesticide residues in surface waters and in particular in ponds used for fish farming, constitute because of their toxicity and their persistence a real threat to the health safety of populations. In fact, fish farming has been considerably increasing these recent years in many countries in the world, notably in Côte d'Ivoire, due to the agricultural diversification policy and the promotion of aquacole production [8]. This aims, on the one hand, improving the productivity and satisfaction of nutritional needs of the populations in fish and other halieutic resources and, on the other hand, sustains national economics by creating new jobs and reduces poverty.

In ZEPREGUHE, village 9 km far from Daloa, in the central west of Côte d'Ivoire, the fish farming ponds are for most located in shallows that are the receptacle of solid and liquid urban waste and of water leached from phytosanitary products used in agricultural farms upstream. This situation brings about worrryness due to the harm to the population indirectly exposed to pesticide residues and TMEs through the consumption of fish from these ponds.

The objective of this work is to evaluate, on the one hand, the levels of identified pesticide residues and, on the other hand, those of researched TME (lead, cadmium, mercury and arsenic) in the waters of ponds used for fish farming in Zépréguhé, a locality located 9 km from the town of Daloa in the centre-west of Cote d'Ivoire.

2. Material and Methods

2.1. Study Area

The fish farm concerned by this study is located in Zépréguhé, in the communal territory of Daloa, 9 km far from the city on the road to Bouaflé (**Figure 1**). This farm is a supply source for Daloa. Where the demand is so high due to the population growth. In fact, Daloa is the third big city in the country with estimated population of 245,360 persons in 2014 an area of 9650.75 ha.

2.2. Study Matrix

This study is about the analysis of water taken from fish farming ponds in diversion connected to a river. **Figure 2** shows the area of ponds in diversion among the fifteen (15) that the farm visited.

2.3. Methods

2.3.1. Water Sampling

Water samplings have been made in five (5) ponds in the fish farming used for this study. For each of the ponds, three (3) samples per type of contaminant sought corresponding to three (3) randomly selected sampling points were collected. Thus, a total of thirty (30) samples have been taken fifteen (15) samples for the TMEs proportions and fifteen (15) others for the search for pesticide residues. All these water samples were collected using a Niskin bottle placed at 0.20 meters (m) below the surface of the pond water body. They have been put in amber glass bottles and plastic vials for the samples respectively for the pesticide residue and the TMEs samples were before being transported and stored at −4˚C in the laboratory.

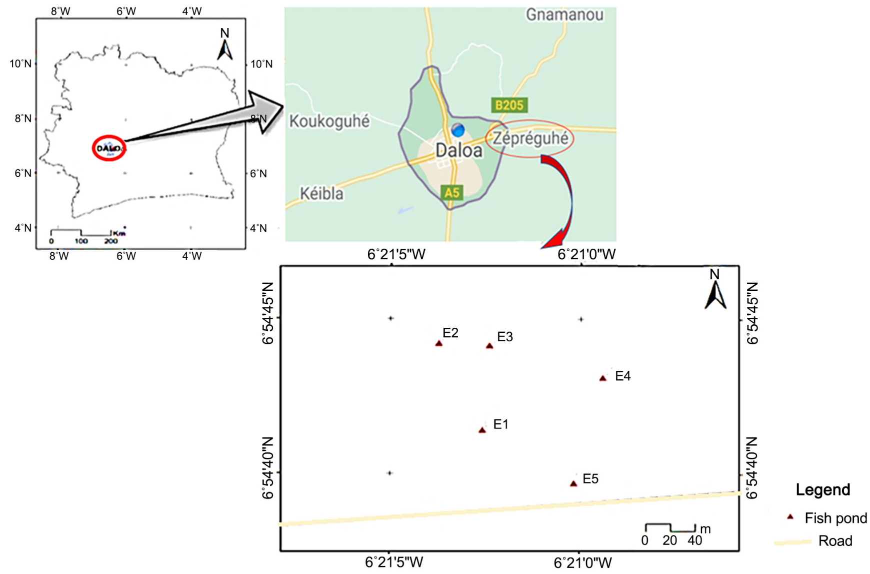

Figure 1. Location map of the study area and sampling sites.

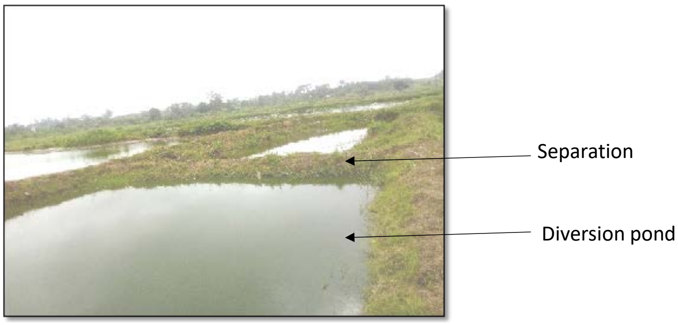

Figure 2. Ponds in diversion in a fish farm of Zépréguhé.

2.3.2. Extraction and Purification of Pesticide Residues

The analysis of pesticides in water needs a pre-treatment, consisting in filtering the water sample on a fiber glass of special use 0.01 μm diameter. After comes the stage of the extraction of the pesticide residues from the water matrix. The method used in our case is liquid-liquid extraction [9] using Merck brand (Darmstadt, Germany) dichloromethane solution with purity ≥ 99% as solvent. Before coming to the chromatographic analysis, the extracts are then purified and evaporated to dryness at 35˚C for 15 min and taken with 2 mL of hexane (≥98%) also provided by Merck. This analysis is the last step of the process and involves the stage of identification and purification. It has been made with a gaseous phase chromatographer coupled with a mass spectrometer (GC/MS). The injection volume is 1 mL.

2.3.3. Metals Dosing

The samples have probably been filtered a paper filter Watchman 0.45 μm before adding nitric acid 65% for 1L of solution in order to come Varian Spectra 110 atomic absorption spectrophotometer to determine the concentrations of metals researched.

2.3.4. Statistical Analysis

For data exploitation, Statistical analysis was done using the STATISTICA 7.1 (one-way ANOVA, LSD test for homogeneous groups) and MATLAB 6.0.1 (neural network). The descriptive statistic permitted us to determine the maximum and minimum concentrations, the average concentrations and the standard deviations of the pesticide residues detected in the samples analysed. The conformity of the concentrations was possible by comparing an average to a standard.

3. Results and Discussion

3.1. Identification and Levels of Pesticide Residues in Analyzed Water Samples

The chromatographic analysis made on the samples of fish farming of ZEPREGUHE revealed the presence of nine (9) pesticide residues. These are α-HCH (lindane), heptachlor, aldrin, β-endosulfan, PP-DDD, endosulfan-sulfate, α-endosulfan, cypermethrin and methoxychlor. They are all from the organochlorin family except the cypermethrin which is a pyrethroid (Table 1). Most of these pesticides detected are insecticides that are used in the spraying of coffee and cocoa farms close to fish farmings. And the presence of these substances pond water could be explained on the one hand by the action of the wind that may have directed the pesticide particles contained in the insecticides directly into the ponds during spraying [10]; and, on the other hand, by the action of rainwater that washes up the substances applied to the plantations into the water bodies of the river which supplies the fish farm. Among the pesticides detected, some are forbiden because of their toxicity and ecotoxicology. Their presence in the water shows the fraudulent use of their formulations containing these substances. Traoré and collabotaters have also noted this fraudulent use of organochlorins (endosulfan, lindan, heptachlor) in coffee and cocoa production areas [11]. That is so frightening because some studies classify most of the organochlorins among the endocrinious subversives and the carcinogen molecules [12] [13].

Table 1. Average concentrations of pesticide residues identified in the pond waters analysed.

	Average concentrations (µg/L)				
Pesticides residues	**Fishpond 1**	**Fishpond 2**	**Fishpond 3**	**Fishpond 4**	**Fishpond 5**
α-HCB (Lindan)	0.0905 ± 0.0003[d]	0.0071 ± 0.0002[a]	0.0076 ± 0.0001[b]	0.0236 ± 0.0002[c]	0.1016 ± 0.0002 [e]
Heptachlor	0.3307 ± 0.0001[a]	0.0168 ± 1E-04[b]	nd	0.0491 ± 1E-04[c]	nd
Aldrin	nd	nd	nd	nd	0.2725 ± 0.0002
β-endosulfan	0.015 ± 0.0003[b]	0.0409 ± 0.0002[c]	0.0085 ± 0.0001[a]	0.1477 ± 0.0001 [e]	0.0809 ± 0.0001[d]
PP-DDD	0.0187 ± 0.0001[c]	0.015 ± 0.001[b]	0.158 ± 0.0015 [e]	0.0755 ± 0.0001[d]	0.001 ± 0.001[a]
Endosulfan-sulfate	nd	0.0064 ± 0.0001[a]	nd	0.0094 ± 0.0001[c]	0.018 ± 0.0001[b]
α-endosulfan	0.0909 ± 5.7735 E-05[c]	0.8038 ± 0.0001 [e]	0.0231 ± 1E-04[a]	0.1279 ± 1E-04[d]	0.0513 ± 8.498E-18[b]
Cyperméthrin	nd	nd	0.07 ± 0.001	nd	nd
Methoxychlor	0.0251 ± 0.0001[a]	0.0605 ± 0.0001[c]	0.1179 ± 0.0001 [e]	0.0455 ± 0.0001[b]	0.099 ± 0.0001[d]

LOQ = 0.018 µg/L.

The residues have been detected in more than 50% of the samples analysed with some concentrations superior to, in most cases the quantification limit (LOQ).

Among the nave (9) pesticide residues detected, five (5) are found in all the waters of all the ponds. These are: lindan (α-HCB), β-endosulfan, PP-DDD, α-endosulfan and methoxychlor. Moreover, among these compounds, α-endosulfan is the molecule with the highest average concentration, with 0.8038 μg/L detected in Pond 2. This value is higher than the maximum permissible concentration of 0.1 μg/L of alpha or beta endosulfan in surface water defined byWorld Health Organization [14] or European Directive 2008/105/EC for 41 substances or groups of substances. The risk of indirect contamination of populations is therefore real since it has been shown that endosulfan is not only a very persistent molecule in the environment but also has a high capacity to bioaccumulate in aquatic organisms, particularly fish, with bioconcentration factor values sometimes ranging between 2400 and 11,000 for whole fish [15].

3.2. Total Load of Pesticide Residues in the Different Ponds

Table 2 shows the level of contamination per pond by doing the sum of concentrations of the residues detected in the water matrix. Comparing total concentrations from each pond, the following order is obtained: [Pond 3] < [Pond 4] < [Pond1] < [Pond 5] < [Pond 2]. The concentration of pesticide residues in the different ponds could be linked to the acreage and depth of ponds.

3.3. Level of Pond Water Contamination by Trace Metal Elements

The dosage of pond water by the spectroscopy of atomic absorption (SAA) has shown that this water contains trace metal elements sought after which are lead, cadmium, mercury and arsenic. The average concentrations of these TMEs are spread in Table 3.

The results indicate that the pond waters studied have all the same contamination level to the trace metal elements, because statistical analysis has shown that, there is no striking difference between the samples for the different concentrations of TMEs (statistically identical with $P > 0.05$). In fact, all the ponds are close to rubber, coffee and cocoa farms, that are maybe sources of contamination in TME with the use of fertilisers and agrochemicals [16] [17].

These fish farmings are vessel of wastewater from the keeping up of these farms upstream. Also, runoff water could carry in its passage hydrocarbons and other waste from garages, landfills and households, and loaded with trace elements to flow into the river that feeds these ponds. In terms of global concentrations, when the cumulative concentrations of detected TMEs are calculated per pond, Table 3 also shows that the pond (pond5) has the highest level of TME contamination. The explanation for this lies in the location of the different ponds in relation to the potential sources of contamination. Indeed, among the five (5) ponds studied, pond (E5) is the one closest to the road that adds to the

Table 2. Average total pesticide residues concentrations detected per pond.

	Fishpond 1	Fishpond 2	Fishpond 3	Fishpond 4	Fishpond 5
Total load (μg/L)	0.5709	0.9505	0.3805	0.4787	0.6243

Table 3. TME levels in the various water samples.

	TME concentrations (μg/L)				
	Pb	Cd	Hg	As	Global concentration
P1	1.215 ± 0.1	0.791 ± 0.02	0.434 ± 0.3	9.496 ± 0.2	11.936
P2	1.355 ± 0.2	0.878 ± 0.1	0.477 ± 0.3	8.679 ± 0.7	11.388
P3	1.600 ± 0.1	0.862 ± 0.1	0.476 ± 0.3	9.437 ± 0.4	12.375
P4	1.510 ± 0.3	0.862 ± 0.1	0.784 ± 0.6	8.763 ± 0.2	11.919
P5	2.391 ± 0.5	0,846 ± 0.1	0.476 ± 0.2	9.497 ± 0.8	13.210
n	15	15	15	15	_
Average concentrations	1.614 ± 0.491	0.847 ± 0.074	0.529 ± 0.336	9.174 ± 0.588	_

n: number of samples; P: ponds.

other sources of pollution that the whole fish farm is confronted with. And this position makes it (pond E5) more vulnerable to pollution from car traffic, especially through vehicle exhaust fumes which contain traces of metals alongside. According to some authors [18], fuels contain mercury (Hg), cadmium (Cd), copper (Cu) and lead (Pb) in their composition, although the presence of this last element in the composition of fuel is increasingly questioned in recent years.

Comparing these average contents with the standards in use, it appears clearly through **Figure 3** that except lead, the average concentrations of TMEs in the pond water are all superior to threshold values [19]. The content in arsenic (As) is about four times superior to norm. In fact, the histogram (**Figure 3**), reveals that the average concentration in lead (1.6142 μg/L), remains low compared to the requirements fixed to 10 μg/L. This result conforms to that Diop and collaborators [20], obtained in Dakar in 2014 that evaluating the contamination and the speciation of trace metals in a river containing fish alife, obtained that the average lead (Pb) oscillated between 0.047 and 3.87 μg/L. This result shows that the samples taken would not present any risk of infection or lead contamination in relation to the standard set. On the other hand, the levels of mercury (0.529 μg/L), cadmium (0.847 μg/L) and arsenic (9.174 μg/L) obtained are respectively higher than the reference values set (0.1 μg/L; 0.2 μg/L; 2 μg/L). These results are worrying insofar as cadmium poisoning could cause cancer effects in exposed individuals and lead to endocrine and/or immune system dysfunction in children [21]. Mercury and arsenic are also known to be acutely toxic at low doses, causing infections of the cardiovascular system and other serious illnesses in humans who are exposed indirectly through the consumption of fish in which these contaminants accumulate [22] [23].

3.4. Distribution of TME in the Samples

Figure 4 presents through the cloud of points the concentration levels of the metallic trace elements studied (Pb, Hg, Cd, As) in each of the fifteen (15) samples. The decreasing order of average concentration of the molecules studied are as follows: [As] > [Pb] > [Cd] > [Hg]. Arsenic is the composite that presents the highest contents with a maximum concentration reaching 9.497 µg/L. Anyway, there is agreat difference between the concentration level of arsenic and that of the three (3) other metals studied, as shown in Figure 4. This preponderance of arsenic in the water could be due not only to the regular use of fertilisers, herbicides or insecticides in the surrounding plantations, but also to the dust heaps or leaching and drainage water from the sand extraction activity carried out near the ponds. Arsenic accumulates naturally in magmatic and sedimentary rocks [24], and sand is usually produced by the weathering and erosion of rocks.

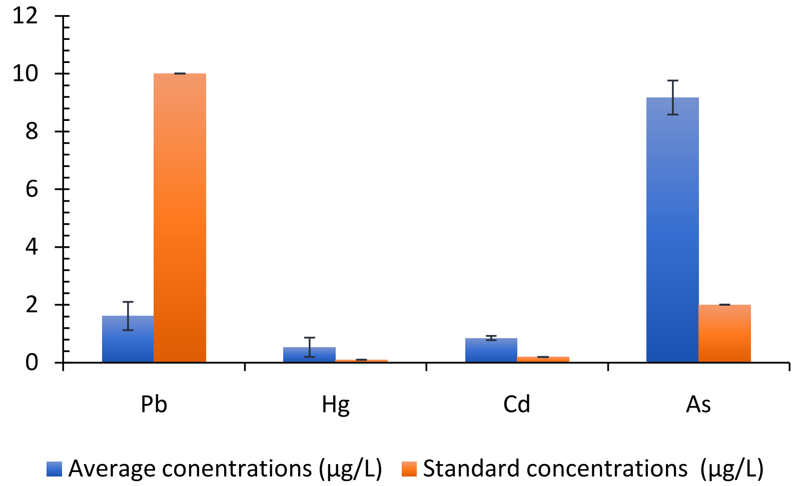

Figure 3. Comparison of TME levels in fishponds waters with the standard concentrations [19].

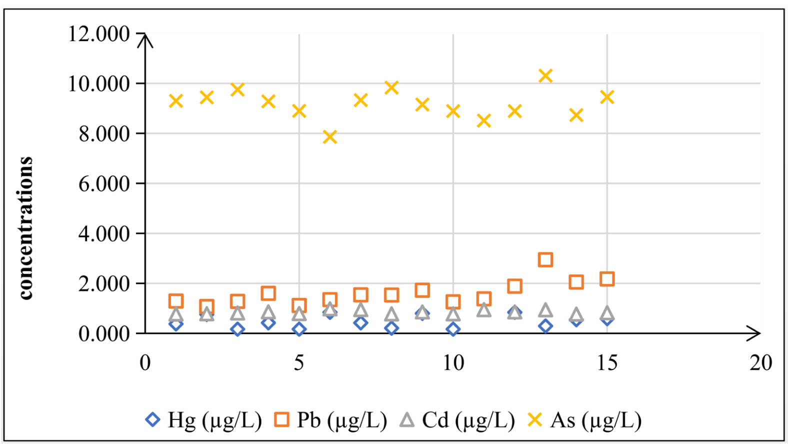

Figure 4. Scatterplot of trace elements in the collected water samples.

4. Conclusions

This study shows that water taken from fish farming ponds of ZEPREGUHE (Daloa) contains pesticide residues with concentrations of certain identified molecules above the current health safety standard. The compounds obtained are essentially from the organochlorin family, with the exception of cypermethrin which is a pyrethroid. The maximum average concentration was obtained for α-endosulfan with a value of 0.8038 µg/L, exceeding the maximum permissible concentration of 0.1 µg/L for this same compound.

These waters also contain trace metals (Pb, Cd, Hg, As) at average levels exceeding the acceptable limit values, except for lead. Arsenic is the compound with the highest levels, with a maximum concentration of 9.497 µg/L. This study showed that the water sampled from the ponds used for fish farming is harmful to aquatic life.

Conflicts of Interest

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

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