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Assessment of metallic pollution (Hg, Pb, Cd, Cu) in water and sediments of fish ponds located in a lowland of the city of Daloa

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ABSTRACT

The assessment of metal pollution in water and sediments of four fish ponds located in the city of Daloa was determined. For this purpose, water and sediment samples were taken from these ponds for the determination of Hg, Pb, Cd and Cu using the Atomic Absorption Spectrophotometer (AAS). Thus, the results of the analyses show that the water quality of the different fish ponds is influenced by the variation of physico-chemical parameters and that these waters are vulnerable to organic and inorganic pollution. Furthermore, these results also show that Cu (5.039 $mg.L^{-1}$) and Hg (5.191 $mg.L^{-1}$) are the most accumulated heavy metals in the water of these fish ponds. For the sediments, Cu (708.909 $mg.kg^{-1}$) and Pb (1.22 $mg.kg^{-1}$) are the most accumulated. The order of preferential accumulation of heavy metals in the water of these fish ponds is as follows: [Cu]>[Hg]>[Pb]>[Cd]. For sediments, the order of preferential accumulation of heavy metals is as follows: [Cu]>[Pb]>[Hg]>[Cd]. These results show that whatever the matrix studied, Cu is the most predominant metal. Furthermore, the values of the geo accumulation index (I_{geo}) show a high intensity of Hg and Cu pollution in fishpond sediments. These two heavy metals present dangers and risks of bioaccumulation, due to their presence and high accumulation, for the fish produced in these fishponds.

1. Introduction

Fishponds are farming systems with widely recognised biodiversity [1]. However, chemical pollutants such as heavy metals influence the water and sediment quality of fishponds, thus affecting aquaculture products [2]. Indeed, the low production and quality of aquaculture products are partly related to the physico-chemical quality of the production environment [1-3].

Thus, for the development of freshwater fish farming in ponds, it is important to determine the physico-chemical quality and to secure the water bodies with respect to their exposure to these pollutants. Heavy metals generally enter aquatic environments through atmospheric deposition, erosion of the geological matrix or through anthropogenic activities such as the discharge of industrial effluents, domestic wastewater, mining waste or the use of pesticides and inorganic fertilisers [3]. These pollutants are substances that can have a toxic effect on aquatic fauna, even at low doses [4]. Their presence in fish ponds would have an impact on the trophic chain and therefore a danger for humans who are exposed to them when eating fish from these fish ponds ([2], [5]).

It is therefore important to determine the level of heavy metal concentration in fish farming environments because of their vulnerability to metal pollutants on the one hand and the impact that these will have on the fauna of these environments on the other. [6]. The objective of this study is to evaluate the degree of metallic pollution in mercury (Hg), lead (Pb), cadmium

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(Cd) and copper (Cu) in the water-sediment matrix of four fish ponds.

2. Materials and Methods

2.1. Location and characterization of fish ponds

The work focused on four (4) fish ponds located in the town of Daloa, which is the capital of the Haut-Sassandra region (central-western Côte d'Ivoire). The town of Daloa is the economic centre of the region and belongs to the Lobo basin, which is located between 6°05' and 6°55' west longitude and between 6°02' and 7°55' north latitude. The climate is hot and humid with rainfall varying between 1000 and 1500mm/year. There are two rainy seasons (April-July) and (September-November) and two dry seasons (December-March) and (July-September). The temperature varies between 18 and 36 degrees. The relief is marked by granitic plateaus of 200 to 300 m in altitude and separated by lowlands (talwegs) [7]. There are fish farms with an intensive production system on the almost extensive lowlands and wetlands. The fish ponds in this study are located in a lowland bordered by houses in the upstream part of its catchment area, maize, rice, cassava and yam plantations. As these fishponds are located in a wetland (lowland), they are fed by spring water and a river. Figure 2 shows the geographical location and outline of the different ponds.

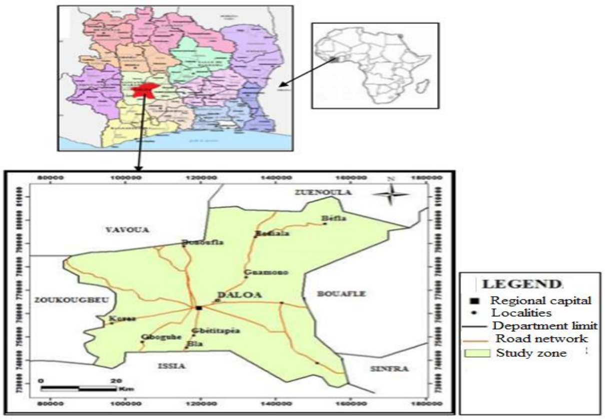

Figure 1: Location of the study area

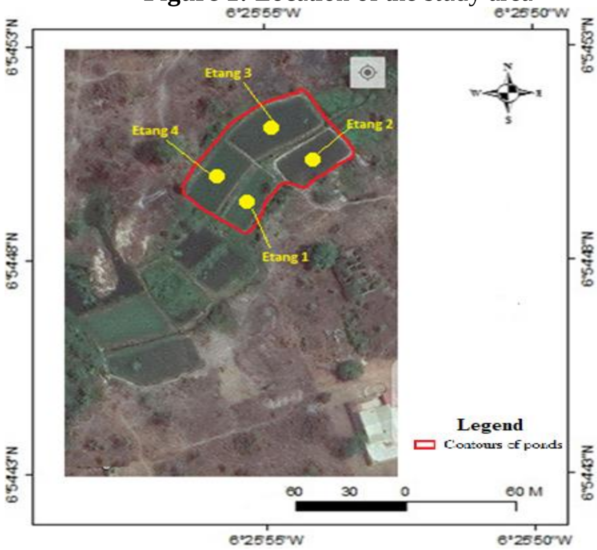

Figure 2: Location of study fish ponds

2.2. Study matrix

The study matrix consists of water and sediment from fish ponds (Figure 3).

Figure 3 : (a)-Pond 1, (b)- Pond (2); (c)- Pond 3; (d)- Pond 4

2.3. Sampling

The water was collected in plastic pots of 0.5 L capacity which were previously washed with 10% nitric acid and rinsed 3 times with distilled water. The water was collected at a depth of approximately 10 cm below the water level of the fish ponds. The different water samples were then acidified with 1 mL of concentrated nitric acid to stabilise them during storage in the laboratory at -4°C until analysis by AAS. The sediments were collected manually with latex gloves from the different fish ponds. They were placed in plastic food bags for the laboratory. A total of 32 samples, including 16 sediment samples and 16 water samples, were collected for heavy metal analysis in the laboratory (Figure 4).

Figure 4 : (a)-Sediment samples; (b)-Water samples

2.4. Mineralization and Analysis

Before the AAS analysis, all water samples were filtered through 45 µm Whatman paper to remove unwanted particles. The sediment samples were oven dried at 80 °C for 24 hours. They were then sieved to obtain a fine fraction with particles smaller than 200 µm in diameter. The digestion method used was the total decomposition method recommended by Tessier and *col* [8].

2-5. Evaluation of the metal pollution intensity

To assess the intensity of metal pollution, the geo-accumulation index I_{geo} was calculated. This empirical index compares a given concentration to a value considered as the geochemical background. Furthermore, Müller [9] defined a scale with six geo-accumulation index classes (Table I). We calculate the I_{geo} with the following formula : $I_{géo} = \log_2\left(\frac{C_n}{1{,}5B_n}\right)$

C: concentration measured in the sample; B, geochemical background; $\log_2$: base 2 logarithm; **n** : element considered; **1.5**: exaggeration factor of the geochemical background, the function of which is to take into account the natural fluctuations of the geochemical background.

Table I: Classes defined by the geoaccumulation index

Values of the I_{geo} index	Classes I_{geo}	Pollution intensity
$I_{geo}>5$	6	Extreme contamination
$4<I_{geo}\leq5$	5	High to extreme contamination
$3<I_{geo}\leq4$	4	Heavy contamination
$2<I_{geo}\leq3$	3	Moderate to heavy contamination
$1<I_{geo}\leq2$	2	Moderate contamination
$0<I_{geo}\leq1$	1	Without slight contamination
$I_{geo}\leq0$	0	Contamination free

2.6. Statistical data processing

The graphic plots were made using the Excel 2016 spreadsheet. A logarithmic transformation ($\log([\text{Metal}]+1)$) was carried out in order to reduce the heterogeneity of the variance observed at the level of the concentrations of the different samples and to better represent them graphically. A *Fisher Snedecor F* test was used to compare the difference observed between the concentration levels of heavy metals studied in the different fish ponds.

3. Results and Discussion

3.1. Results

3.1.1. Physico-chemical parameters of the fish pond environment

Figure 5 shows the variation of the pH of the water in the different fish ponds. Table ٢ lists the values of some physico-chemical parameters of these different fish ponds such as: temperature, conductivity, dissolved oxygen saturation rate, TDS.

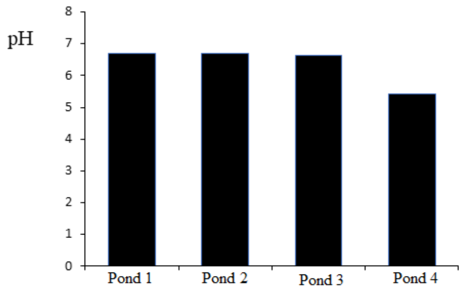

Figure 5: Average pH values of fish pond water

Table ٢: Values of the physico-chemical parameters of the water in the study ponds

Fish ponds	Physico-chemical parameters			
	T (°C)	Conductivity (µS.cm^{-1})	O_2 saturation rate (%)	TDS (mg.L^{-1})
Pond 1	27.9	35.7	126.3	16.3
Pond 2	27.7	**78.7**	**139.3**	**39.3**
Pond 3	**28.8**	49.3	90.3	25.3
Pond 4	26.7	38.7	87.7	19.0

The observation of the histograms in Figure 5 shows that the pH values measured in the water of the fish ponds are between 5.43 and 6.68 . These results show that the water in the fish ponds is acidic. Furthermore, Table II shows that the average minimum and maximum temperatures are 26.7 °C and 28.8 °C respectively; the average dissolved oxygen saturation rate is between 87.7% and 139.3%; and finally, the average TDS values are between 16.3 mg.L^{-1} and 39.3 mg.L^{-1}. Of the four ponds, the values obtained for ponds 1, 3 and 4 are below the minimum limit value of 50 µS.cm^{-1}. However, the value obtained for pond 2 (78.7 µS.cm^{-1}) is above the minimum limit value. The dissolved oxygen saturation flux values recorded in the ponds are all above the recommended limit value for natural waters (50%).

3.1.2. Levels of ETM concentration in fish ponds

- In water

The results of the concentration levels of the different heavy metals studied measured in the water of the fish ponds are presented in Figure 6.

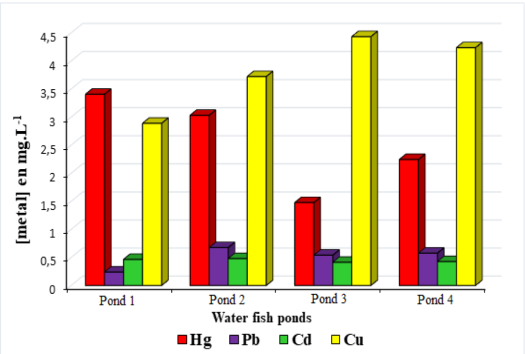

Figure 6: Average concentration levels of Pb, Hg, Cd and Cu in the water of the study fish ponds

The histograms in Figure 6 show that all the heavy metals investigated in the study were detected in the water of the different fish ponds at different concentration levels. It can also be observed that Cu and Hg are the most concentrated and detected heavy metals in the different waters studied. The maximum concentration levels recorded in the different samples for these two metals are respectively 5.039 mg.L^{-1} for Hg and 5.191 mg.L^{-1} for Cu. Furthermore, this figure reveals the order of preferential accumulation of heavy metals in the water for each fish pond, which is as follows :

- Pond 1 : [Hg]>[Cu]>[Cd]>[Pb];
- Pond 2 : [Cu]>[Hg]>[Pb]>[Cd];
- Pond 3 : [Cu]>[Hg]>[Pb]>[Cd];
- Pond 4 : [Cu]>[Hg]>[Pb]>[Cd];

Thus, in general for fish ponds, the order of preferential accumulation of heavy metals in water is as follows: [Cu]>[Hg]>[Pb]>[Cd]. Furthermore, the statistical analysis of variance applied to the concentrations of heavy metals in the different waters of the fish ponds shows that the differences observed between the concentration levels of the metals (Hg and Cd) and their distributions in the waters are not significant, the *Fisher F*-test is below the 5% threshold ($F_{calculated} > F_{005}$). However, the observed differences between the concentration levels of the metals (Pb and Cu) in the pond waters are significant at the 5% level ($F_{calculated} < F_{005}$).

- <u>In sediments</u>

The results of the concentration levels of the different heavy metals detected in the fishpond sediments are presented in Figure 7.

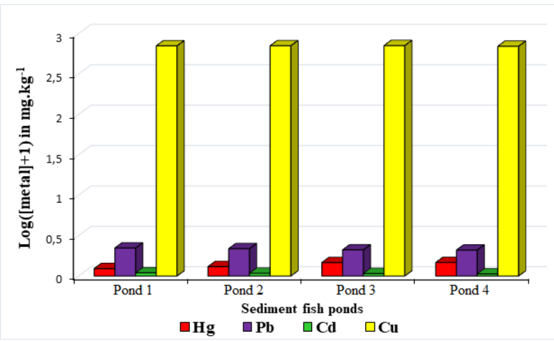

Figure 7: Average concentration levels of Pb, Hg, Cd and Cu in fishpond sediment

The figure above shows that the heavy metals investigated were also all detected in the sediments of the different fish ponds studied. Cu is the most accumulated metal in the sediments of these fish ponds with a maximum average concentration of 708.909 $mg.kg^{-1}$. A high concentration of Pb is also found in these ponds. The maximum concentrations recorded in the different samples for Cu and Pb are 717.122 $mg.kg^{-1}$ and 2.406 $mg.kg^{-1}$ respectively. Thus, the order of preferential accumulation of heavy metals in the sediments is as follows :

- Pond 1 : [Cu]>[Pb]>[Hg]>[Cd];
- Pond 2 : [Cu]>[Pb]>[Hg]>[Cd];
- Pond 3 : [Cu]>[Pb]>[Hg]>[Cd];
- Pond 4 : [Cu]>[Pb]>[Hg]>[Cd];

In general, the order of preferential accumulation of heavy metals in the sediments of different fish ponds is as follows: [Cu]> [Pb]>[Hg]>[Cd].

Furthermore, the *Fisher Snedecor F*-test applied to the distribution of heavy metal concentrations in the different fish pond sediments shows that the differences observed between the concentration levels of the different heavy metals and their distribution in the studied pond sediments are not significant. at 5% ($F_{calculated} > F_{005}$).

3.1.3. Comparison of heavy metal concentration levels with the current WHO standard

Tables ٣ and ٤ show the different average concentrations calculated in the water and sediment of the fish ponds respectively, in relation to their standards.

Table ٣: Average concentrations of heavy metals and their standard [10] in water.

Heavy metals	Calculated mean concentration ($mg.L^{-1}$)				Standard in $mg.L^{-1}$
	Pond 1	Pond 2	Pond 3	Pond 4	
Hg	3.406	3.031	1.476	2.244	0.006
Pb	0.239	0.675	0.540	0.576	0.010
Cd	0.465	0.479	0.413	0.426	0.003
Cu	2.888	3.721	4.432	4.235	2.000

Table ۴ : Average concentrations of heavy metals and their standard [10] in sediments

Heavy metals	Calculated mean concentration ($mg.kg^{-1}$)				Standard in $mg.kg^{-1}$
	Pond 1	Pond 2	Pond 3	Pond 4	
Hg	**0.235**	**0.307**	**0.465**	**0.469**	0.150
Pb	1.22	1.178	1.105	1.094	30.000
Cd	0.094	0.080	0.072	0.060	0.250
Cu	**703.123**	**705.222**	**708.909**	**694.906**	35.000

Examination of Table III reveals that in the waters of the fish ponds, all the heavy metals studied have concentration levels above the standard for the protection of water and aquatic organisms [10]. Also, Table IV shows that in sediments, only Hg and Cu have concentration levels above the current standard for each metal in sediments.

3-1-4. Geo-accumulation index for metal pollutants

Table V shows the geo-accumulation (I_{geo}) index values for the heavy metals studied in the various fish ponds. This index is used to assess the pollution intensity of the fish pond sediments by heavy metals..

Table ۵: Geo-accumulation index (I_{geo}) values for heavy metals in fish ponds

	I_{geo} values			
Fish ponds	**Hg**	**Pb**	**Cd**	**Cu**
Pond 1	3.48	-2.39	1.32	7.07
Pond 2	4.02	-2.26	0.79	7.03
Pond 3	3.63	-1.90	0.81	7.01
Pond 4	3.94	-2.79	0.90	7.02

The analysis of Table V shows positive I_{geo} values calculated for the heavy metals (Hg, Cd and Cu) measured in the sediments of the different fish ponds. This table also shows negative I_{geo} values calculated only for the metal Pb. This gives the ranges of Igeo values for each metal studied :

$I_{geo(\mathbf{Cu})}>7$; $3< I_{geo\ (\mathbf{Hg})}<4$; $0< I_{geo(\mathbf{Cd})}<2$; $I_{geo(\mathbf{Pb})}<0$

The intervals of I_{geo} values allow to find the different classes of intensity of metal pollution of the sediments for each fishpond which are listed in the following Table ٦.

Table ۶: Intensity classes of metal pollution of sediments in fish ponds

	Metal pollution intensity classes			
Fish ponds	**Hg**	**Pb**	**Cd**	**Cu**
Pond 1	Classe 4	Classe 0	Classe 2	Classe 6
Pond 2	Classe 5	Classe 0	Classe 1	Classe 6
Pond 3	Classe 4	Classe 0	Classe 1	Classe 6
Pond 4	Classe 4	Classe 0	Classe 1	Classe 6

3.2. Discussion

The assessment of water pollution in the different fish ponds was based on the measurement of physico-chemical and chemical parameters that can be indicators of a more or less good water quality. All of these elements make it possible to evaluate the degree of pollution of the watercourses and to assess their capacity for self-purification. For example, the pH values indicate that the water in fishponds is only slightly acidic and tends to be neutral (pH almost 6.7). However, the reproduction of most species in an aquatic environment is possible for pH values between 6 and 7.2 (weakly acidic to neutral). Above pH = 9, many species are killed according to the quality standards recommended for freshwater to protect aquatic life [11]. In particular, acidic water increases the risk of metals being present in a more toxic ionic form. A high (basic) pH increases the concentrations of ammonia, which is toxic to fish [12]. Furthermore, the low acidity of the water in the various ponds can be explained by the chemical quality of the substrate of these ponds. According to Faurie et al. [12], the pH of continental waters is linked to the soil structure. According to this author, the pH of continental waters is lower than 7 with a non-calcareous soil whose cation exchange capacity is mainly composed of H^+ ions. The results obtained for temperature show a minimum of 26.7 °C and a maximum of 28.8 °C. The temperature of the water plays an important role, for example, in the solubility of salts and gases, including, among others, the oxygen necessary for the balance of aquatic life. It increases the speed of chemical and biochemical reactions by a factor of 2 to 3 for a temperature increase of 10 degrees Celsius (°C). According to Lwamba and *col* [13], the variation in surface water temperature is closely related to solar radiation. However, these temperatures slightly above 25°C, according to the ANRH of the Algerian Republic [14], do not present any danger for aquatic beings. Moreover, these high values could be explained by the degree of insolation and the shallow depth of the fish ponds [2]. This observation was made by Akatumbila et al [15] in the study of the urban river Gombe in Kinshasa and by Rahmouni [16]. The conductivity study showed us that the average conductivities of the waters of fishponds 1, 3 and 4 are all lower than 50 µS/cm except for fishpond 4 (78.7 µS/cm). These results show a very low mineralization of these waters. In fact, the electrical conductivity of the natural waters is between 50 and 1500 $\mu S.cm^{-1}$. The minimum values recorded for the electrical conductivity of the waters could be attributed to the precipitation that caused a dilution phenomenon, thus reducing the content of dissolved salts, and therefore the conductivity ([11], [17]). On the other hand, the high conductivity and TDS values observed in fishpond 2 are believed to be the result of a massive influx of terrigenous material transported by runoff [2]. The dissolved oxygen saturation values recorded in the ponds are all above the recommended limit value for natural waters (50%), which shows that the waters of the various fish farms are suitable for the life and production of aquatic organisms such as fish. Indeed, the closer the dissolved oxygen concentration is to saturation, the greater the capacity of the aquatic environment to absorb pollution. However, the values of all the physico-chemical parameters make it possible to predict the accumulation of certain metals preferentially in the environment of these fish ponds. The different levels of heavy metal concentrations detected in the sediments and water of these fish ponds show the state of metallic contamination of these ponds, and therefore their vulnerability to non-biodegradable pollutants. Concentration levels of heavy metals in the water that are higher than the norm would indicate that these waters are receiving pollutants from the surrounding activities in the catchment. Indeed, all the fish ponds are located near anti-pollutant activities such as: vegetable, maize, banana, cassava, and yam plantations which are likely sources of heavy metal contamination. These crops are vectors of pollutants in the use of fertilisers and phytosanitary products [2]. In sediments, the preferential state of metallic contamination in Hg and Cu is due, on the one hand, to the nature of the soil and the pH of the water. In neutral or basic water, metals precipitate and accumulate mainly in the solid phase (sediment) [17]. On the other hand, the regular use of herbicides and pesticides in the market gardens around the fish ponds [2]. Furthermore, the study indicates that there is no significant difference for Hg and Cd, but for Pb and Cu there is a significant difference of 5%. The contamination of the sediments and pond water by the various heavy metals studied would be linked to the still persistent effect of the input of raw wastewater of domestic and agricultural origin from the village of Gbokora, from the surrounding dwellings and from the use of phytosanitary products in the surrounding market gardening, which are sources of organic and inorganic pollutants, particularly Cu and Hg ([2], [4], [18]) The Igeo index values show a high intensity of Hg and Cu pollution in the sediments of fishponds. For Hg, we find respectively class 4 (ponds 1, 3, 4) and 5 (pond 2) and class 6 for Cu (all ponds).

This shows a high contamination of Hg and an extreme contamination of Cu in the sediments. These results show that these two metals would present risks of bioaccumulation by living organisms in the environment with these toxics. Furthermore, the metal pollution intensity class for Pb (class 0) means that there is no Pb pollution in the sediments. There is therefore no risk of metallic bioaccumulation of this toxic substance by organisms in the environment (fish). Classes 1 (ponds 2, 3 and 4) and 2 (pond 1) determined for Cd allow us to deduce a low metallic contamination of this metal, or even a moderate contamination. These classes of low intensity of metallic pollution would be justified by the fact that the fish ponds are located far from the road traffic and industrial activities of the city of Daloa.

4. Conclusion

- The waters of the fish ponds are all weakly acidic and not very mineralized. However, they are suitable for living and producing fish.

- Cu is the most accumulated metal in water and sediment. While the CD is the weakest accumulated. Thus, the order of preferential accumulation of heavy metals in the study fish ponds is as follows :

  - In water : [Cu]>[Hg]>[Pb]>[Cd].
  - In the sediments : [Cu]>[Pb]>[Hg]>[Cd].

- The values Igeo of the Igeo index clearly show a high intensity of Hg and Cu pollution in the sediments of the tanks.

- This high level of Hg and Cu pollution of sediments and fish pond water is linked to the still persistent effect of inputs from raw wastewater of domestic and agricultural origin and surrounding anthropogenic activities.

- The intensity of pollution of Cu, Hg, and Cd raise fears of risks of bioaccumulation and therefore health risks. However, there is no immediate risk of Pb bioaccumulation by organisms in this aquatic environment (fish).

5. Conflict of Interests :

......The authors declare that there is no conflict of interest or plagiarism.

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