LEAD CONCENTRATIONS IN SEDIMENTS AND MOLLUSC GASTROPOD FROM VRIDI CANAL, CÔTE D’IVOIRE

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ABSTRACT

Lead (Pb) is one of the most frequent and toxic contaminant in the environment. It can be bioaccumulated by marine organisms through contaminated sediments as well as their food chains. The current study aimed at investigating Pb occurrence in the sediments and gastropod P. haemastostoma from Vridi Canal. Sediment samples were taken using a Van Veen steel grab of 0.02 m² area, sealed in plastic bags and transported to the laboratory at 4 °C. Gastropod P. haemastostoma species were collected manually using gloves, and then placed in polyethylene plastic bags. The different concentrations were determined using atomic absorption spectrometer Varian AA 20. The results showed seasonal variability of Pb concentrations in sediments and P. haemastostoma. In the both matrices, Pb exhibited the same trend in the distribution between the seasons. This study also mentioned that sediments were highly contaminated by Pb (54.27-134.71 mg/kg). Vridi Canal was found to be one of the most contaminated seaport area. Pb levels (49.55-104.19 mg/kg) in P. haemastostoma exceeding the maximum permitted levels according to the United Nations Food and Agriculture Organization (FAO). This research demonstrated that sediments having lower ecological risk may be resulting in lower tissue Pb of P. haemastostoma.

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Keywords: Metal Pb, sediment, P. haemastostoma, seasonal variation.

INTRODUCTION

Lead, known to be toxic metal with no nutrient values, finds its way into the aquatic environment via atmospheric inputs as well as from leaded gas leaking from boats (Berto et al., 2012). Its presence in water systems, even at low concentrations causes its incorporation into the food chain, which could result in a wide variety of adverse effects in organisms and humans (Baby et al., 2010; Youssoa et al., 2011; Kantati et al., 2013; Zhang et al., 2017; Gope et al., 2017). However, determination of lead contamination level in aquatic system is important in order to control its pollution in the environment. Several studies have shown that tropical estuarine sediments were highly...
contaminated by Pb (Chakraborty et al., 2015; Kouassi et al., 2015; Yao and Kouassi, 2015; Chen et al., 2016; Botwe et al., 2017). However, these studies have not focused on seasonal accumulation of Pb in seaport sediments. Studies on the assessment of Pb contamination in tropical seaport sediments are in its infancy.

In Côte d’Ivoire, Vridi Canal is the unique way to enter and exit of Abidjan seaport area (Kouakou et al., 2016a). The intense ship traffic and the high fishing fleet increase the potential risk of lead contamination in the surface sediments of this area. More recently, in order to enlarge the Vridi Canal, intense dredging has become a very common activity leading to relevant sediment resuspension from which Pb can be easily released into water column (Xie et al., 2016). Therefore, it is crucial to assess Pb concentration in Vridi seaport sediments.

Pb accumulated in sediments could be released into water column under the variation of various physical and chemical parameters such as pH, ionic strength. Thus, Pb release into water column could be accumulated by biota. For this reason, many researches were carried out on Pb concentration in organisms such as gastropod mollusks (Xiaobo et al., 2009; Ragi et al., 2017; Baltas et al., 2017; Mejdoub et al., 2018). These studies showed those gastropods Pb concentrations exceeding WHO safe limits. Some gastropods species represent a source of cheap protein for the population. This is the case of Vridi Canal where gastropods P. haemastostoma are highly consumed by habitants. Moreover, Kouakou et al. (2016a) have reported high levels of Cd and Zn in P. haemastostoma in Vridi Canal. However, there is no report about Pb in the tissues of P. haemastostoma in this area. This study aimed at investigating the concentrations of lead simultaneously in sediments and in the tissues of P. haemastostoma from the Vridi Canal. To address this objective: (i) the seasonal variations of Pb concentrations in sediments and in P. haemastostoma were assessed, (ii) the relationship between lead content in the sediments and its bioaccumulation in P. haemastostoma was investigated, and (iii) the ecological risks (Er) of sediments and the bioaccumulation factor (BAF) for Pb were determined.

MATERIALS AND METHODS

Description of the study area

This study focused on an important Canal of Abidjan seaport (the economic capital of Côte d’Ivoire). Vridi Canal is an artificial Canal created in 1954 and located in the southern part of Abidjan (Kouakou et al., 2016a, b). It is chosen because of its proximity to most of the industrial and maritime activities taking place, such as maritime transport and fishing, and the company of oil Refinery. This Canal possesses a navigable depth of 15 m with a length of 2.7 km, and a width of about 370 m. It receives domestic raw sewage, household waste, and industrial wastes from its neighbourhood (Kouakou et al., 2016a).

Sampling and treatment of sediment

The sediment samples were collected between February 2015 and September 2015 (dry season, rainy season and flooding season) from different sites (Figure 1). Three significant stations representative of each site were selected upstream, midstream, and downstream. Sediment samples were collected at each station using a Van Veen stainless steel grab of 0.02 m² area, following USEPA (2001). Then sediment samples were put into small plastic bags and kept in a cooler at 4 °C. All samples were transported to laboratory and subsequently stored in a freezer at -20 °C. The sediments samples were treated according to the treatment method described by Saleem et al. (2015).

pH was determined using standard procedures (Radojevic and Bashkin, 1999). Organic carbon was determined using Walkey-Black method (Radojevic and Bashkin, 1999). The pH was measured using 1:2 sediment, water ratio with the pH meter. Grain size distribution is one of the most important characteristics of sediment. Protocol used to separate the different sediment is the
pipette method of Robinson-Köl n (Radojevic and Bashkin, 1999).

A mass of 0.2 g of each of the homogenized sediment was digested in closed Teflon bomb with a mixture of 1 ml of aqua regia (HNO₃: HCl; 1:3, V/V) and 3 ml of HF, heated to 100 °C during 3 h in a water bath. After cooling, a volume of 20 ml of H₃BO₄ (140 g/L) was added to each Teflon bomb to mask free fluoride ions in solution and re-dissolve fluoride precipitates (Kouassi et al., 2015). The final volume was made up to 50 ml with 2% ultrapure HNO₃. The solutions were filtered and stored in polyethylene flasks for later determination of lead content.

**Sampling and treatment of gastropod**

*Purpurea haemastostoma* was collected from the same sites and during the same seasons as for sediments. Gastropod *P. haemastostoma* species were collected manually using gloves, and then placed in polyethylene plastic bags (Bakary et al., 2015). The individuals were selected for the following sizes of shells: 4 cm for *P. haemastostoma*. Approximately 144 of gastropod samples were collected between February 2015 and September 2015. After sampling, the samples were treated according to Chiffoleau (2003) before analysis.

**Total digestion of the soft tissues of gastropod**

The digestion of soft tissues was made according to the method described by Chiffoleau (2003). 0.2 g of each of the homogenized soft tissues was placed in a Teflon bomb, then 4 ml of concentrated HNO₃ (65%) was added and held for all night for a pre-digestion and digested on a water bath (above 100 °C) for 3 h. After cooling, the solution was filtered, stored in polyethylene flasks and made the filtrate up to 50 ml with deionized water. Blank digestion was also made to quantify possible contamination.

**Determination of lead concentration**

Lead contents were determined by using an air-acetylene flame atomic adsorption spectrometer (Varian SpectraAA 20). The detection limit was 0.003 mg/kg. In addition, accuracy and precision of analysis was checked by replicate measurements of standard reference materials (BCSS-1, National Research Council Canada, DORM-2 dogfish muscle). The measured concentrations fell within the range of certified values, and the recoveries varied between 94% and 108%.

**Bioaccumulation factor (BAF) and ecological risk index (Eᵣ)**

The accumulation of Pb from sediment in the gastropod *P. haemastostoma* was estimated according to the following BAF equation:

\[
BAF = \frac{C_{\text{gastropod}}}{C_{\text{sediment}}} \tag{1}
\]

Where \( C_{\text{gastropod}} \) (mg/kg) and \( C_{\text{sediment}} \) are the concentrations of Pb in *P. haemastostoma* and sediment, respectively. When BAF value exceeds 1, metal is likely to concentrate in *P. haemastostoma* relative to the sediment.

Ecological risk associated with the presence of Pb in sediment was calculated using the following equations developed by Hakanson (1980).

\[
C^{i}_f = C^i_i \times C^{i}_c \tag{2}
\]

\[
E^{i}_r = T^{i}_r \times C^{i}_f \tag{3}
\]

Where \( C_i \) is the contamination factor of Pb in the sediment sample, \( C_i \) is the analyzed Pb concentration (mg/kg) in the sediment sample, and \( C_n \) is the background concentration of Pb (17 mg/kg) in the Upper Continental Crust given by Wedepoh (1995). \( E_r \) is the ecological risk index of Pb and the toxicity coefficient \( T_r \) represents the toxicity and biological sensitivity to Pb. The value of \( T_r \) for Pb is 5 (Hakanson, 1980).

An \( E_r \) value < 40 corresponds to low risk; 40 < \( E_r \) < 80 to moderate risk; 80 < \( E_r \) < 160 considerable risk; 160 < \( E_r \) < 320 to high risk, and \( E_r \geq 320 \) to very high risk (Hakanson, 1980).
Statistical analysis

The analysis of variance (ANOVA one way) was used to evaluate the difference between the months. Then, Tukey test (Honest significant difference) was performed whenever significant difference was found in ANOVA. Differences were considered significant at $p$ values < 0.05. Statistical analyses (mean value, minimum, maximum, and correlation) were carried out with Statistica 7.1 software.

Figure 1: Map of the study area showing sampling sites.
RESULTS
Physico-chemical parameters and sediment grain sizes
The physico-chemical parameters of sediment samples are given in Table 1.

The averages values of pH, and TOC varied between 7.41± 0.31 and 8.42 ± 0.19, and between 0.28 ± 0.24% and 0.94 ± 0.8%, respectively. Sediment texture results indicated that sediments were mainly composed by sand particles with an average percentage ranged from 56.77 ± 5.14% to 89.69 ± 4.14% (Table 1).

Sediment texture results showed that pH, TOC and sediment grain size composition varied significantly with the seasons.

Total concentrations of Pb in sediments and bioaccumulation of Pb in P. haemastostoma
The seasonal variation of Pb concentration in Vridi Canal sediments is given in Figure 2. The ranges of Pb concentrations were (108.84 ± 37.87 – 134.71 ± 54.77) mg/kg, (52.65 ± 21.50 – 72.23 ± 19.08) mg/kg and (92.24 ± 28.34 – 115.35 ± 28.32) mg/kg, during the dry season (February-March), the rainy season (April–June) and the flood season (July-September), respectively. These values were higher than the pre-industrial values (17 mg kg⁻¹) in the Upper Continental Crust (UCC) (Wedepohl, 1995). Significant differences (ANOVA, p < 0.05) were observed between Pb concentration in the dry season and the rainy season, and Pb concentration in the rainy season and the flood season.

As displayed in Figure 2, the average concentrations of lead in the soft tissues of P. haemastostoma vary from 49.55 ± 21.49 mg/kg (May) to 104.19 ± 28.32 mg /kg (August). During the sampling period, in P. haemastostoma Pb contents exceeded the maximum permissible levels (2 mg/kg) according to the United Nations Food and Agriculture Organization (FAO). Total concentration of Pb in P. haemastostoma showed significant differences (ANOVA, P < 0.05) between the dry and rainy seasons, and between the rainy and flood seasons.

Relationship between Pb in sediment and Pb bioaccumulation in P. haemastostoma
The linear regression showed a significant correlation (r² = 0.82; N = 72) between Pb concentrations in the sediments and P. haemastostoma Pb concentrations (Figure 3). Pb bioaccumulation in P. haemastostoma gradually increased with the increasing concentrations of Pb in the sediments.

Correlation between bioaccumulation factor (BAF) and ecological risk index (Er)
Table 2 gives the values of bioaccumulation factor (BAF) and ecological risk index (Er). Average BAF values were ranged from 0.74 ± 0.35 (March) to 0.97 ± 0.30 (April), with no significant difference (ANOVA, p < 0.05) between the seasons. BAF of Pb indicated values lower than the unity during the sampling period. The ecological risk index (Er) values for Pb varied between 15.48 ± 6.15 (April) and 39.62 ± 10.06 (March). The average values of Er were significantly lower (p < 0.05) in the rainy season compared to those in the dry and flood seasons. The Er values were lower than 40, indicating low risk for Pb in sediments of Vridi Canal. Figure 4 shows the linear regression between BAF and Er. The results revealed that there was not significant correlation (r²= 0.056; N=72) between BAF and Er.
Table 1: Physico-chemical parameters and sediment grain sizes.

|       | PH     | TOC (%) | Clay (%)   | Silt (%)  | Sand (%)  |
|-------|--------|---------|------------|-----------|-----------|
| February | 8.06 ± 0.60 | 0.72 ± 0.47 | 13.04 ± 2.75 | 26.12 ± 3.67 | 60.84 ± 5.29 |
| March   | 8.42 ± 0.19   | 0.28 ± 0.24   | 5.08 ± 1.75   | 23.60 ± 5.98   | 71.32 ± 5.83   |
| April   | 8.01 ± 0.35   | 0.86 ± 0.20   | 20.67 ± 6.70   | 49.11 ± 14.76  | 69.79 ± 8.85  |
| May     | 7.73 ± 0.59   | 0.94 ± 0.80   | 4.39 ± 0.85    | 8.20 ± 2.94    | 87.41 ± 3.25  |
| June    | 7.77 ± 0.43   | 0.85 ± 0.23   | 4.54 ± 1.72    | 5.77 ± 3.51    | 89.69 ± 4.14  |
| July    | 7.35 ± 0.43   | 0.85 ± 0.23   | 30.15 ± 5.84   | 43.27 ± 5.78   | 73.42 ± 5.07  |
| August  | 7.59 ± 0.55   | 0.75 ± 0.14   | 11.90 ± 3.03   | 28.22 ± 4.51   | 59.88 ± 5.59  |
| September | 7.41 ± 0.31  | 0.76 ± 0.22   | 13.45 ± 3.80   | 29.77 ± 5.50   | 56.77 ± 5.14  |

TOC: Total Organic carbon. Physico-chemical parameters are significant different between the seasons at p < 0.05. Sediment grain sizes are significant different between the seasons at p < 0.05.

Figure 2: The concentration of lead (mg/kg dry weight) in sediment and in P. haemastostoma. Pb concentrations in sediment are significantly different between the seasons at p < 0.05; Pb concentrations in P. haemastostoma are significantly different between the dry and rainy, and, between the rainy and flood seasons at p < 0.05.
Figure 3: Linear regression between Pb concentration in sediment and Pb concentration in *P. haemastostoma*. Correlation is significant at \( p < 0.05 \).

Figure 4: Linear regression between bioaccumulation factor (BAF) and ecological risk index (\( E_r \)). R\(^2\) = 0.056.
Table 2: Results of bioaccumulation factor (BAF) and ecological risk index (\(E_r\)).

|       | Er         | BAF       |
|-------|------------|-----------|
| February | 32.01 ± 11.17 | 0.95 ± 0.02 |
| March   | 39.62 ± 10.06  | 0.74 ± 0.35 |
| April   | 15.48 ± 6.15    | 0.97 ± 0.30 |
| May     | 15.96 ± 6.15    | 0.90 ± 0.09 |
| June    | 21.24 ± 5.40    | 0.92 ± 0.05 |
| July    | 33.45 ± 9.43    | 0.86 ± 0.16 |
| August  | 33.93 ± 9.43    | 0.91 ± 0.10 |
| September | 27.13 ± 8.33   | 0.95 ± 0.03 |

BAF: Bioaccumulation Factor; Er: ecological risk index of Pb in sediment; Er is significantly different between the seasons at \(p < 0.05\).

DISCUSSION

Physico-chemical parameters and sediment grain sizes

Significant seasonal variability of physico-chemical parameters and sediment grain sizes was found between the dry season and the rainy and flood seasons. Vridi Canal is dominated by marine water from Atlantic Ocean. The intrusion of marine water increases pH values (Kumar et al., 2015). The pH values during the study period indicated that the surface sediments are basic character. This could be due to the contribution of marine water. A sedimentation medium usually has a pH between 6 and 8. It has been reported that calcite is a carbonate mineral which is pH sensitive. In marine water (pH > 7), calcite is precipitated almost entirely. Therefore, it could be explained the basic character of sediment. In Vridi Canal, the dry season is characterized by the maximum intrusion of marine waters from the Atlantic Ocean which could explain the highest pH values. The low percentages of TOC obtained could be due to the sediments texture. In aquatic environment, fine particles (clays and silt) are responsible for the conservation of organic matter in sediments. These sediments are composed mainly of sand particles (Table 2). Therefore, they are poor in organic matter (Chuan et al., 2016). Difference of fine particles content among the seasons could indicate that Vridi Canal receive different type of sediments. These sediments probably derived from anthropogenic discharges, weathering processes and Ebrie lagoon during the flooding season.

Seasonal variation of Pb concentration in sediments

Pb concentration in the sediments varied significantly during the seasons. Metal accumulation in sediment could be influenced by the physico-chemical parameters and the sediment grain sizes (Li et al., 2017). Our study showed seasonal variation of physico-chemical parameters (pH, TOC) and fine particles (silt and clay), which could explain Pb seasonal variability in sediments. However, correlation analysis between physico-chemical parameters (pH, TOC), fine particles (silt and clay) and Pb concentrations in sediments should be conducted for further investigations in Vridi Canal. Seasonal variation of Pb was also reported in seafloor sediments from the East China Sea (Li et al., 2017), which corroborates our observations.

The high concentrations obtained during the dry and flooding seasons could be explained by the phenomena of adsorption
due to the physico-chemical conditions. For example, the high pH in the dry season highly allows the fixation of Pb on sediments (Binkowski, 2017). Low concentrations of Pb in sediment during the rainy season (April to June) could be due to the diffusion phenomena (Binkowski, 2017). Pb concentrations obtained in this study could be compared with those found in marine sediments in Taiwan (31-140 mg/kg) (Chen et al., 2016) and in Australia (27-120 mg/kg) but higher than results reported by Vodopivez et al. (2015) (4.9-5.8 mg/kg) in marine sediments in Argentina, by El Taher et al. (2018) in Qusie seaport in Egypt (48.2 mg/kg) and by Choi et al. (2012) in HaengamMan seaport in South Korea (29.3 mg/kg). Accordingly, these results indicate that Vridi Canal could be considered as one of the most contaminated seaport area.

In this study, the significant high Pb concentrations in the sediments are probably originated from anthropogenic activities including waste disposal, maritime activities, and boat traffic (Bakary et al., 2015). Vridi Canal is the area where cruise boats and deep draft vessels daily transit the water of the harbour in Abidjan seaport (Kouakou et al., 2016a). It has been reported that the navigation of deep draft vessels leads to an intense sediment resuspension in seaport (Martínez-Soto et al., 2016). Therefore, input of Pb from sediments in Vridi Canal can occur by the sediment resuspension. Pb release from sediment could be accumulated by organisms such us gastropod species.

**Seasonal variation of Pb concentrations in P. haemastostoma**

*P. haemastostoma* is consumed by the surrounding population of Vridi Canal. The levels of Pb (26.83 - 212.28 mg/kg) exceeded the maximum permissible levels (2 mg/kg) according to the United Nations Food and Agriculture Organization (FAO), indicating that it consumption constitute a risk for human consumption. Pb concentrations in *P. haemastostoma* were higher than those (1.16 - 2.76 mg/kg) in Ashtamudi estuary (India) by Ragi et al. (2017).

Pb concentrations in *P. haemastostoma* differed significantly from one season to another. The seasonal variation of Pb in gastropods might be due to the environmental conditions. It has been reported that when the environmental conditions fluctuate, the tolerance ranges and optima of organisms can shift or be exceeded; causing changes to the metal accumulation levels (Murray et al., 2013). In our study, sediments physico-chemical parameters varied significantly according to the seasons. This could explain in part the seasonal variability of Pb concentrations in *P. haemastostoma*. Other factors such as age, size, growth cycle, and feeding habits could also influence Pb accumulation in gastropods species as reported by Xiaobo et al. (2009). Therefore, further studies in Vridi Canal including the effect of age, size and growth cycle will be necessary. Xiaobo et al. (2009) and Saha et al. (2016) observed that Pb levels in marine organisms were influenced by the seasons in Yangtze Estuary (China) and Bengal Bay (India), respectively, which corroborates our observations.

The total concentrations of Pb in *P. haemastostoma* and sediments showed similar seasonal patterns, because it was higher in the dry season, lower in the rainy season and medium in the flooding season. We concluded that Pb concentrations in the both matrices varied significantly among the seasons.

**Relationship between Pb in sediment and Pb bioaccumulation in P. haemastostoma**

Molluscs are favoured as environmental monitors due to their sessile nature, cosmopolitan abundance and their ability to concentrate contaminants while maintaining a high tolerance (Xiaobo et al., 2009; Ragi et al., 2017). The extent of incorporation of Pb in soft tissues of the gastropod from sediments depends on Pb concentrations in the sediments. Gastropod *P. haemastostoma* species are known to bioaccumulate contaminants (Kouakou et al.,
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2016a) at water sediment interface via filter feeding. In this study, Pb accumulation in soft tissues of *P. haemastostoma* increased with the increasing total concentration of Pb in the sediments. The plausible pathway of Pb bioaccumulation by *P. haemastostoma* could be explained by the fact that aquatic organisms filter in and out surrounding water for food (Chakraborty et al., 2015). Sediments particles (suspended) in the water enter inside the organism during the filter finding. Pb associated with finer sediment particles also enters inside the organisms (Chakraborty et al., 2015).

A significant correlation also reported between Pb concentrations in the sediments and in *P. haemastostoma* showed that this specie accumulated Pb depending to its exposure to this metal. In addition, *P. haemastostoma* was sedentary, abundant in this study area and tolerant to high concentrations of Pb (Hamza-Chaffai, 2014). Based on the present evaluation which satisfied the criteria of bioindicator of metals pollution, *P. haemastostoma* can be used as bioindicators of pollution for lead.

**Ecological risk (Er) and Bioaccumulation factor (BAF)**

BAF is commonly used to estimate contaminant loads in aquatic organisms. BAF results indicated low tendency of Pb to be accumulated in the gastropod *P. haemastostoma*. These results might also indicate that *P. haemastostoma* present a lower level of bioconcentration, which could have a lower environmental impact on the studied aquatic ecosystem. Xiaoobo et al. (2009) observed high tendency of Pb to be accumulated in gastropod *P. Onchidium struma* in Beibao Harbor (China), which not corroborates our findings. According to Er values no ecological damage should be observed at the Pb concentration in the sediments from Vridi Canal. This study also mentioned that Pb bioaccumulation factor was not correlated with its ecological risk index, suggesting that sediments possessing lower ecological risk may be resulting in lower tissue Pb of *P. haemastostoma*. Therefore, correlation between BAF and Er can be used to examine the transfer of Pb to sediment to *P. haemastostoma* in the Vridi Canal. We concluded that the higher concentrations of Pb observed in *P. haemastostoma* could be derived from others sources (e.g water and food). However, Pb chemical speciation study is necessary to better understand its fate, bioavailability and toxicity in seaport sediments.

**Conclusion**

This study has shown that Pb concentrations in sediments and *P. haemastostoma* varied significantly according to the seasons. Sediments and *P. haemastostoma* from Vridi Canal are highly contaminated by Pb, indicating the influence of anthropogenic activities. The gastropod *P. haemastostoma* can be used as bioindicators of Pb pollution and it may be risky for human when it is consumed. This research also demonstrated that the correlation between bioaccumulation factor (BAF) and ecological risk index (Er) can be used to predict accumulation of Pb in gastropod *P. haemastostoma* in the Vridi Canal. However, for better understanding of Pb fate, bioavailability and toxicity, complementary study including Pb chemical speciation should be investigated.

**COMPETING INTERESTS**

The authors declare that they have no conflict to interest

**AUTHORS’ CONTRIBUTIONS**

KAR, NLBK, EKK, AT, BKY and KA conceived and planned the experiments. KAR, EKK, carried out the experiments. KAR, NLBK, BKY, AT and KA planned and carried out the statistical analyses. KAR, NLBK, EKK, AT, BKY and KA contributed to sample preparation. KAR, NLBK, EKK, AT, BKY and KA contributed to the interpretation of the results. KAR and NLBK took the lead in writing the manuscript. All authors
provided critical feedback and helped shape the research, analysis and manuscript.

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