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Speciation of Heavy Metals in Benin Aquatic Systems: Case of Cotonou Channel

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ABSTRACT

The voltammetry methods have revealed in the water of the Cotonou channel, the presence of organic and inorganic complexes of metals, such as: Zn-Carbonate, Zn^{2+}, $ZnSO_4$, Zn-OM, Cu-Carbonate, Cu^{2+}, $Cu(OH)_2$, Cu-OM, Pb-Carbonate, Pb^{2+}, Pb-OM, Cd-Carbonate, Cd^{2+}, and Cd-OM. Their concentrations were variable with the water pH and depended on the season. At pH values ranging 6.5 - 7.2, metals were complexed by carbonate ions present in the water. Zinc is predominantly present as Zn^{2+} in the rainy season and Cu^{2+} levels were decreasing when pH was increasing. 80% of the total lead appeared to be complexed as Organic matter complex lead (Pb-OM), and cadmium which, unlike other metals, was mainly present in free Cd^{2+} form.

1. Introduction

Metals in water, sediments and living organisms are found in different chemical forms. According to Blanquet et al.[1], the inorganic complexes mostly present in water are: CuS; CuO; $Cu(OH)^+$; $Cu(OH)_2$; $CuFeS^+$; $CuCO_3$, $CuCOZn^+$; ZnS; ZnSO4; $Zn(OH)^+$; $ZnCl^+$; $ZnCO_3$, Pb^{2+}; PbS; $PbCl^+$; $PbCl^+$; $PbCl_2$, $Pb(OH)^+$; $Pb(OH)_2$; PbO, Cd^{2+}; $CdCl^+$; $CdCl_2$, CdS, $Cd(HS)^+$; $Cd(OH)^+$, $Cd(OH)_2$, $CdCO_3$, etc. Complexation phenomena involving metals are governed by a set of physicochemical parameters. These modify the speciation of the metals that is to say that, they influence the distribution of the different metallic chemical forms, but also act on their assimilation by the living organisms. Among these parameters, mention may be made for pH, redox potential and, of course, available ligands quantity or complexing capacity [2].

The Cotonou Channel is affected by human activities with significant contents of toxic heavy metals (Cadmium, Copper, Lead and Zinc) [3]. It is 400 meters long, 300 meters wide with a depth of 5 to 10 meters. It is the seat of the mixture of fresh water and sea water. That confers to this aquatic ecosystem, an ecological, environmental and economic importance through the nutritional quality of its fisheries resources; on the international market, like its shrimps on the European market ([4] and [5]).

Today, the Cotonou Channel seems to be losing its economic appeal because of its high level of pollution, due to the various dumping of waste. Numerous economic activities are carried out, and its west bank is home to the Dantokpa international market and a craft center for dyeing and tinplate making in Gbogbanou. Users of this Benin largest market have been generating for many years high quantities of solid waste that covered the lagoon bankets. The outlets of urban wastewater collectors are connected to the channel and make the pollution level very alarming [6]. According to Vissin et al. [7], these forms of pollution, both organic and chemical, would lead to a contamination of fish species by toxic metals (Pb, Cd, Cu, and Zn). In fact, toxicity, mobility and bioavailability of a metal in water depend on its physicochemical forms and its affinity for the other water constituents ([8] and [9]). Knowledge of the speciation of metals in solution is of considerable interest to characterize and possibly treat polluted water [10]. Thus, our work aims at determining the total contents of each metal element, its different chemical forms, and the spatiotemporal variation of these parameters in the channel waters in relation to the pH of the medium. Specifically, we focused our study on identifying the chemical forms under which the metals were predominating in water and determining pH influence on the toxicity of metals in the channel.

2. Material and methods

2.1. Sampling sites

Tableau 1. Geographical coordinates of sampling sites.

Sites	Sites names	Geographical coordinates	
		X	Y
S1	Gbogbanou	04° 37'692''N	07°03'970''E
S2	Missèbo	04°37'817''N	07°03'664''E
S3	Hotel du lac	04°38'471''N	07°02'979''E
S4	D pêche	04°38'234''N	07°03'256''E
S5	Dédokpo	04°37'963''N	07°03'865''E
S6	Kpankpan	04°37'884''N	07°04'293''E
S7	Teintuerie	04°37'837''N	07°04'593''E
S8	HLacomè	04°37'775''N	07°05'990''E
S9	Ladji	04°37'487''N	07°05'785''E
S10	Hindé	04°37'521''N	07°04'948''E
S11	Sofrado	04°37'576''N	07°04'857''E
S12	Embacardère	04°37'604''N	07°04'456''E

Source : our study

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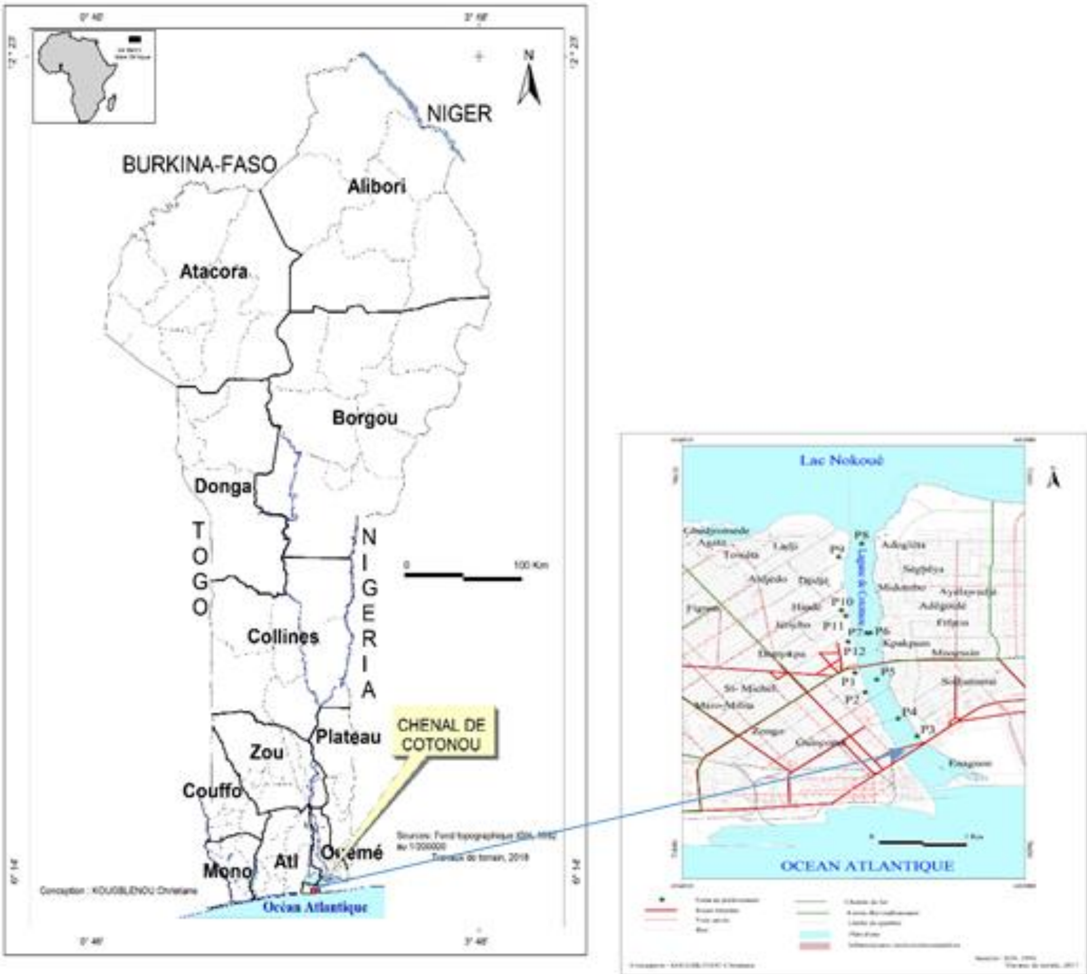


Figure 1. Location of sampling sites.

Twelve (12) sites in the Cotonou Channel were sampled for water analysis. These were named from P1 to P12 located in Figure 1 and whose geographical coordinates are mentioned in Table 1. These study sites are located in the vicinity of both banks and represent places of potential waste inputs in the channel. Four water sampling campaigns were conducted during rainy seasons (July-September 2017) and the high dry season (November 2017-January 2018). Collected water samples were immediately stored in 4°C cold equipment and transported and yielded from light to the laboratory where samples were analyzed for metal speciation.

2.2. Physico-chemical analyses

Prior to heavy metal determination processes, physico-chemical parameters such as temperature, potential Hydrogen (pH) and electrical conductivity of the water were measured in situ using a Hanna Instruments HI 8014 portable digital multi-parameter. In order to appreciate their probable control potential of these physico-chemical parameters on heavy metal speciation and distribution in water. Then, speciation and determination of heavy metal such as lead, cadmium, copper and zinc were performed in the laboratory using the OVA-300 voltammetric analyzer. The electro-analytical method used consists in measuring the flow of current resulting from the reduction or oxidation of the test compounds present in solution under the effect of a controlled variation of the potential difference between two specific electrodes. Before measurement, water sample is purged with a stream of inert gas (N_2 or Ar) to remove dissolved oxygen therein. This operation is necessary because oxygen in a relatively large concentration (between 5×10^{-4} and 8×10^{-3} mol/L in saturated solution with air) interferes with the metals by its electro-activity [11].

2.3. Statistical analyses

The measurement of each parameter on each sample was made three times in a row. The resulting data were processed using Microsoft Excel 2013 and SPSS 16.0 software. SPSS 16.0 software was used for statistical analysis of data for t-test averaging and Duncan's variance analysis. A probability less than 0.05 was considered significant.

3. Results and discussion

The results of the physicochemical analyses on the twelve sites are interpreted according to the water quality assessment criteria.

3.1 Physico-chemical characteristics

➢ **Temperature**

The temperature of the water is an ecological factor which causes important ecological repercussions [12]. Temperature values obtained per season at the twelve sites (Figure 2) oscillate between 26°C and 29.4°C with an average value of 28.32 ± 0.93°C in July and September 2017 (during rainy season) in one side, and between 27.5°C and 30.9°C with an average of 29.53 ± 0.94°C in November 2017 and January 2018 (in dry season). Overall average water temperatures in the study areas seem to be related to weather conditions because the surface layer is subjected to the direct influence of climate which is characterized by two alternate rainy seasons and two dry seasons.

As such these temperature values can affect the pH of water, the chemical and biochemical reactions, the development and the growth of the living organisms in the water, in particular the micro-organisms, and consequently the distribution of different forms of metals [13].

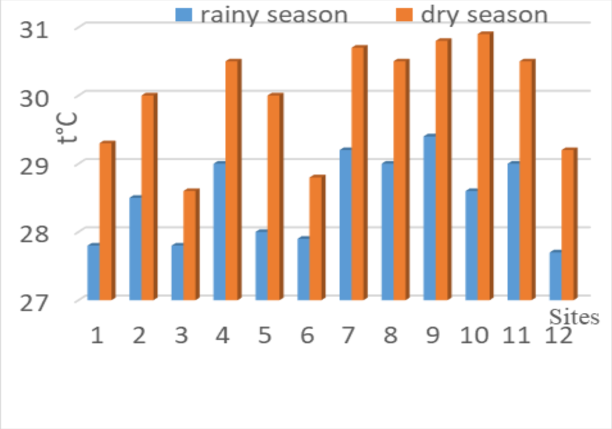


Figure 2. Distribution of average temperature.

➢ **Electrical conductivity**

Figure 3 shows the mean values of water conductivity at the twelve sampling sites. Electrical conductivity is a numerical expression of the ability of a water sample to conduct electrical current. Its measurement thus makes it possible to appreciate the degree of mineralization of water where most of the dissolved materials are in the form of electrically charged ions which act each by their specific conductivity. As results, it was observed that, in rainy periods the minimum value (1410 µS/cm) was measured at the site S9 and the maximum value (1610 µS/cm) at the site S11. While in drought the minimum value (1360 µS/cm) was registered at the site S4, the maximum value (2100 µS/cm) on the site S1.

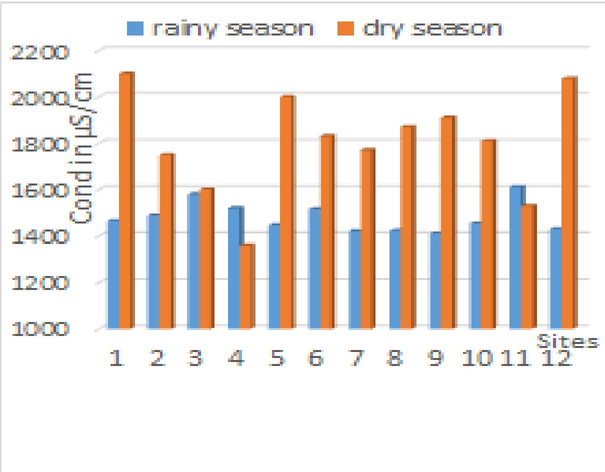


Figure 3. Distribution average conductivity.

The average values recorded (Fig.3) show significant variations, especially in the dry season with a maximum value of 2100 µS/cm and 1611 µS/cm in the rainy season. These values were far higher than those previously found in the same aquatic medium by other authors, such as Vissin et al. [7] who found a maximum of 1016 µS/cm in August, and Youssao et al. [5] whose studies showed a maximum value for conductivity around 1968 µS/cm in the dry period. In spite of the conductivity decrease during the rainy season compared to the dry season, values obtained for our water samples sometimes were higher than those of natural waters, which ranged 50-1500 µS/cm. This observation corresponded to an event of sewage discharges with significant variations in dissolved salts that aquatic organisms generally cannot withstand. The site of fabric dyeing in Gbobganou (S1) was also an important source of salts discharges in the channel waters.

➢ **Hydrogen potential (pH)**

Figure 4 shows variations of average pH for water at the twelve sampling sites submitted to investigations. pH is a fundamental parameter whose values determine the evolution direction for many physico-chemical processes occurring in aquatic environments [14]. The data obtained for the Cotonou Channel waters were ranging 6.5-7.7 during dry season and 7.4-8.3 during rainy season. Globally for any season considered, the pH values were suitable for the pH normal range in surface water systems where biological tissues could easily develop [15]. However, pH values were varying from one site to another, depending on the kinds of anthropogenic activities conducted nearby. If some wastewaters from SOBEBRA breweries industry affected the pH values in the channel, it was also important to mention that alkaline wastewaters from the Gbogbanou artisanal tinplate sites (site S1) contributed to increase the pH of the channel water in these places.

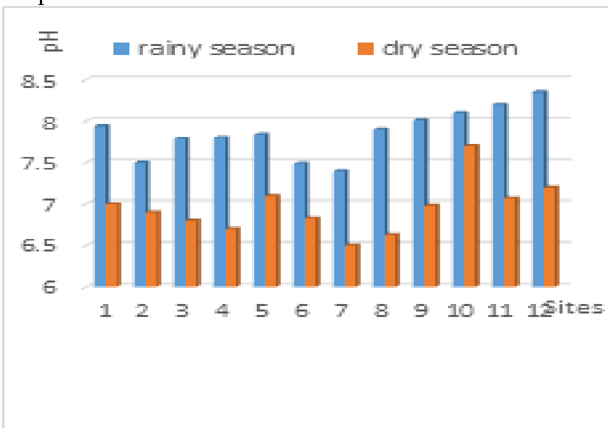
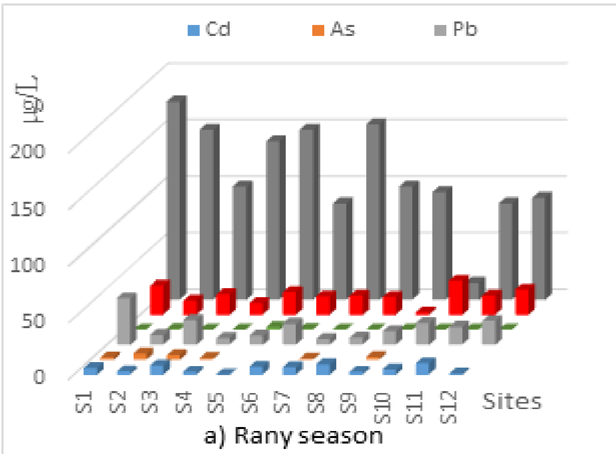


Figure 4. Distribution of average pH.

3.2 Heavy metals measurements

➢ **Total metals concentrations**

Figure 5 shows the evolution tendancy for heavy metals concentrations during two sampling campaigns: July-September 2017 for wet season, and November 2017-January 2018 for dry season. Comparison of the concentrations of the total element metals revealed that the zinc element predominated over all other metals (Copper, Lead, Cadmium, Chromium and Arsenic) in the dry season and the rainy season, with concentrations values ranging from 15 µg/L (S10; Hinde site) to 175 µg/L (S1, Gbogbanou Site). Except for arsenic and chromium, the highest values were observed for copper (30 µg /L), lead (41µg/L) and cadmium (10µg/L) at the Gbogbanou site. As observed above for the pH and electrical conductivity values, this site is strongly dominated, not only by tinning and dyeing activities, but also by the repair of obsolete electrical and electronic equipment (dragging sometimes on the ground), which are important sources of toxic metals in the channel waters.



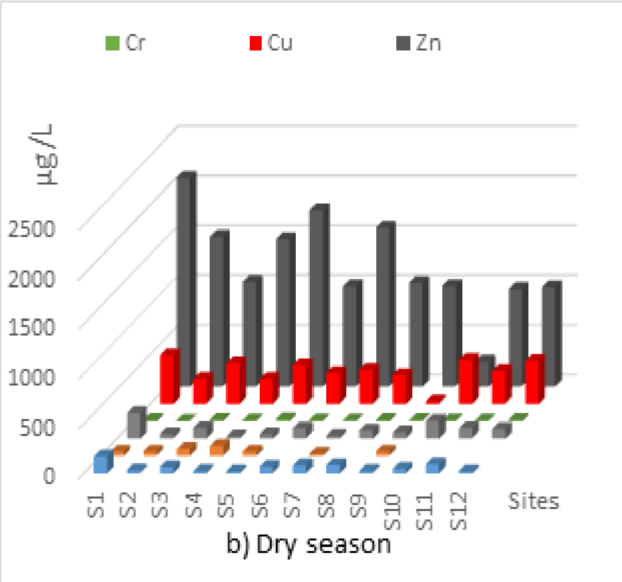


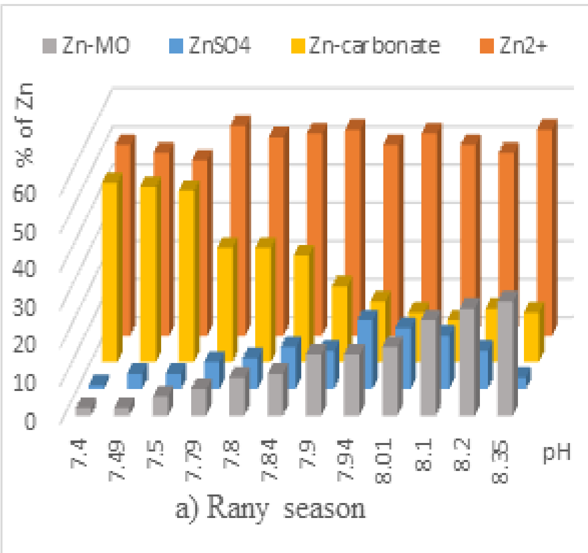
Figure 5. Distribution of average total metal concentration in the rainy and dry season.

➢ **Chemical forms of metals in Cotonou channel waters**

As the metal behavior in natural systems evolutes with their chemical forms [1], our investigations were also focused on the qualitative and quantitative metal speciation, for zinc, copper, lead, and cadmium. As results, Fig. 6 - 9, relating to the relative proportions of the metal forms within each element, made it possible to identify the majority and minority forms according to the physicochemical conditions of the metal.

Zinc metal

The chemical forms identified for zinc are: Zn-carbonate, Zn^{2+}, Zn-SO_4, Zn-OM. In rainy season, Zn^{2+} was the predominant form of zinc and represented more than 50% of the total concentration of zinc, whatever the pH values. In contrast, in the dry season the pH values affected the distribution of zinc forms, so that at pH between 6.5 and 7.0 Zn-carbonates predominated when the zinc form complexed with the organic matter (as Zn-OM) increases in concentration with pH, and Zn-SO_4 oscillating with the pH during the two seasons. These observations are consistent with the results obtained by Bourg et al. [11] who conducted similar studies on the Lot River in southwestern France.



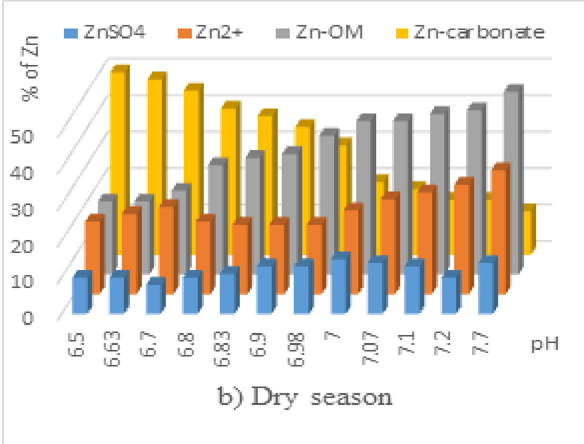


Figure 6. Distribution of the chemical forms Zinc in the Rainy and dry season.

Copper metal

According to figure 7, the copper element was identified in water samples in different forms such as: Cu-carbonate, Cu^{2+}, $Cu(OH)_2$, and Cu-OM, during the 4 sampling campaigns (July 2017-September 2017 and November 2017-January 2018). Among the various forms of copper, the complexed organic matter Cu (Cu-OM) predominates over the others and represents 55% of the total in rainy season and 80% in dry season. In addition, both Cu^{2+} and $CuCO_3$ levels decrease during the two seasons when the pH of the water increases; $Cu(OH)_2$ remaining almost non-existent during the dry period.

According to Montinaro et al. [16], the Cu^{2+} ion is more toxic than all the other forms of copper; so, it could be concluded that the water pH increases were accompanied with the decreases of the total copper toxicity.

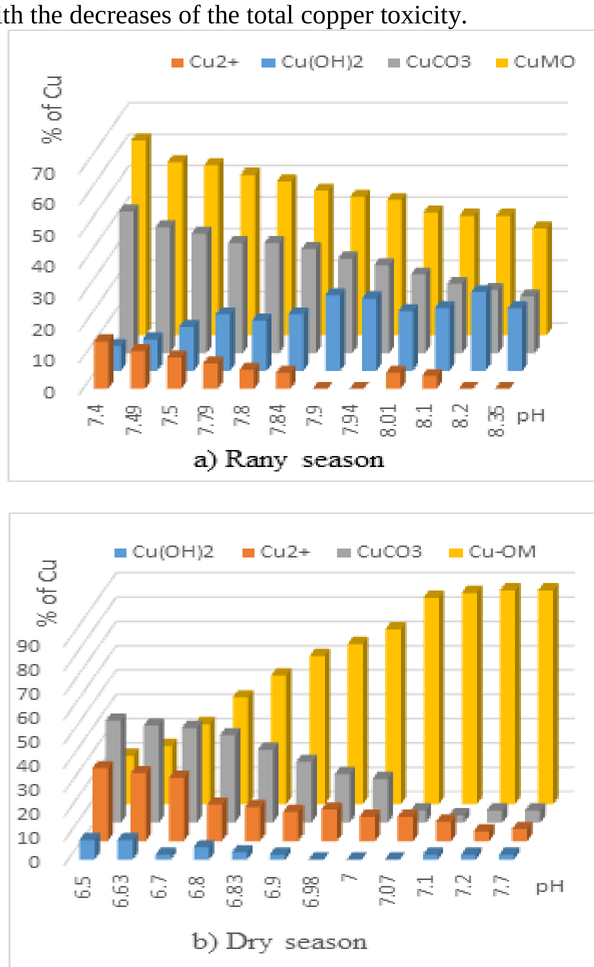


Figure 7. Distribution of the chemical forms copper in the rainy and dry season.

Lead metal

In the water samples lead appeared in different forms such as Pb-carbonate, Pb^{2+}, and Pb-OM. Analysis of the shape of the figure 8 showed that the concentrations of the Pb-OM form represented 75% of the Pb total levels for the two first sampling campaigns and 80% of the total concentration for the two last campaigns. At the time, about 15% of the total lead concentration represented lead carbonate which decreased with pH increase. It was also observed that Pb^{2+} occupied 10% of the the total lead and its concentrations varied irregularly with the pH values.

In view of these observations, it is possible to hypothesize that organic matter controls the speciation of lead in water, and that Pb complexed with organic matter (Pb-OM) is the most toxic form of lead in water [17].

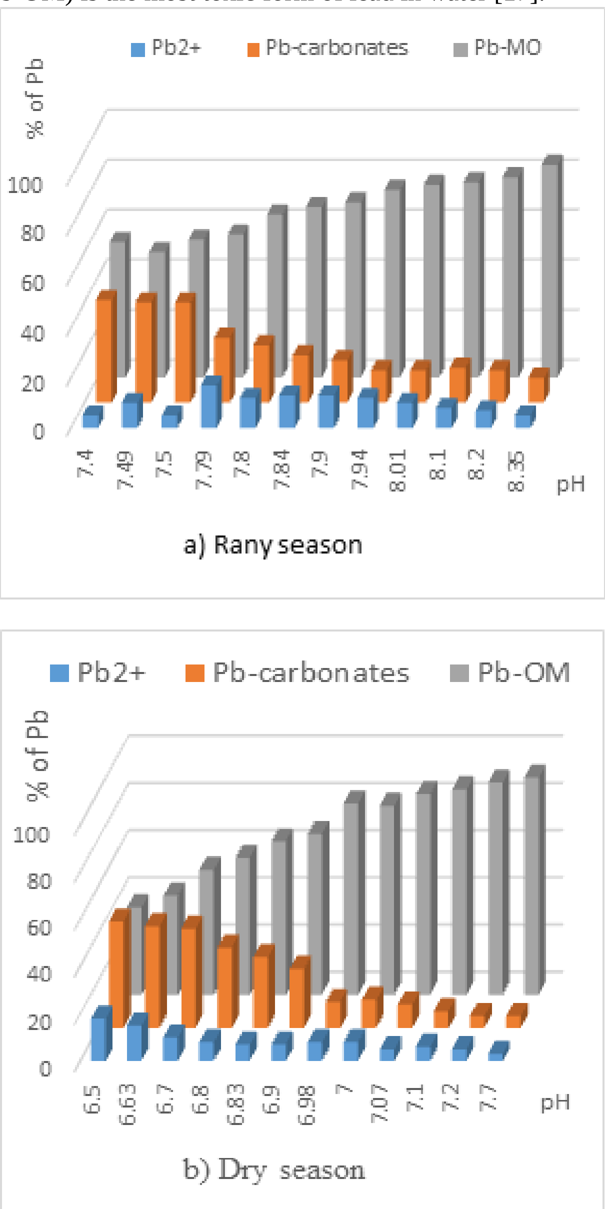


Figure 8. Distribution of the chemical forms lead in the rainy and dry season.

Cadmium

In figure 9 the cadmium element was represented by the three main chemical forms: Cd-carbonate, Cd^{2+}, Cd-OM. The Cd^{2+} form represents more than 80% of the total cadmium concentration. The Cd-OM evolution shape was the same for the 4 sampling campaigns, whereas Cd-carbonate decreased with the pH increase. So, cadmium speciation revealed that it appeared both in free, complexed Dissolved Organic matter and carbonate complexed forms. Unlike other metals, the Cd^{2+} free form predominated preferentially at all sites and regardless of pH. In general, free metal ions in solution are the most bio-available chemical form and therefore the most likely to be toxic [18].

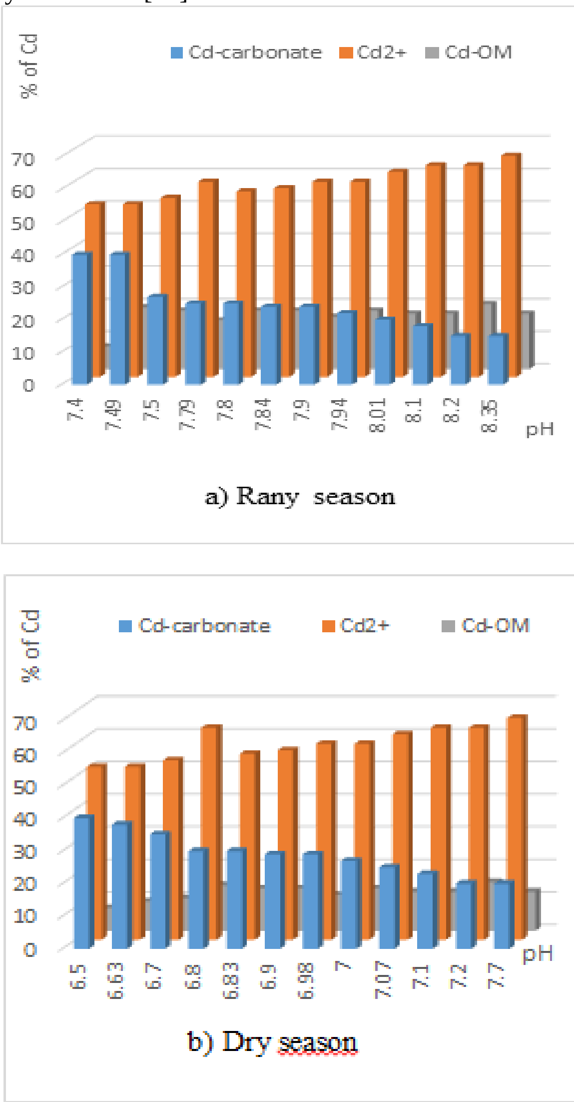


Figure 9. Distribution of the chemical forms cadmium in the rainy and dry season.

Conclusion

The distributions of the metal forms vary with the physicochemical conditions, in particular the pH of the water. In fact, the present study has shown for all the metallic elements investigated that the metal forms complexed with the organic matter predominated on other forms, whatever the pH. They are followed in terms of abundance by the carbonated metals whose concentrations decreased with the increase of the water pH.

As regards their toxicity for living organisms, it was noted that Pb-OM, Cd^{2+}, $ZnSO_4$ and Cu^{2+} appeared as the most toxic chemical species among the identified forms.

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