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Lou Brou Cécile Kouamé, Natchia Aka, Emile B. Bolou-Bi, Bi Tié Albert Goula, Alexandre Livet, et al.. Determination of Source and Control Factors of Trace Metals (Cd, Zn, Cu, Cr, Ni and Pb) Bioaccumulation in Tilapia Fish of the Ebrié Lagoon (Côte d'Ivoire). International Journal of Sciences, 2020, 10.18483/ijSci.2276 . hal-02524536

HAL Id: hal-02524536

<https://hal.u-pec.fr/hal-02524536>

Submitted on 30 Mar 2020

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Determination of Source and Control Factors of Trace Metals (Cd, Zn, Cu, Cr, Ni and Pb) Bioaccumulation in Tilapia Fish of the Ebrié Lagoon (Côte d'Ivoire)

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Abstract: Lagoon water as sources of trace metals contamination in Tilapia fish as well as the physico-chemical parameters controlling the bioaccumulation of trace metals were determined in the Ebrié lagoon. For this, trace metals contents (Cd, Zn, Cu, Cr, Ni and Pb) were measured in the water, sediments and flesh of the tilapia fish of the Ebrié lagoon. In addition, physico-chemical parameters (pH, salinity, dissolved oxygen and redox potential) were determined in the lagoon waters during two hydrological seasons: the dry season and the rainy season. The results obtained showed that the sediments of the Ebrié lagoon constituted a real trap for the studied trace metals (very high Rd). The bioaccumulation factors (BAFs) of all trace metals in lagoon water column were higher than those of the sediments, reflecting an intense bioaccumulation, from the water column ($BAF_{water} > 1 > BAF_{sed}$). However for Cd, the BAF_{water} and BAF_{sed} values were less than 1. Zn was the most bioaccumulated metal in fish, while the lowest bioaccumulated Cd. The decrease in dissolved oxygen favored the increase of Cr contents in tilapias and the retention of Zn in sediments. The increase of the pH as well as the decrease of the redox potential had led to the decrease of the Ni contents in the Tilapias. Nevertheless, the fish flesh Tilapias of the lagoon Ebrié, was not toxic to consumers.

Keywords: Metals, Tilapia sp., Bioaccumulation, Ebrié Lagoon, Abidjan

Introduction

Trace metals are naturally present in the environment in low concentration but human activities increase their concentration in various environment compartments (Sharma et al 2003; Thi et al 2018). In aquatic environments, trace metals are predominantly in particulate forms and tend to accumulate in sediments (Tessier, 2015). From these sediments, trace metals can be released into the water and then contaminate living organisms in this aquatic system through various processes (Borgmann et al 1993). Indeed, as the metals are non-biodegradable, they can bioaccumulate in living organisms, and then biomagnify along the trophic chain to become a health problem for humans (Agah et al., 2009). In aquatic organisms, the biological accumulation of metals can be from water, food or sediment (Dedeh et al 2015). After absorption by living organisms,

metals are able to generate neurological, renal, hepatic, genetic, reproductive system and many other diseases (Amiard et al 1987; Miquel, 2000; Sanders et al 2008; Cambier, 2009; Bohic et al., 2011; Liu et al 2011). These processes are even more accentuated with the mobility of metals. Their mobility increases by the passage from the colloidal and particulate form to the dissolved form, and the physicochemical parameters that influence most of this type of exchange in water. (Billon et al 2010).

Fish accounts for 20 % of animal protein intake worldwide. It is rich in essential nutrients, making it one of the most traded food items in the world (FAO, 2012). Fish are often at the top of the aquatic food chain and can concentrate large amounts of metals in their habitat (Mansour and Sidky, 2002). In addition, fish is one of the most sensitive indicators of trace

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Published at: <http://www.ijsciences.com/pub/issue/2020-03/>

DOI: 10.18483/ijSci.2276; Online ISSN: 2305-3925; Print ISSN: 2410-4477



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metals pollution and the potential risk of human consumption (Authman et al 2015; Ezemonye et al 2019). Several recent studies have revealed that fish living in polluted waters accumulate various concentrations of trace metals (Authman et al 2015; Thi et al., 2018).

The trace metal in aquatic environment derived from human activity. In the case of Ebrié lagoon, the successive and massive rejection of urban and industrial waste in the lagoon resulted in a gradual accumulation of trace metals in the lagoon compartments. Thus, various studies have revealed a dramatic deterioration of the water quality of the Ebrié lagoon and a significant contamination of the sediments by the trace metals (e.i. Scheren et al 2004; Soro et al., 2009), with contents up to 110 mg.kg^{-1} in the sediments (Wognin et al., 2017) and $288 \text{ }\mu\text{g.l}^{-1}$ in the water column. Currently, metal concentrations in sediments have reached a high enough level to consider the Ebrié lagoon as contaminated with trace metals and potentially toxic to lagoon organisms (Ahoussi et al., 2012; Kouamé et al., 2016). Despite the numerous studies carried out on the trace metals in the Ebrié lagoon, very little research has been focused on the mode of ingestion and factors controlling the contamination of living organisms (fish) by the trace metals in the Ebrié lagoon. Indeed, tilapias are pelagic fish that feed on phytoplankton, zooplankton, insects and insect larvae, contained in the water column by filtration (Bwanika et al 2004; Semyalo et al., 2011). However, according to Youssao et al., (2011), the diet and the diffusion processes of trace metals by the cutaneous barrier are possible mechanisms at the origin of the bioconcentration of metals in these fish.

The Ebrié lagoon represents an enormous economic potential for the district of Abidjan because it is used as sources of fish products to supply urban markets (nearly 20% of domestic fish production for the domestic market) (FAO, 1997). Any contamination of fish products by trace metals would therefore be a district-wide environmental and health issue. In this context, this study has been conducted to highlight a potential contamination of fish products through the characterization of distribution ratios (Rd) and bioaccumulation factors (BAFs) of the sediments, column of water and fishes. The main objective of this article is to find the origin of trace metals ingested by fishes living in lagoon water, i.e. the preferential compartment, from which the fish will accumulate the metals and to determine the physicochemical conditions (pH, redox potential, Salinity and dissolved oxygen) favoring contamination of fish.

1. MATERIAL AND METHODS

Studied site

The study was carried out in the Ebrié Lagoon, located in the south of Côte d'Ivoire (Figure 1). This

lagoon is parallel with the equator, and it coordinates are $5^{\circ}20'$ and $5^{\circ}10'$ N and $3^{\circ}40'$ and $4^{\circ}50'$ W. The study area covers an area of 560 km^2 and is 140 km long. Its width does not exceed 7 km, and its mean water volume is estimated at approximately $2.7 \times 10^9 \text{ m}^3$, with an average depth of 4.8 m (Varlet, 1978). The Ebrié Lagoon is fed with freshwater by the Agnéby, Mé and Comoé rivers. The lagoon has been in permanent contact with the Atlantic Ocean since 1950 by the artificial channel of Vridi. As part of this study, eight (8) sites were selected for sample collection, including seven (7) in the District of Abidjan and one (1) in Cosrou Bay. Cosrou Bay is located about 90 km west of the Abidjan area and is considered a control site. These sampling sites were chosen on the basis of the morphological and hydrobiological criteria proposed by Durand and Guiral (1994), which stipulate that the Abidjan zone is under the influence of the sea and that of Cosrou is stable, with little influence from marine waters and freshwater inputs. This choice is also motivated by the fact that these two zones are very different from the point of view of urbanization: Abidjan is very urbanized and Cosrou is purely rural.

Sampling and preparation of samples

Samples of sediments, water and fishes (*Tilapia guineensis*) were collected during two sampling campaigns in the dry season (February 2017) and then in the wet season (July 2017). The sediments were collected using a Van Veen grab sampler and was stored in Falcon® tubes at -18°C until analysis. In the laboratory, the sediment samples were dried and finely ground for analysis.

Water samples were taken from the water column at each site using a 2-liter Niskin® bottle. Then, the samples were transferred to Nalgene® polyethylene bottles, previously rinsed with a 5 % acid solution and distilled water in the laboratory and rinsed again with an aliquot of the sample from the site before sampling. In the laboratory, the water was vacuum filtered using the Whatman® filtration system and using a nylon filter ($0.45 \text{ }\mu\text{m}$ diameter). The filtered samples were stored in Falcon® tubes in the freezer until analysis.

The fish samples were obtained at each site by collecting fish from traditional fishermen living around the lagoon. Fish were transported in refrigerated recipients (4°C). In the laboratory, the flesh of fishes was delicately separated from the skeleton. These fish flesh samples were then freeze-dried using a lyophilizer Alpha 1-2®, and then the samples were finely ground and stored before analysis.

Chemical analyses of samples

In situ parameter measurements in water column

During both field seasons, the pH, redox potential and dissolved oxygen were measured *in situ* using the multiparameter BANTE 900P[®]. The salinity of the samples was determined using a multiparamètre HANNA HI 9828[®]. The determination of these parameters was based on an aliquot of the samples taken at each site and at each depth of the water column.

Trace metals contents in all samples

The metal contents (Pb, Cd, Cu, Cr, Ni and Zn) were determined in the different samples collected (sediments, water and fish):

Solid samples were mineralized by humid digestion before the determination of the metal contents. About 200 mg of previously dried and ground material is introduced into a 50 ml teflon digestion tube. Then, 1 ml of hydrogen peroxide (H₂O₂) suprapur[®] and 3 ml of nitric acid (HNO₃) suprapur[®] were added to these samples. This mixture is left at room temperature for 24 hours. After closing the digestion tube, the mixture is placed in a DigiPep[®] oven whose temperature is increased gradually until a plateau of 120 °C and maintained for 4 hours. After cooling, the mineralized solution obtained is evaporated to dryness and the residue is then taken up in 1 ml of nitric acid (HNO₃) suprapur[®] and heated again at 75

°C for 24 hours. After cooling, the solution is filtered into 50 ml volumetric flasks. The volume of the solutions is adjusted to the gauge line and then homogenized by manual stirring. The metals concentration in sample are determined using an SPECTROBLUE[®] induced plasma optical emission spectrometer (ICP-OES), in addition to lagoon water filtered and acidified with suprapur[®] nitric acid.

Parameter calculation

The trace metal distribution ratios (Rd) are defined as the ratio of the contents of metal in two various compartments. This ratio reflects the ability of moving of trace metal from one compartment to another in the same environment. The trace metal distribution ratios (Rd) between two different compartments of the lagoon were determined based on the obtained contents after the analyses is calculated as following relation:

$$Rd = \frac{\text{Metal content in sediment}}{\text{Metal content in water}}$$

Bioaccumulation factor (BAF) describes the ability of an element to be transferred from one lagoon compartment to fish. In other words, the BAF is the ratio of the contents of the element between the compartment considered and the living organisms (Fishes). The bioaccumulation factors of metal (BAF) in fishes were calculated for each compartments following this relation:

$$BAF = \frac{\text{Metal content in Fish}}{\text{Metal content in a given compartment (sediment or water)}}$$

Data treatment

The results were statistically processed using XLSTAT software version 2018. For Physical and chemical characteristics, each analysis was performed in triplicate. Significant differences between each sample were determined by analyzing the variance (one-factor ANOVA) and by the Tukey HSD test (significance threshold of $P < 0.05$, with $n=3$). The Pearson correlation coefficient was calculated between the physical and chemical characteristics of the medium and the metal content of the different compartments of the studied lagoon for each sampling point.

RESULTS

Physico-chemical parameters of water in Ebrié Lagoon

The pH values ranged from 6.75 ± 0.30 to 7.89 ± 0.09 , with an average of 7.62 ± 0.25 in the dry season and 7.44 ± 0.34 in the rainy season. The lowest pH was measured in the waters of Cosrou site during the rainy season, and the highest pH at Yopougon site during the dry season. There was no significant difference between the samplings sites according to

ANOVA and the Tukey test ($p = 0.05$) (Figure 2A).

The redox potential (Eh) values of the lagoon waters ranged between -46.67 ± 6.45 mV and 19.63 ± 15.72 mV, with an average of -35.12 ± 9.49 mV and -23.07 ± 19.99 mV in the dry season and the rainy season, respectively. The lowest Eh value was measured in the waters of Yopougon site during the dry season and that of the highest Eh was measured at Cosrou site during the rainy season. The difference was not significant between sampling site, except for the Cosrou site (control site) at rainy season, according to ANOVA and the Tukey test ($p = 0.05$) (Figure 2B).

The salinity values ranged from 0.05 ± 0.00 ppm to 35.23 ± 2.15 ppm, with an average of 27.16 ± 11.12 ppm and 10.86 ± 7.31 ppm in the dry season and the rainy season, respectively. The lowest salinity was measured in the waters of the Cosrou site during the rainy season, while the highest salinity was observed at the Port site during the dry season. The difference was not significant between sampling sites, with the

exception of the Cosrou site (control site) in all seasons, according to the ANOVA and the Tukey test ($p = 0.05$). (Figure 2C).

The dissolved oxygen levels (DO) ranged from $3.95 \pm 0.18 \text{ mg.l}^{-1}$ to $8.78 \pm 2.66 \text{ mg.l}^{-1}$, with an average of $6.86 \pm 1.18 \text{ mg.l}^{-1}$ and $5.07 \pm 0.67 \text{ mg.l}^{-1}$ in the dry season and the rainy season. The lowest DO value was measured in the waters of the Biétri site during the rainy season, and the highest DO at the site of Koumassi in the dry season, but the difference was not significant according to ANOVA and the Tukey test ($p = 0.05$) (Figure 2D).

Trace metals contents in the different compartments (sediment, water, fish) of the Ebrié Lagoon

In Sediment samples

The Cd content was only detected during the rainy season, in the sediments of three sites with $259 \pm 67 \text{ } \mu\text{g.kg}^{-1}$ at Marcory, $1178 \pm 76 \text{ } \mu\text{g.kg}^{-1}$ at Koumassi and $592 \pm 108 \text{ } \mu\text{g.kg}^{-1}$ at Cocody. According to ANOVA and the Tukey's test ($p = 0.05$) (Figure 3A), trace metal contents were different from each other in these three sites. Zinc contents in sediments ranged from $8988 \pm 42 \text{ } \mu\text{g.kg}^{-1}$ to $320582 \pm 3017 \text{ } \mu\text{g.kg}^{-1}$, with a maximum at Cocody and a minimum at Port and Cosrou. The Zn contents obtained were significantly different whatever the sampling site, according to ANOVA and the Tukey test ($p = 0.05$) (Figure 3B). The Cu contents of the sediments ranged from $0 \text{ } \mu\text{g.kg}^{-1}$ to $53126 \pm 1096 \text{ } \mu\text{g.kg}^{-1}$, with a maximum at Cocody and Biétri and a minimum at Port. However, the Cu contents were generally different between sites, according to ANOVA and Tukey's test ($p = 0.05$) (Figure 3C). The Cr contents of the sediments ranged from $10152 \pm 101 \text{ } \mu\text{g.kg}^{-1}$ to $98493 \pm 430 \text{ } \mu\text{g.kg}^{-1}$, with a maximum in Cocody and a minimum at Port. The Cr contents obtained were generally different whatever the sampling sites, according to ANOVA and Tukey's test ($p = 0.05$) (Figure 3D). The Ni contents in the sediment ranged from $2089 \pm 376 \text{ } \mu\text{g.kg}^{-1}$ to $40566 \pm 267 \text{ } \mu\text{g.kg}^{-1}$, with a maximum in Biétri and a minimum in Cosrou. The Ni contents obtained were generally different whatever the sampling sites, according to the ANOVA and Tukey's test ($p = 0.05$) (Figure 3E). The Pb content was detected only in the sediments collected at Cocody, with a value of $20446 \pm 1820 \text{ } \mu\text{g.kg}^{-1}$ (Figure 3F).

In water samples

The Cd contents in the water column ranged from $1.38 \pm 0.22 \text{ } \mu\text{g.l}^{-1}$ to $1.87 \pm 0.14 \text{ } \mu\text{g.l}^{-1}$, with a maximum at Marcory and a minimum at Cosrou. However, the difference between sites are not significant according to ANOVA and Tukey's test ($p=0.05$) (Figure 4A). The Zn contents in the water column ranged from

$0.90 \pm 0.98 \text{ } \mu\text{g.l}^{-1}$ to $11.34 \pm 15.61 \text{ } \mu\text{g.l}^{-1}$, with a maximum at Cocody and a minimum at Biétri, but there was no difference whatever the sampling sites, according to ANOVA and Tukey's test ($p=0.05$) (Figure 4B). The Cu contents in the water column ranged from $0.71 \pm 0.36 \text{ } \mu\text{g.l}^{-1}$ to $3.95 \pm 3.01 \text{ } \mu\text{g.l}^{-1}$, with a maximum at Marcory and a minimum at Yopougon, but there was no difference between sites, according to ANOVA and Tukey's test ($p=0.05$) (Figure 4C). The Cr contents in the water column ranged from $0.29 \pm 0.07 \text{ } \mu\text{g.l}^{-1}$ to $2.39 \pm 2.29 \text{ } \mu\text{g.l}^{-1}$, with a maximum at Port and a minimum at Marcory, but there was no difference between sites, according to ANOVA and Tukey's test ($p = 0.05$) (Figure 4D). The Ni levels in the waters ranged from $0.71 \pm 0.41 \text{ } \mu\text{g.l}^{-1}$ to $7.66 \pm 4.00 \text{ } \mu\text{g.l}^{-1}$, with a maximum at Marcory and a minimum at Biétri, but it did not there was no difference between sites, according to ANOVA and Tukey's test ($p = 0.05$) (Figure 4E). The Pb contents in the water ranged from $1.49 \pm 0.72 \text{ } \mu\text{g.l}^{-1}$ to $6.21 \pm 4.19 \text{ } \mu\text{g.l}^{-1}$, with a maximum at Marcory and a minimum at Koumassi, but it was not there was no difference between sites, according to ANOVA and Tukey's test ($p = 0.05$) (Figure 4F).

In fish samples

Fish Cd contents ranged from $2 \times 10^{-1} \pm 9 \times 10^{-3} \text{ } \mu\text{g.kg}^{-1}$ to $9 \times 10^{-1} \pm 16 \times 10^{-3} \text{ } \mu\text{g.kg}^{-1}$, with a maximum at Banco and a minimum at Koumassi. Outside Biétri (dry season), Yopougon (rainy season) and Banco (dry season), Cd contents were identical between sites, according to ANOVA and Tukey's test ($p = 0.05$) (Figure 5A). The Zn levels in fish ranged from $672 \pm 2 \text{ } \mu\text{g.kg}^{-1}$ to $2594 \pm 0 \text{ } \mu\text{g.kg}^{-1}$, with a maximum at Banco and a minimum at Cosrou. The Zn levels were different at all sites, according to ANOVA and Tukey's test ($p = 0.05$) (Figure 5B). The levels of Cu in fish ranged from $30 \pm 25 \times 10^{-2} \text{ } \mu\text{g.kg}^{-1}$ to $138 \pm 1 \text{ } \mu\text{g.kg}^{-1}$, with a maximum at Marcory and a minimum at Yopougon. The difference in Cu levels was significant between sites, according to ANOVA and Tukey's test ($p = 0.05$) (Figure 5C). Levels of Cr in fish ranged from $4 \pm 36 \times 10^{-2} \text{ } \mu\text{g.kg}^{-1}$ to $9 \pm 38 \times 10^{-2} \text{ } \mu\text{g.kg}^{-1}$, with a maximum at Banco and a minimum at Biétri, however, these levels were identical between sites, except Banco, according to ANOVA and Tukey's test ($p = 0.05$) (Figure 5D). Fish Ni levels ranged from $14 \times 10^{-2} \pm 1 \times 10^{-2} \text{ } \mu\text{g.kg}^{-1}$ to $125 \pm 5 \times 10^{-1} \text{ } \mu\text{g.kg}^{-1}$, with a maximum at Cosrou and a minimum at Cocody. According to ANOVA and Tukey's test ($p = 0.05$), The Ni levels were not significantly different at all sites except Cosrou (Figure 5E). The Pb levels in fish ranged from $46 \times 10^{-2} \pm 2 \times 10^{-2} \text{ } \mu\text{g.kg}^{-1}$ to $12 \pm 72 \times 10^{-2} \text{ } \mu\text{g.kg}^{-1}$, with a maximum at Marcory and a minimum at Cocody, still in the rainy season. There was no difference between sites, except Marcory (rainy season) and Koumassi, according to ANOVA

and Tukey's test ($p=0.05$) (Figure 5F).

Transfer of trace metals between each compartment in the Ebrié Lagoon

Trace metals distribution ratios (Rd)

Calculated Rd indicate that these ratios are all greater than 1 suggesting that trace metals are strongly retained by sediments. In details, the distribution ratios (Rd) of Cd in the three sites at which Cd contents were detected in the sediments, were 172 ± 45 at Marcory, 724 ± 94 at Koumassi and 409 ± 78 at Cocody. (Figure 6A). The Rd of Zn ranged from $4 \times 10^4 \pm 2 \times 10^4$ to $2 \times 10^5 \pm 3 \times 10^5$, with a minimum at Cosrou and a maximum at Biétri (Figure 6B). The Rd of Cu ranged from 0 to $58 \times 10^3 \pm 14 \times 10^3$, with a minimum at Port and a maximum at Biétri (Figure 6C). The Rd of Cr were between $7 \times 10^3 \pm 7 \times 10^2$ and $2 \times 10^5 \pm 5 \times 10^4$, with a minimum at Cosrou and a maximum at Marcory (Figure 6D). The Rd of Ni varied from $10^3 \pm 3 \times 10^2$ to $46 \times 10^3 \pm 2 \times 10^4$, with a minimum at Cosrou and a maximum at Biétri (Figure 6E). As for Pb, Rd at Cocody was $10 \times 10^3 \pm 4 \times 10^3$ (Figure 6F).

Bioaccumulation factors (BAFs) in fishes

Water column bioaccumulation factors (BAF_{water}) of Cd ranged from 0.12 ± 0.01 to 0.60 ± 0.08 , with a minimum at Koumassi and a maximum at Banco (Figure 7A). The factors of bioaccumulation of Cd with respect to sediment (BAF_{sed}) were $2 \times 10^4 \pm 1 \times 10^5$ for Koumassi, $1 \times 10^3 \pm 3 \times 10^4$ for Marcory and $7 \times 10^4 \pm 1 \times 10^4$ for Cocody (Figure 7B). Cd has not bioaccumulated in the flesh of fish, either from the water column or sediment, at all sites ($BAF_{sed} < BAF_{water} < 1$), however BAF_{water} is much higher than BAF_{sed} .

The BAF_{water} of Zn ranged from 128 ± 176 to 1295 ± 740 , with a minimum in Cocody and a maximum in Koumassi, while BAF_{sed} is between $38 \times 10^4 \pm 2 \times 10^5$ and $13 \times 10^2 \pm 13 \times 10^4$, with minimum at Cocody and a maximum at Cosrou. Bioaccumulation of Zn in fish was very strongly from the water column ($BAF_{water} > 1 > BAF_{sed}$) at all sites (Figure 8A and 8B).

The BAF_{water} of Cu ranged from 12 ± 9 to 99 ± 24 , with a minimum and a maximum at Marcory in the dry season and the rainy season, respectively. While the BAF_{sed} of the Cu oscillated between 0 and $15 \times 10^3 \pm 4 \times 10^3$ with a minimum at Port and a maximum at Cosrou. The bioaccumulation of Cu in fish was very strongly from the water column ($BAF_{water} > 1 > BAF_{sed}$) at all sites (Figure 9A and 9B).

The BAF_{water} of Cr ranged from 2.34 ± 2.25 to 21.27 ± 5.17 , with a minimum at Port and a maximum at Marcory, while BAF_{sed} of Cr ranged from $5 \times 10^$

$5 \pm 4 \times 10^{-6}$ to $6.7 \times 10^{-4} \pm 1 \times 10^{-5}$, with a minimum at Biétri and a maximum at Cosrou. The bioaccumulation of Cr in fish was very strongly from the water column ($BAF_{water} > 1 > BAF_{sed}$) at all sites (Figure 10A and 10B).

The BAF_{water} of Ni ranged from 0.09 ± 0.03 to 58.89 ± 12.22 , with a minimum at Cocody and a maximum at Cosrou, while BAF_{sed} of Ni ranged from $1 \times 10^{-5} \pm 6 \times 10^{-7}$ to $6 \times 10^{-2} \pm 1 \times 10^{-2}$, with a minimum at Cocody and a maximum at Cosrou. Bioaccumulation of Ni in fish was very strongly from the water column ($BAF_{water} > 1 > BAF_{sed}$) at all sites (Figure 11A and 11B).

The BAF_{water} of Pb ranged from 0.18 ± 0.12 to 3.68 ± 1.77 , with a minimum at Marcory and a maximum at Koumassi, and the BAF_{sed} of the only site of Cocody was equal to $23 \times 10^{-6} \pm 2 \times 10^{-6}$. However, bioaccumulation of Pb in fish was from the water column ($BAF_{water} > BAF_{sed}$) (Figure 12A and 12B).

Discussion

Content of trace metals in various compartments of Ebrié Lagoon

The results of analyzes of sediments show that for metals, the sediments of the Ebrié lagoon are not toxic to benthic organisms, compared to the values of Threshold to Effect Concentration (TEC) and Probable Effect Concentration (PEC), except, Zn and Cr, who are above the effect concentration threshold (CBSQG, 2003). (Table 1). Our results are consistent with those of Kouame et al (2016). Our values are higher than of Coulibaly et al. (2012) ones for Cd and Zn, while for Cu and Pb, our results are higher. The metal contents obtained from the sediments of the Ebrié lagoon in our study are higher than those of the sediments of the Swan lagoon in China (Hu et al 2019). The sediments of the Ebrié lagoon are less polluted in Cd, Cu and Ni compared to Chilika lagoon in India (Nazneen et al 2018). On the other hand, the sediments of the Ebrié lagoon are more polluted in Zn than the sediments of the Chilika lagoon (Nazneen et al 2018) (Table 1).

The trace metal concentrations determined on the Ebrié lagoon water samples remained low for all sites. The comparison of the results of the trace metals contents in water with the quality criteria of brackish water has revealed that waters of the Ebrié lagoon are not toxic for living organisms according to the metals contents obtained. All levels remained below the guideline values defined for chronic and acute toxicity in brackish and salt water (MDDEP 2009). Our values are much lower than those obtained by Coulibaly et al. (2012) from Biétri bay

(Ebrié Lagoon). and those of the waters of the Lomé lagoon obtained by Ayah et al 2015 (Table 2). The levels obtained in the waters of the Ebrié lagoon remained much lower than that of the sediments. This is justified by the very high R_d values for all metals in the Ebrié lagoon. Indeed, sediments constitute an almost ultimate trap of particles which pass through the water column (Chapman et al., 1998).

Currently, the lack of standards in Côte d'Ivoire does not limit the consumption of fish. However, these contents compared to the reference values established by the International Communities (Table 3), show that the fish of the Ebrié lagoon, are not toxic for human consumption, except Zn. The Zn in fish was very much higher than the reference values, about 5 times (Table 3). According to Kouassi et al. 2018, Zn could present a high risk for the biota of the Ebrié lagoon. According to their results on the mobility of metals in the Ebrié lagoon, Zn is the metal that forms labile complexes.

Effect of physico-chemical conditions on Tilapia fish contamination.

The bioaccumulation of metals in an aquatic environment is a function of the characteristics of this environment (Maruszczak, 2010), the metal chemistry (Pichard et al., 2005), and also the mode of feeding of the living organism (Bottin et al 2014). The chemistry of metals in the Ebrié lagoon, shows that these metals preferentially accumulate in sediments. This is justified by the R_d greater than one (1) obtained. Our results are in the same direction as those of Coulibaly et al (2012), whose distribution ratios of the contents obtained between the sediments and the water, were beyond 1 (Table 4). However, our R_d were much higher than those of Coulibaly et al (2012). Our R_d compared to those of another Lagoon of the Gulf of Guinea, shows that the sediments of the Ebrié lagoon retain more Zn, Ni and Pb than those of the Kpeshie lagoon in Ghana (Addo et al 2011) (Table 4). In general, the BAFs values of metals imply bioaccumulation from the column ($BAF_{water} > BAF_{sed}$). Our results are in accordance with the studies of Coulibaly et al (2012). The bioaccumulation factors of metals in fish from the Ebrié lagoon compared to those of a hydrosystem with different characteristics such as Wadi Hanifah (Saudi Arabia) (Abdel-Baki, et al, 2013) shows that the bioaccumulation of metals from the column is more intense in the Ebrié lagoon than in Wadi Hanifah. However, the bioaccumulation of metals from sediments is higher in Wadi Hanifah than in the Ebrié lagoon (Table 4).

In the Ebrié lagoon, the preferred site for Cd accumulation is sediment according to the high

values of R_d obtained. This means that the portion of Cd that is soluble in water is very low, according to the observation of Yao and Kouassi (2015). This also explains the non-significant variation in Cd contents obtained in the water column, despite the fact that Cd was not detected in the sediments of several sites. BAF_{water} and BAF_{sed} from Cd do not imply bioaccumulation by water and sediment compartments. However, Cd can bioaccumulate via the trophic chain (Bottin et al 2014), because of the diet of tilapias. Nevertheless, our results based on the calculation of Pearson correlation coefficient between total metals contents in all compartments and chemical parameters (Table 5) showed no correlation between these parameters (Table 5), other parameters could favored the contamination of Tilapias by Cd. It should be noted that in a reducing and alkaline conditions, Cd precipitates under the form of Cd sulfate (CdS) or Cd hydroxide (CdOH) (INERIS, 2006). Indeed, the redox potential in the Ebrié lagoon is a reducing potential and its pH tends towards alkalinity.

Zinc appears to be the most bioaccumulative element in fish. He had the highest BAFs among the metals studied. Our results are coherent with those of Falusi and Olanipekun (2007). In addition, Zn is considered a high-risk element for biota in the Ebrié lagoon (Kouassi et al. 2018). Indeed, Zn is able to form labile complexes in the water column that are easily bioaccumulable in living organisms. Indeed, BAF_{water} was much higher than BAF_{sed} , which means the water column as the source of bioaccumulation of Zn in fish. Moreover, Tilapias fish are filter feeders and their main habitat is the water column (Semyalo et al 2011). The indirect contribution of sediments to the bioaccumulation of Zn should not be neglected because of the diet of tilapia, consisting of phytoplankton and zooplankton (Semyalo et al 2011), which can draw their Zn content from sediment (Lewis and Syvitski, 1983). However, the passage of Zn from sediments to the water column or its maintenance in solution is conditioned by the low pH (acid pH) and the oxidizing condition (INERIS, 2005). Even though the pH of the lagoon waters is not acid (on average 7.5), the dissolved oxygen seems negatively control the Zn content in the sediments of the Ebrié lagoon ($r = -0.498$) (Table 5). Although the accumulation of zinc in the body is regulated for many species (eg molluscs, crustaceans, fish and mammals (INERIS, 2005)), it would be important to control the influx of Zn into the Ebrié lagoon, in order to avoid possible Zn poisoning if its content increases further in the sediments and the conditions of the lagoon become oxidizing.

Like other metals, Cu was found preferentially in

sediment than in water column in the Ebrié lagoon according to R_d much higher than 1. These observations are with the study of ATSDR (1990) which states that in water, Cu is mostly in particulate form. Indeed, once entering the water, Cu tends to settle, precipitate or adsorb on solid particles. The absorption of Cu by an organism depends on its chemical form and its oxidation state, since the complexed copper is less toxic than the copper in the ionic state (INERIS, 2005). Generally, these processes represent a transfer of Cu to less bioavailable and less toxic forms (ECI, 2018). These processes are reversible and depend to certain parameters such as pH. When pH is above 6, there is an increase in binding sites for Cu due to the increase in negative charges on solid particles (Youcef and Achour, 2006). That is not the case for our study because, the pH are higher than 6 whatever the sampling sites. There was no correlation between the different Cu contents and the parameters studied (Table 5). Despite the low levels of Cu in the water column of the Ebrié lagoon, the bioaccumulation of Cu in the tilapias come preferentially from water column

Chromium generally exists in two stable forms: Cr(III) and Cr(VI). The first is generally in particulate form (INERIS, 2014), while the second is very mobile (Desjardin, 2002), but it is rapidly reduced in Cr(III) under anaerobic conditions by microbiological processes (Desjardin, 2002; Gorny et al., 2016) or physico-chemical (Gorny et al., 2016). According to the diagram of Pourbaix of Cr in water (Kotas and Stasicka, 2000), the trivalent form would be the preferential form present in the Ebrié lagoon, according to the redox potential and pH. It is coherent with the high value of R_d obtained with our results. Despite the low content of Cr in the water column, dissolved Cr has actively bioaccumulated in fish. This is probably due to the way tilapia feeds, by the phenomenon of biomagnification along the food chain (Oeil, 2006), tilapias being inhabitants filterers in the water column and consumers of phytoplankton and zooplankton. However, the algae are able to bioconcentrate up to 3.10^4 times the Cr in an environment polluted by Cr according to Pichard et al 2005. While the fish itself is able to bioaccumulate Cr(III) While the fish itself is able to bioaccumulate more Cr (III) than Cr(VI) (Pichard et al 2005). According to Table 5, bioaccumulation of Cr in tilapia would be negatively controlled by dissolved oxygen ($r=-0.612$). This means that when the Ebrié lagoon is well oxygenated, the bioaccumulation of Cr in the fish will decrease. However, according to Pichard et al 2005), it is under anaerobic conditions that Cr(VI) is largely transformed into Cr(III).

According to the R_d obtained for Ni in our results, the particle form of Ni is very high compared to its dissolved form. In addition, according to the pH/Eh diagram of Ni in the Ebrié lagoon, Ni^{2+} is the Ni species present in the water. Thus, it can be adsorbed or associated with solid particles and this is conditioned by the pH values of the medium (INERIS, 2006). In the range of pH 5 to 9, Ni is adsorbed on solid particles (oxides of iron, manganese, organic or inorganic ligands). pH in the Ebrié lagoon are in this range and it's coherent to the very high distribution ratios obtained. Our results are consistent with the study of Lapointe and Couture, 2010. According to these authors, water was the main source of bioaccumulation of Ni in fish feeding. In addition, the dissolved form of Ni is more easily absorbed by living organisms than its less soluble forms. Our results based on the calculation of Pearson correlation coefficient between total metals contents in all compartments and chemical parameters (Table 5) showed that the bioaccumulation of Ni in the Tilapias is negatively controlled by the pH ($r = -0.711$) and positively by Eh ($r = 0.795$). The increase in pH leads to a decrease in the toxicity of Ni (Pyle et al 2002; Kozlova et al 2009), but for this, the pH should be between 7 and 8.4 (Pyle et al 2002). This can be explained the obtained value for Ni BAFs in Cosrou with the highest value in comparison of the sites in Abidjan (Figure 11A and 11B) with a pH below 7 for Cosrou (Figure 2A).

Lead (Pb) is known for firmly bound to sediment particles. The Pb tends to be removed from the water column by migrating to sediments by adsorption, precipitation and reaction processes with water ions and oxides (INERIS, 2016). However, the amount of Pb remaining in solution will depend on the pH. At pH levels ≥ 6.6 , the various Pb compounds can be precipitated (Cossa et al 1993). This explains the very high R_d value obtained at the Cocody site. Cocody is the only site where Pb was detected in sediments (Figure 3F) with a pH above 6.6 (Figure 2A). However, no relationship between Pb levels and the parameters studied was found (Tableau 1). BAFs of Pb obtained, involves bioaccumulation, coming from the water column. Our results are coherent with the studies of (Cossa et al 1993), which show that the transport of Pb in dissolved form is the mechanism that promotes the penetration of Pb into living organisms.

Conclusion

The results show that the sediments of the Ebrié lagoon constituted a real trap for the studied TMs (very high R_d). In general, the bioaccumulation factors of the water column were higher than those of the sediments, for all metals, reflecting an intense bioaccumulation, from the water column. Zn was the

most bioaccumulated metal in fish, while the lowest bioaccumulated Cd. The decrease in dissolved oxygen favored the increase of Cr contents in tilapias and the retention of Zn in sediments. The increase of the pH as well as the decrease of the Eh had led to the decrease of the Ni contents in the Tilapias. Nevertheless, the fish flesh Tilapias of the lagoon Ebrié, was not toxic to consumers.

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| Metals contents in sediment (µg.kg ⁻¹) | Ebrié lagoon (Present Study) | Ebrié lagoon (Bietry Bay) (Coulibaly et al 2012) | Chilika lagoon (India) (Nazneen et al 2018) | Swan Lagoon (China) (Hu et al 2019) | Reference contents (CBSQG, 2003) | |
|--|------------------------------|--|---|-------------------------------------|----------------------------------|--------|
| | | | | | TEC | PEC |
| Cd | 676 | 580 | 3500 - 4600 | 280 | 990 | 4980 |
| Zn | 136268 | 87580 | 52700 - 103600 | 21800 | 121000 | 459000 |
| Cu | 30663 | 42150 | 88200 - 141800 | 9900 | 31600 | 149000 |
| Cr | 62373 | - | - | 15000 | 43400 | 111000 |
| Ni | 20673 | - | 29700 - 145800 | - | 22700 | 48600 |
| Pb | 20446 | 58470 | 11300 - 116100 | 13030 | 35800 | 128000 |

Table 1. Average metals contents (µg.kg⁻¹) in Ebrié Lagoon sediments compared to some global hydrological systems

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| Metals contents in water ($\mu\text{g.L}^{-1}$) | Ebrié lagoon (Present Study) | Ebrié lagoon (Bietry Bay) (Coulibaly et al 2012) | Lomé Lagoon (Togo) (Ayah et al 2015) | Reference contents (MDDEP, 2009) | |
|---|------------------------------|--|--------------------------------------|----------------------------------|----------------|
| | | | | Chronic toxicity | Acute toxicity |
| Cd | 1.510 | 100 | 0.850 | 9.300 | 43.000 |
| Zn | 3.087 | 17040 | 56.600 | 81.400 | 89.900 |
| Cu | 1.471 | 9430 | 15.850 | 3.100 | 4.800 |
| Cr | 1.072 | - | 14.320 | 49.700 | 1092.000 |
| Ni | 2.819 | - | 0.270 | 8.280 | 74.850 |
| Pb | 2.825 | 3530 | 5.690 | 8.100 | 209.000 |

Table 2. Average metals contents ($\mu\text{g.L}^{-1}$) of Ebrié Lagoon water compared to some global hydrological systems.

| Metals contents in fish ($\mu\text{g.kg}^{-1}$) | Average content in fish flesh | | recommended limit |
|---|-------------------------------|--|---------------------|
| | Ebrié lagoon (Present Study) | Ebrié lagoon (Bietry Bay) (Coulibaly et al 2012) | |
| Cd | 0.37 | 70.00 | 50 (CE, 2006) |
| Zn | 1297.00 | 11700.00 | 200 |
| Cu | 52.38 | 5520.00 | 30 000 (FAO), 1983) |
| Cr | 6.07 | - | 50 |
| Ni | 11.22 | - | 200 (WHO, 2005) |
| Pb | 2.64 | 450.00 | 300 (CE, 2006) |

Table 3. Average metal contents ($\mu\text{g.kg}^{-1}$) of Ebrié Lagoon fish (*Tilapia* sp.) compared with those of some global hydrological systems

| Parameter | | Cd | Zn | Cu | Cr | Ni | Pb | Reference |
|----------------------------|-----------------------------|--------|--------|--------|--------|--------|---------|------------------------|
| BAF_{water} | Ebrié Lagoon | 0.25 | 614 | 41 | 7.372 | 5.675 | 1.063 | this study |
| | Ebrié lagoon (Bietry Bay) | 0.70 | 0.69 | 0.59 | - | - | 0.13 | (Coulibaly et al 2012) |
| | Wadi Hanifah (Saudi Arabia) | 0.12 | - | 0.04 | 0.028 | - | 0.024 | Abdel-Baki et al 2011 |
| BAF_{sed} | Ebrié Lagoon | 0.0006 | 0.0243 | 0.0029 | 0.0002 | 0.0043 | 0.00002 | this study |
| | Ebrié lagoon (Bietry Bay) | 0.12 | 0.13 | 0.13 | - | - | 0.01 | (Coulibaly et al 2012) |
| | Wadi Hanifah (Saudi Arabia) | 9.52 | - | 9.1 | 41.66 | - | 62.5 | Abdel-Baki et al 2011 |
| Rd | Ebrié Lagoon | 435 | 71868 | 23533 | 79443 | 11724 | 10122 | this study |
| | Ebrié lagoon (Bietry Bay) | 5.80 | 5.14 | 4.47 | - | - | 16.56 | (Coulibaly et al 2012) |
| | Kpeshie Lagoon, (Ghana) | 800 | 0.019 | - | 187610 | 6585 | 679 | Addo et al 2011 |

Table 4. Bioaccumulation factor of metals in fish (*Tilapia* sp) and distribution ratios compared with those of some global hydrological systems.

Determination of Source and Control Factors of Trace Metals (Cd, Zn, Cu, Cr, Ni and Pb) Bioaccumulation in Tilapia fish of the Ebrié lagoon (Côte d'Ivoire)

| Variables | DO | Salinity | pH | Eh | Cd _{fish} | Zn _{fish} | Cu _{fish} | Cr _{fish} | Ni _{fish} | Pb _{fish} | Cd _{water} | Zn _{water} | Cu _{water} | Cr _{water} | Ni _{water} | Pb _{water} | Cd _{sed} | Zn _{sed} | Cu _{sed} | Cr _{sed} | Ni _{sed} | Pb _{sed} |
|---------------------|---------------|---------------|---------------|--------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|
| DO | 1 | | | | | | | | | | | | | | | | | | | | | |
| Salinity | 0,361 | 1 | | | | | | | | | | | | | | | | | | | | |
| pH | 0,268 | 0,758 | 1 | | | | | | | | | | | | | | | | | | | |
| Eh | -0,342 | -0,682 | -0,951 | 1 | | | | | | | | | | | | | | | | | | |
| Cd _{fish} | -0,183 | 0,286 | 0,204 | -0,095 | 1 | | | | | | | | | | | | | | | | | |
| Zn _{fish} | -0,465 | -0,368 | -0,029 | 0,117 | -0,107 | 1 | | | | | | | | | | | | | | | | |
| Cu _{fish} | -0,185 | 0,038 | 0,247 | -0,223 | -0,271 | 0,480 | 1 | | | | | | | | | | | | | | | |
| Cr _{fish} | -0,612 | -0,181 | -0,235 | 0,430 | 0,576 | 0,376 | 0,024 | 1 | | | | | | | | | | | | | | |
| Ni _{fish} | 0,065 | -0,412 | -0,711 | 0,795 | -0,030 | 0,022 | -0,181 | 0,265 | 1 | | | | | | | | | | | | | |
| Pb _{fish} | 0,140 | -0,132 | 0,123 | -0,110 | -0,265 | 0,373 | 0,836 | 0,009 | 0,039 | 1 | | | | | | | | | | | | |
| Cd _{water} | -0,404 | -0,140 | -0,113 | 0,213 | -0,276 | 0,287 | 0,139 | 0,246 | -0,122 | -0,063 | 1 | | | | | | | | | | | |
| Zn _{water} | -0,420 | -0,353 | -0,157 | 0,145 | -0,066 | 0,243 | -0,189 | 0,200 | -0,057 | -0,233 | 0,127 | 1 | | | | | | | | | | |
| Cu _{water} | 0,038 | 0,405 | 0,161 | -0,123 | -0,048 | -0,294 | 0,042 | 0,095 | -0,204 | -0,129 | 0,548 | 0,115 | 1 | | | | | | | | | |
| Cr _{water} | -0,082 | -0,214 | 0,065 | -0,072 | -0,010 | 0,401 | 0,345 | 0,132 | 0,224 | 0,376 | -0,300 | 0,147 | -0,267 | 1 | | | | | | | | |
| Ni _{water} | -0,466 | -0,287 | -0,202 | 0,268 | -0,280 | 0,402 | 0,441 | 0,287 | -0,112 | 0,286 | 0,880 | 0,053 | 0,403 | -0,259 | 1 | | | | | | | |
| Pb _{water} | -0,299 | -0,006 | -0,064 | 0,053 | -0,242 | 0,182 | 0,249 | 0,043 | -0,263 | 0,024 | 0,790 | 0,084 | 0,591 | -0,343 | 0,828 | 1 | | | | | | |
| Cd _{sed} | -0,363 | -0,446 | -0,142 | 0,135 | -0,233 | 0,272 | 0,279 | 0,008 | -0,151 | 0,155 | 0,196 | 0,202 | -0,148 | -0,031 | 0,317 | -0,061 | 1 | | | | | |
| Zn _{sed} | -0,498 | 0,069 | 0,090 | -0,100 | 0,296 | -0,072 | -0,070 | 0,146 | -0,447 | -0,264 | -0,008 | 0,414 | 0,023 | -0,404 | 0,058 | 0,097 | 0,307 | 1 | | | | |
| Cu _{sed} | -0,401 | 0,188 | 0,141 | -0,134 | 0,461 | -0,181 | -0,115 | 0,207 | -0,466 | -0,278 | 0,030 | 0,155 | 0,082 | -0,515 | 0,079 | 0,116 | 0,190 | 0,933 | 1 | | | |
| Cr _{sed} | -0,400 | 0,095 | 0,187 | -0,196 | 0,323 | -0,129 | -0,096 | 0,125 | -0,537 | -0,235 | 0,098 | 0,201 | 0,047 | -0,480 | 0,134 | 0,151 | 0,252 | 0,914 | 0,946 | 1 | | |
| Ni _{sed} | -0,211 | 0,030 | 0,206 | -0,214 | 0,179 | -0,106 | 0,055 | -0,009 | -0,509 | 0,011 | 0,293 | -0,143 | -0,008 | -0,455 | 0,340 | 0,256 | 0,204 | 0,557 | 0,724 | 0,768 | 1 | |

Table 5. Pearson correlation coefficient (n-1) between total metals contents in all compartments (sediment, water column, fish), chemical parameters (pH, Eh, salinity and dissolved oxygen contents) based on 24 observations for all sampling sites. Values in bold are different from 0 to a level of significance of alpha = 0.05.

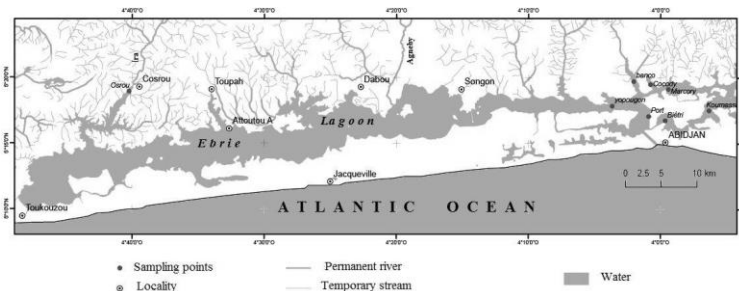


Figure 1. Localization map of the different sampling sites of the Ebrié Lagoon.

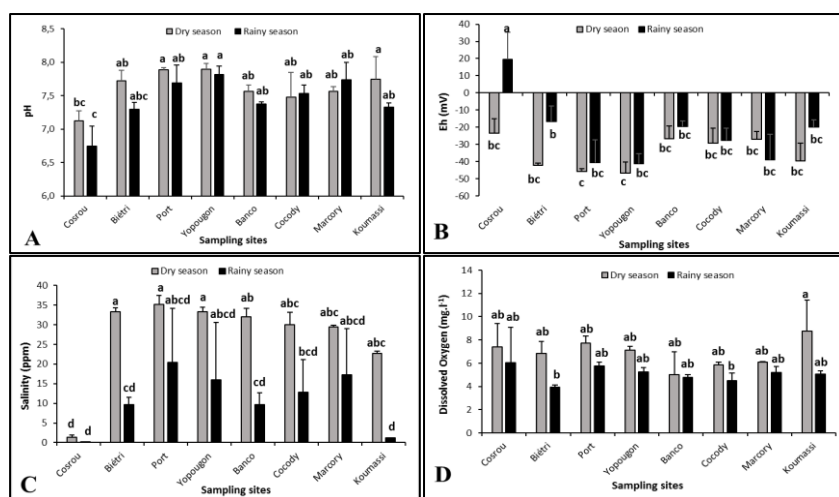
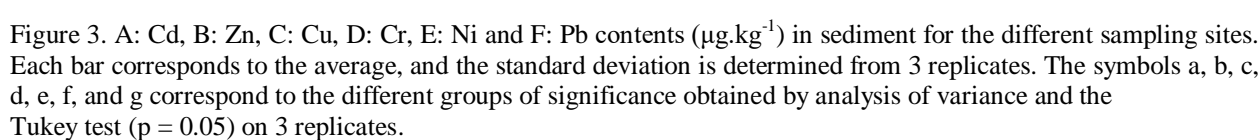


Figure 2. Variation of the physico-chemical parameters (A: pH, B: redox potential, C: salinity, D: dissolved oxygen content) of the Ebrié Lagoon. Each bar corresponds to the average, and the standard deviation is determined from 3 replicates. The symbols a, b, c and d correspond to the different groups of significance obtained by analysis of variance and the Tukey test (p = 0.05) on 3 replicates.



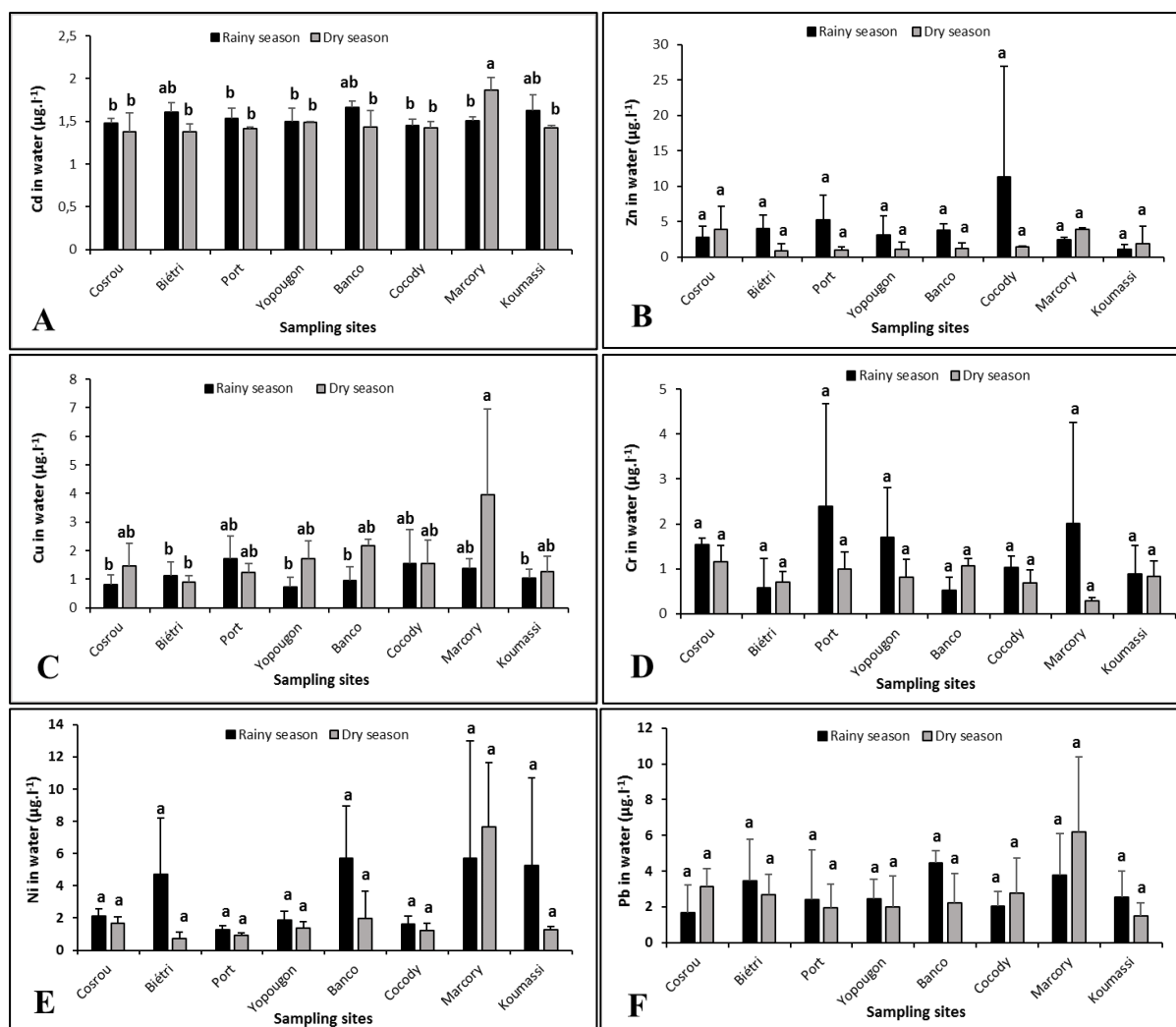


Figure 4. A: Cd, B: Zn, C: Cu, D: Cr, E: Ni and F: Pb contents ($\mu\text{g.l}^{-1}$) in the water column for the different sampling sites. Each bar corresponds to the average, and the standard deviation is determined from 3 replicates. The symbols a, b, c, d, e, f, and g correspond to the different groups of significance obtained by analysis of variance and the Tukey test ($p = 0.05$) on 3 replicates.

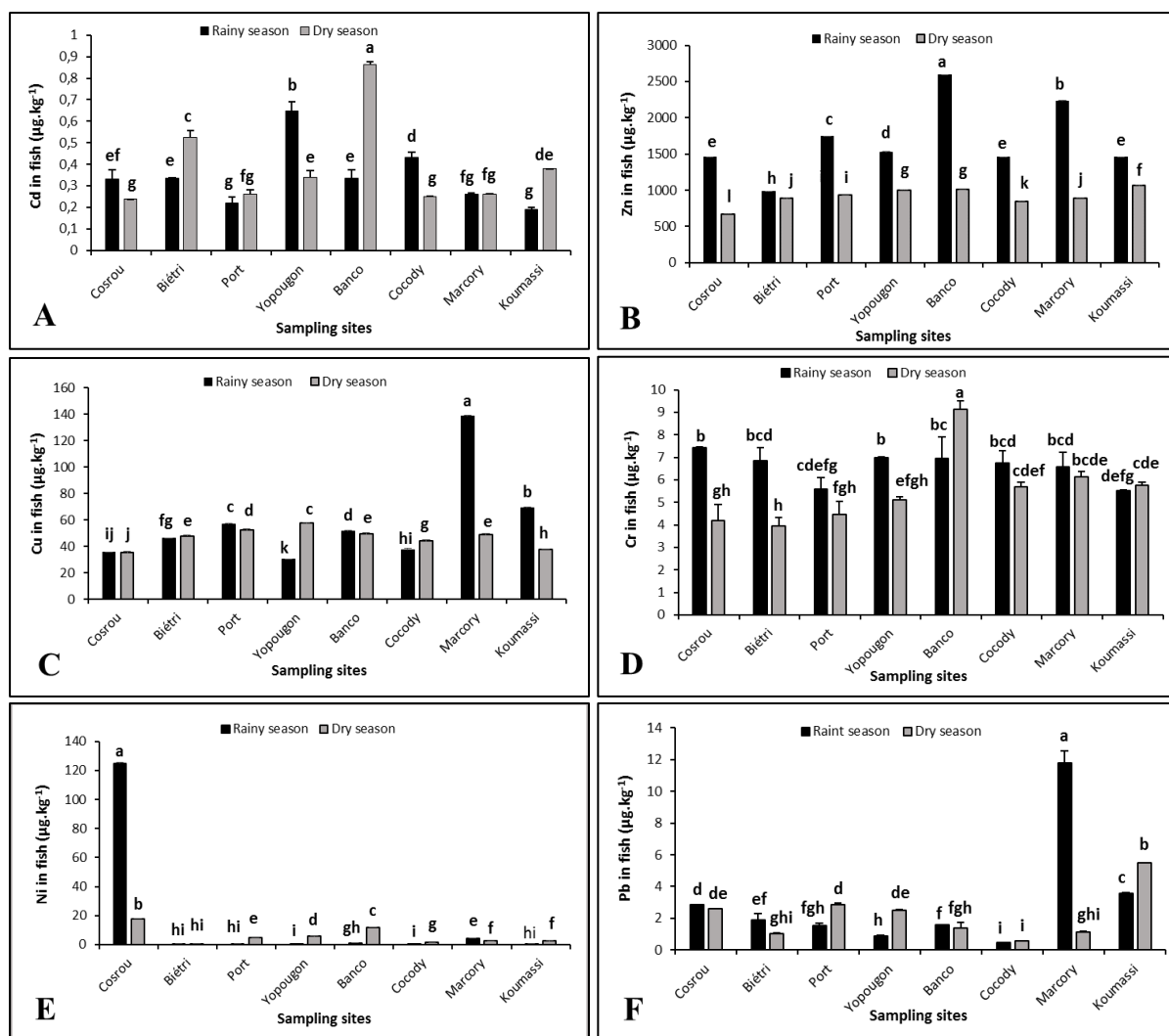


Figure 5. A: Cd, B: Zn, C: Cu, D: Cr, E: Ni and F: Pb contents ($\mu\text{g}\cdot\text{kg}^{-1}$) in fish (*Tilapia*) for the different sampling sites. Each bar corresponds to the average, and the standard deviation is determined from 3 replicates. The symbols a, b, c, d, e, f, and g correspond to the different groups of significance obtained by analysis of variance and the Tukey test ($p = 0.05$) on 3 replicates.

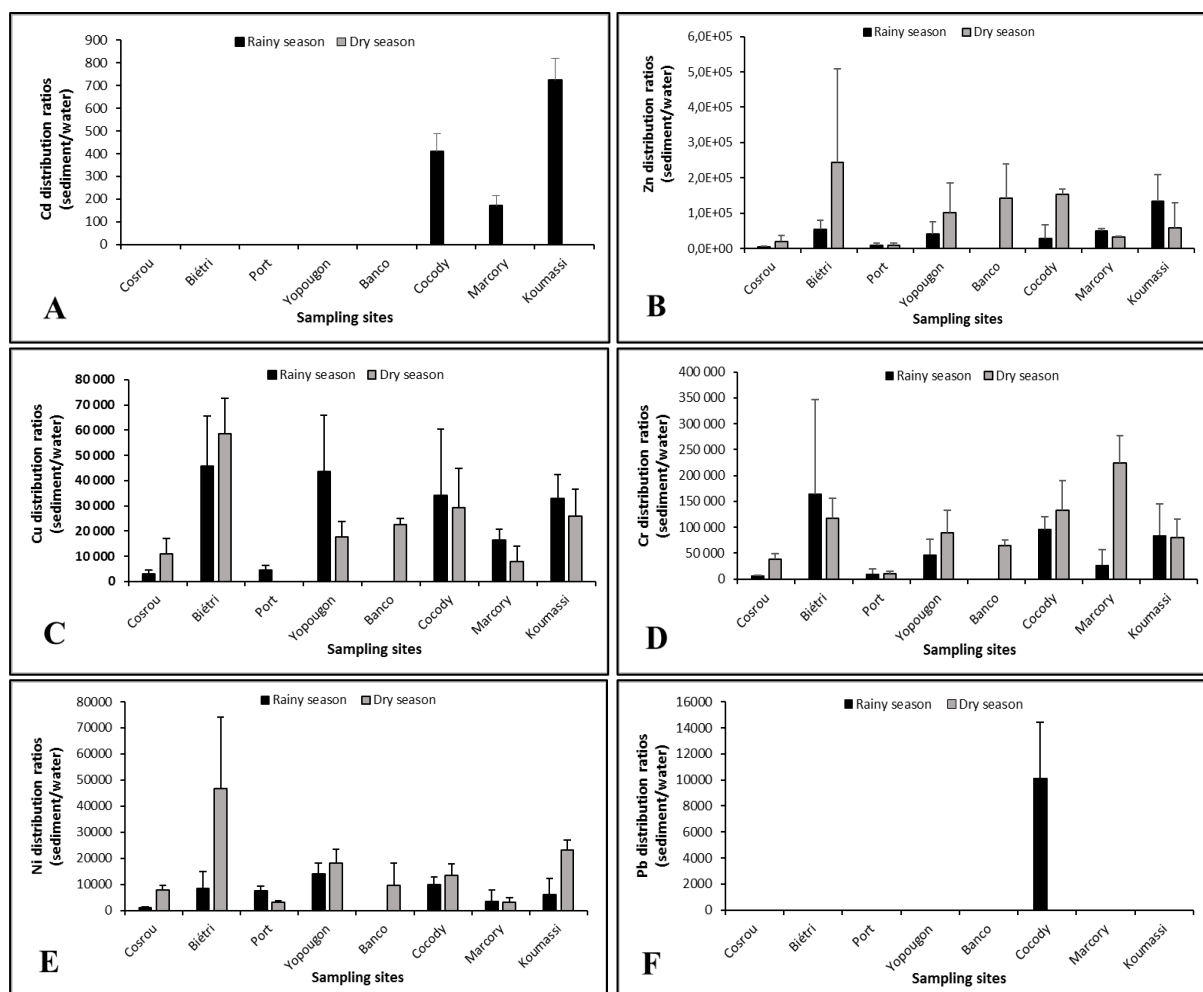


Figure 6. Distribution ratios (sediment/water) of TMEs in the Ebrié Lagoon (A: Cd, B: Zn, C: Cu, D: Cr, E: Ni and F: Pb).

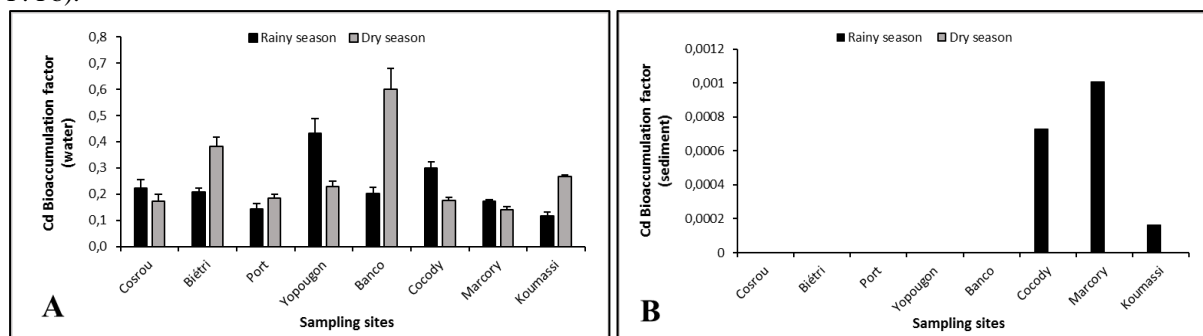


Figure 7. Bioaccumulation factor of Cd in Tilapia (A: sediment, B: water).

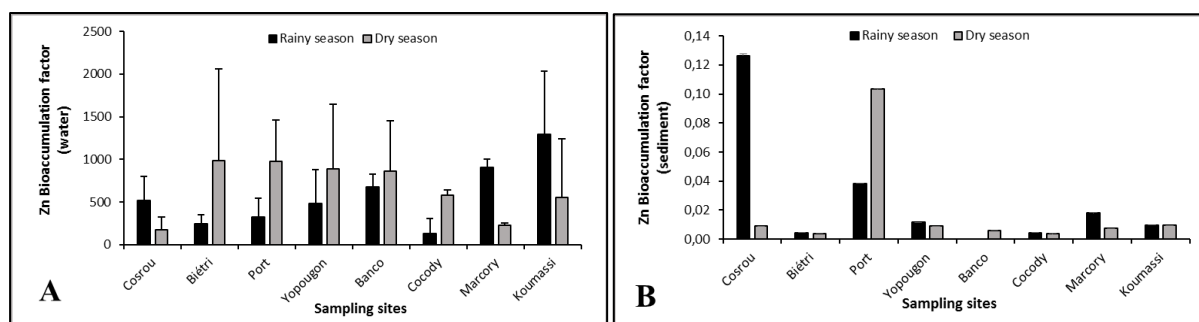


Figure 8. Bioaccumulation factor of Zn in Tilapia (A: sediment, B: water).

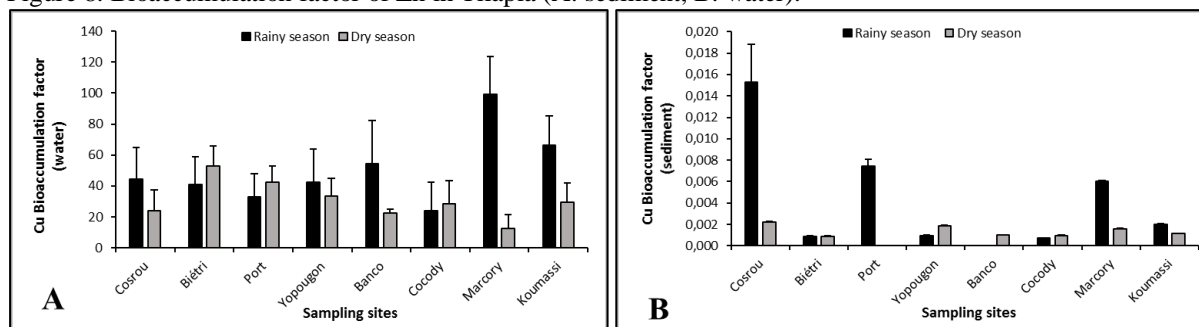


Figure 9. Bioaccumulation factor of Cu in Tilapia (A: sediment, B: water).

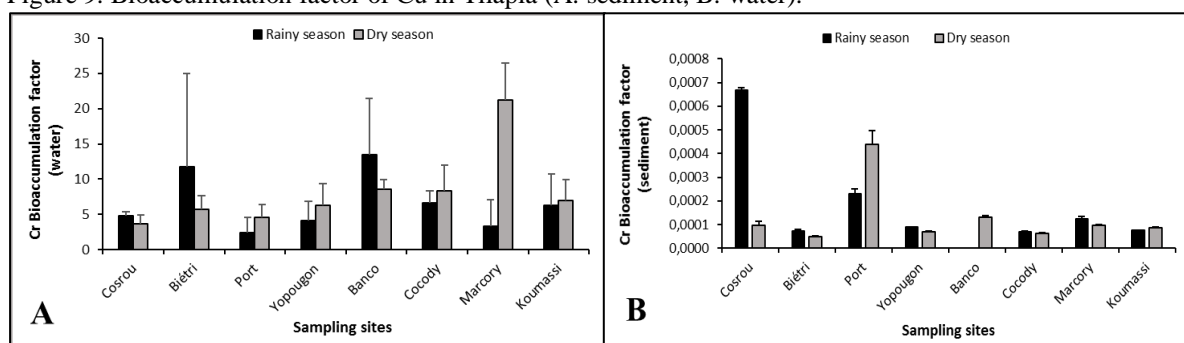


Figure 10. Bioaccumulation factor of Cr in Tilapia (A: sediment, B: water).

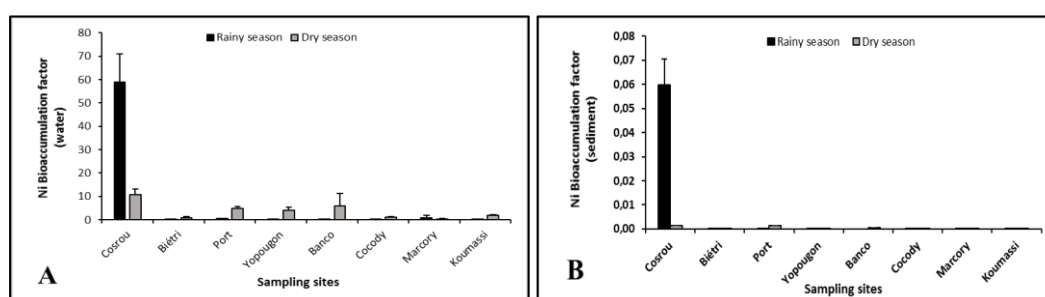


Figure 11. Bioaccumulation factor of Ni in Tilapia (A: sediment, B: water).

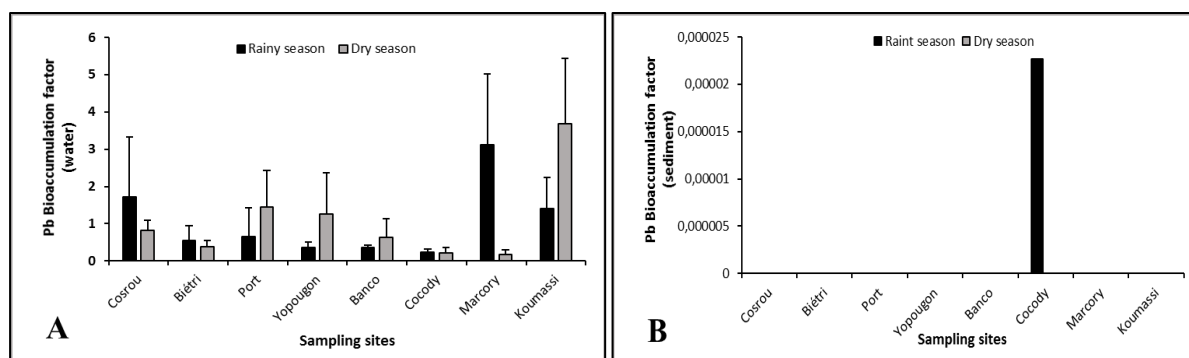


Figure 12. Bioaccumulation factor of Pb in Tilapia (A: sediment, B: water).