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Assessment of Waters Contamination by Nutrients and Heavy Metals in the Ebrie Lagoon (Abidjan, Ivory Coast)

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ABSTRACT

The estuarine part of the Ebrie lagoon, close to the city of Abidjan, is contaminated by several persistent pollutants such as heavy metals, due to discharges from industrial and port wastes, agricultural and urban sewage. Water samples were collected from eighteen stations located in six bays for the analysis of nutrients (NO_2^-, NH_4^+ and PO_4^{3-}) and heavy metals (Pb, Cd, Ni, Mn and Zn). Some important limnological parameters were also measured in situ. The samples were analyzed using colorimetric methods and with an Atomic Absorption Spectrophotometer (AAS) for nutrients and heavy metals, respectively. Levels of temperature, pH, salinity and conductivity were ranged save for aquatic life. Mean values of dissolved oxygen and transparency ranged from 1.62±1.62 to 7.26±2.24 mg L^{-1} and from 0.55±0.43 to 2.36±0.56 m, respectively. According to our data, hypoxia was observed in urban bays, around Abidjan. The analysis of water samples showed NO_2^-, NH_4^+ and PO_4^{3-} levels of mean values 0.152±0.234, 0.857±1.095 and 0.289±0.378 mg L^{-1} and 0.096±0.128, 0.592±0.758 and 0.295±0.393 mg L^{-1} in surface and bottom zones respectively. Highest levels for NH_4^+ and NO_2^- were found in surface waters, while PO_4^{3-} recorded the highest levels in the bottom. For nutrients, significant difference ($p<0.05$) was observed between locations and seasons. The elemental toxicants Pb, Cd, Ni, Mn and Zn were identified in water of mean values 531.12±128.04, 19.19±12.35, 149.52±59.35, 92.80±22.79 and 19336.25±9960.60 μg L^{-1}, respectively. According to the WHO recommended limits, waters collected at Bingerville, farther from Abidjan, were found to be suitable. Therefore, around Abidjan, apart from Mn, waters analyzed were found contaminated by Pb, Cd, Ni and Zn, with significant difference ($p<0.05$) between locations for Pb, Cd, Ni and Zn. Apart from Ni ($p<0.001$), there was no significant difference ($p>0.05$) between seasons, due to continuous inputs of these pollutants in the lagoon through anthropogenic activities during both seasons.

Key words: Nutrients, heavy metals, domestic and industrial, untreated effluents, pollution, toxicity, Ebrie lagoon

INTRODUCTION

Water is the most important natural resource for all forms of life. It's the reason of the development of several human activities (agriculture, industry, transport, fishing, port, etc.) around water points. This also explains the high population densities observed around water sources, in general and particularly in estuaries and coastal areas. Thus, estuaries and coastal areas exhibit a wide array of human impacts (anthropogenic inputs) that can compromise their ecological integrity, because of rapid population growth and uncontrolled development in many coastal regions worldwide. Indeed, many human activities are sources of persistent pollutants that accumulate in the environment, threatening all forms of life (Sarma, 2011; Orlu and Gabriel, 2011). However, depollution of aquatic ecosystems is very expensive and unsupportable by many poor countries (Eneh, 2007; Danh *et al*., 2009). According to many studies, access to safe drinking water is an essential condition for development and fulfillment of human (Water\Health information, 2009; Stone *et al*., 2001; Earthwatch, 2009; WHO/UNICEF, 2008; Oshisanya *et al*., 2011). Therefore, water, main source of life, could rapidly become a source of death (Earthwatch, 2009; Beyersmann and Hartwig, 2008). In estuaries and costal areas, pollution by heavy metals has also been recognized as a serious environmental concern (Dural *et al*., 2007).

In Ivory Coast, since the building of the Abidjan port in 1951 (the most important in West Africa), many industries (more than 80%) are located around this city, the economic capital. These industries used to discharge their effluents in waters of the Ebrie lagoon without any prior treatment. This lack of wastewaters treatments was responsible of the progressive pollution observed in waters of the Ebrie lagoon. Thus, the urban area of the Ebrie lagoon is increasingly contaminated with toxic substances that may affect health and aquatic life (fish, crustaceans, mollusks, etc.,) (Al-Hashem and Brain, 2009). Heavy metals can be accumulated by marine organisms through a variety of pathways, including respiration, adsorption and ingestion (Zhou *et al*., 2001). The levels of heavy metals are also known to increase drastically in coastal environment through anthropogenic activities. This result either with extinction of some non tolerant species from these environments or they cause structural and functional damage to the organisms by interfering with their physiological and biochemical mechanisms. Previous work conducted in the Ebrie lagoon showed the impact of urbanization and industrialization in the environmental degradation (Metongo and Gbocho, 2007; Kone *et al*., 2008; Yao *et al*., 2009; Marcellin *et al*., 2009).

However, there are no reports available regarding the assessment of heavy metals into the Ebrie lagoon waters. The objective of this present study was, therefore, to determine nutrients (NO_2^-, NH_4^+ and PO_4^{3-}) levels and the differences in concentrations of Pb, Cd (non-essential metals) and Ni, Mn, Zn (essential metals) in samples collected in the Ebrie lagoon, around Abidjan. These concentrations were then compared with the recommended maximum levels allowed in waters. It was also to evaluate the degree of heavy metals contamination based on the calculated Contamination Index (CI) and the Mean Contamination Index (MCI). The data of some important physicochemical parameters (temperature, pH, salinity, conductivity, dissolved oxygen and transparency) were also analyzed.

MATERIALS AND METHODS

Collection of water: For this study, a total of 1728 samples were collected (for dissolved oxygen, nutrients and heavy metals) in surface and in the bottom waters of the Ebrie lagoon from February 2008 to December 2009, in eighteen (18) stations, located at a mean distance of 25 to 50 m from domestic and/or industrial inputs. Dissolved oxygen, nutrients and heavy metals were analyzed using two or three replicates per analysis. All sampling equipment were thoroughly washed, rinsed with nitric acid and then with double distilled water. Water samples were collected at surface and at the bottom, using a Niskin bottle (capacity of 2 L, graduated rope with a closing system controlled by a "messenger", allowing the collection of samples at depth). Samples were collected and stored in a cooler at 4°C for later analysis in the laboratory.

Table 1: Names and No. of the sampling stations in the Ebrie lagoon

Bay	Station	Number	Bay	Station	Number
Banco	CARENA	1	Bietri	SIR	9
	Sebroko	2		Bidet	10
	Bolibana	3		Abattoir	11
Cocody	Hotel-Ivoire	4		SIVOA	12
	BNETD	5		Marina	13
	Stade FHB	6		Unilever	14
Milliardaires	S1	15	Marcory	Grand Caniveau	7
	S2	16		Biafra	8
	S3	17	Bingerville	R	18

Location: The Ebrie lagoon has an area of 566 km^2 and stretches on 125 km along the coast of Ivory Coast, between 3°40' and 4°50' West, at latitude 5°50' North (Table 1). Its volume is estimated at 2.5×10^9 m^3, with an average depth of 4.8 m and a few pits near Abidjan (Bay Abou-Abou) that exceed 20 m (Dufour, 1982). This lagoon communicates with the Atlantic Ocean by the Vridi channel, drilled in 1951, for the building of Abidjan port, the most important in West Africa.

Physicochemical characterization: The physicochemical parameters such as pH, salinity, conductivity and temperature were measured in situ with a multi-parameter (type WTW pH/340i). Transparency was determined in situ by diving Secchi Disk. Water samples for the assessment of dissolved heavy metals were previously filtered through 0.45 µm mesh filters and acidified by adding 2 mL of concentrated nitric acid (HNO_3). This treatment was performed to prevent the development of any bacterial activity, flocculation, adsorption and reduction of pollutants on the walls on the vials.

Analysis of water samples: Dissolved Oxygen (DO) and nutrients were measured following "The Standard methods for the Examination of Wastewater", published by the American Public Health Association (APHA *et al.*, 2005). A PerkinElmer Atomic Absorption Spectrophotometer (AAS) Model 3030 with air/acetylene flame was used for analysis of the samples after preparation of calibration standards. Due to expected low concentrations of the metals in the natural water and limited instrument sensitivity, pre-concentration of the water samples was done by evaporating 100 mL of the water to 5 mL on a hot plate. The digestion of the water samples was then achieved by adding 5 mL of concentrated nitric acid (HNO_3) and heating on a hot plate for 30 min. Some 10 mL of concentrated hydrochloric acid (HCl) was added and digestion continued until the solution remained light brown or colorless. The volume was then adjusted to 25 mL with distilled water. Two and often three replicates were used for the different analysis.

The degree of metal pollution was assessed using the Contamination Index (CI) and the Mean Contamination Index (MCI). In the absence of "background levels" (natural content) without anthropogenic inputs, several authors have proposed the calculation of the index of contamination to establish the degree of contamination of a site compared to overall pollution in the whole region (Chafika *et al.*, 2001; Kaimoussi *et al.*, 2002), according to the formula:

$$CI_x(\text{metal y}) = \frac{M_x}{M}$$

where, Mx is metal mean value at station x (mg L^{-1}); M is y mean level for all stations (mg L^{-1}). Mean contamination index (MCI) was determined using the following equation in order to classify the stations:

$$MCI = \frac{\sum_{i=1}^{n} CI_x}{n}$$

where, n is the total number of metals analyzed (for the present study, n = 5).

All statistical analyzes (Mean, standard deviation, One-way ANOVA, Two-way ANOVA, etc.) were performed with STATISTICA software (2005, 7.1 Version), a complete integrated statistical data analysis, charting, database management and data-oriented applications, consisting of a wide range of analytical procedures for basic and advanced scientific applications, commercial, etc. Factorial analysis was necessary to capture the main effects and possible interactions between locations and seasons. Significant treatment means were compared using least significant difference at 5% probability level.

RESULTS AND DISCUSSION

Physicochemical parameters: The Ebrie lagoon is the main receptacle of domestic and industrial effluents, torrents of tropical rainfall, etc. Almost all of these effluents are untreated, leading to the pollution of this ecosystem. The mean values and standard deviations of some immediately measurable chemical and physical characteristic of waters were assessed. Their mean values and standards deviations are presented in Table 2. The highest mean value for temperature was recorded at Abattoir (30.41±1.87°C), while the least (28.24±2.5°C) was recorded at Stade FHB (Bay Cocody). Significant differences were observed between stations in the whole water body ($p<0.05$ and $p<0.01$ in surface and at bottom respectively). Seasonal variations of temperature were found to be significant ($p<0.001$ and $p<0.01$ in surface and at bottom waters, respectively).

Table 2: Analysis of limnological parameters in the Ebrie lagoon (n= 8)

Site	Temperature (°C)	pH	Salinity (%)	Conductivity (mS cm^{-1})	DO (mg L^{-1})	Transparency (m)
CARENA	28.66±1.77	7.36±0.79	1.19±0.94	21.10±16.10	5.15±3.58	1.75±1.56
Sebroko	28.88±1.77	7.68±0.87	1.24±0.95	21.91±16.51	5.02±5.02	0.68±0.45
Bolibana	29.00±1.85	7.57±0.70	1.24±0.96	22.16±16.63	4.19±2.61	0.64±0.52
Hotel-Ivoire	28.46±1.45	7.51±0.50	1.03±0.13	18.16±17.41	3.63±2.34	1.62±1.33
BNETD	28.64±1.87	7.44±0.51	1.07±0.11	18.99±17.39	3.20±2.47	1.21±1.07
Stade FHB	28.24±2.05	7.30±0.52	1.00±0.14	17.80±17.83	1.62±1.62	1.05±1.33
Grand caniveau	28.81±1.72	7.32±0.57	1.04±1.03	18.64±7.76	2.68±2.07	1.29±1.11
Biafra	28.74±1.63	7.34±0.59	1.18±0.97	19.42±17.08	3.57±1.90	1.25±1.27
SIR	29.73±1.20	8.10±0.58	1.44±0.97	25.44±16.22	5.30±3.40	0.65±0.48
Bidet	29.76±1.47	7.84±0.39	1.42±0.95	24.04±16.79	4.23±3.21	0.80±0.63
Abattoir	30.41±1.87	7.98±0.60	1.34±0.98	24.10±16.60	4.53±3.00	0.94±0.77
SIVOA	29.66±2.33	7.66±0.58	1.34±0.92	23.67±15.38	3.75±3.22	1.55±1.46
Marina	29.51±2.32	7.94±0.70	1.40±0.94	24.63±15.55	5.00±3.25	1.10±0.54
Unilever	29.53±2.28	7.98±0.72	1.39±0.98	24.37±16.35	4.05±2.87	0.55±0.43
S1	29.40±0.28	7.88±0.17	1.69±0.43	29.17±07.51	5.61±0.91	2.36±0.56
S2	29.65±0.07	7.66±0.13	1.78±0.53	31.50±08.49	4.37±1.24	1.56±0.82
S3	29.88±1.15	7.50±1.21	1.58±0.14	27.64±22.21	7.26±2.24	2.32±1.24
R	29.15±1.51	7.28±0.33	1.13±0.94	21.76±16.36	5.16±0.96	1.83±0.76

Values are Mean±SD, DO: Dissolved oxygen

The highest mean value for pH was recorded at SIR (8.10±0.58), while the least (7.30±0.52) was recorded at Stade FHB. The highest value of pH observed at SIR (Bay Bietri) may be due to alkahine inputs from refining of petroleum products activities, wastewaters, etc. In surface waters, pH values were not significantly different between locations ($p>0.05$), but in the bottom waters, locations were significantly different ($p<0.01$), due to their individual characteristics (depth, renewal rate, hydrodynamism, chemical characteristics of domestic and industrial inputs, etc.) (Arfi and Guiral, 1994). The pH ranges observed were appropriate for the support of aquatic life (4.50-10.00) (Yao *et al.*, 2009). The highest mean value for dissolved oxygen was recorded at S3 (7.26±2.24 mg L^{-1}), while the least (1.62±1.62 mg L^{-1}) was recorded at Stade FHB, which receives most of the untreated domestic and industrial wastewaters from the north of the city of Abidjan. In surface waters, spatial and seasonal variations of the dissolved oxygen observed were not significant ($p>0.05$). However, in bottom waters, the difference between locations was found significant ($p<0.01$). Significant differences of dissolved oxygen levels were observed between seasons ($p<0.001$), may be due to seasonal variations of loads of organic matter inputs in the Ebrie lagoon. As example, during the rainy season, runoff waters introduced many pollutants loads in the lagoon waters.

The highest mean value for salinity and conductivity was recorded at S2 (1.78±0.53%, 31.50±8.49 mS cm^{-1}), while the least (1.00±0.14%, 17.80±17.83 mS cm^{-1}) was recorded at Stade FHB, more confined and located at the end of Bay Cocody, farther from Vridi channel. In surface waters, salinity and conductivity levels were not significantly different between locations ($p>0.05$), due to the tide which causes dilution of all surface waters of the estuarine area through sea water. At the opposite, values of salinity and conductivity have significantly varied between seasons ($p<0.01$). Indeed, the highest values of salinity were observed during dry seasons, when marine waters dilute the lagoon waters. In contrast, during rainy seasons, fresh waters predominate, which leads to the decrease in salinity. The salinity mean values observed ranged from 1.00±0.14% (Stade FHB) to 1.78±0.53 % (S2), values generally encountered in the literature (Kouassi *et al.*, 2005; Yao *et al.*, 2009). In general, the stations in Bay Milliardaires, more diluted by the waters of marine origin recorded the highest values of salinity and conductivity. In contrast, the lowest values were observed at Station Stade FHB, farther from Vridi channel (Table 2). The highest mean value for transparency was recorded at S1 (2.36±0.56 m), while the least (0.55±0.43 m) was recorded at Unilever. Significant differences of transparency were observed between locations ($p<0.05$). The transparency values in Bay Milliardaires were higher than those observed in urban bays (Table 2). This was the consequence of several untreated (often colored) domestic and industrial effluents inputs into urban bays.

Nutrients

Spatial variations: The highest mean value for ammonium was recorded at Stade FHB (0.615±0.782 mg L^{-1}), while the least (0.001±0.001 mg L^{-1}) was recorded at S2 in surface waters. At the bottom, the highest mean value for ammonium was recorded at S2 (0.909±1.285 mg L^{-1}), while the least (0.001±0.001 mg L^{-1}) was recorded at S1 (Table 3). High concentrations of ammonium observed at Stade FHB were due to the high concentrations of organic matter it contains. This is confirmed by hypoxia that is observed at this station. The high levels of ammonium observed in the bottom in station S2 could be due to mineralization of a considerable amount of organic matter within the sediment, whose products diffuse into the water column. Stations were significantly different ($p<0.05$) in surface, while, at the bottom, no significant differences ($p>0.05$) were observed. For ammonium, the highest values were recorded in the waters of Bays Cocody, Marcory and Bietri. In Bay Bietri and Bay Milliardaires, concentrations of

Table 3: Mean values and standard deviations of nutrients in waters of the Ebrie lagoon (n = 8)

Nutrient		CARENA	Sebroko	Bolibana	Hotel-Ivoire	BNETD	Stade FHB	Grand caniveau	Biafra	R
NH_4^+	Surface	0.250±0.350	0.194±0.241	0.334±0.632	0.127±0.207	0.771±1.303	0.615±0.782	0.209±0.215	0.167±0.136	0.007±0.001
	Bottom	0.058±0.066	0.167±0.299	0.163±0.280	0.076±0.080	0.390±0.888	0.536±0.881	0.241±0.443	0.268±0.583	0.008±0.016
NO_2^-	Surface	0.353±0.364	0.304±0.340	0.327±0.408	0.115±0.137	0.074±0.049	0.203±0.318	0.069±0.029	0.087±0.054	0.031±0.016
	Bottom	0.037±0.024	0.068±0.086	0.161±0.174	0.100±0.079	0.114±0.079	0.135±0.104	0.074±0.040	0.113±0.085	0.032±0.013
PO_4^{3-}	Surface	0.155±0.133	0.155±0.103	0.284±0.164	0.268±0.182	0.361±0.171	0.926±0.831	0.458±0.526	0.203±0.113	0.392±0.014
	Bottom	0.201±0.120	0.173±0.150	0.200±0.077	0.190±0.157	0.196±0.109	0.639±0.629	0.409±0.505	0.214±0.099	0.395±0.022

Nutrient		SIR	Bidet	Abattoir	SIVOA	Marina	Unilever	S1	S2	S3
NH_4^+	Surface	0.109±0.174	0.287±0.481	0.282±0.401	0.220±0.365	0.051±0.069	0.358±0.926	0.004±0.002	0.001±0.001	0.003±0.001
	Bottom	0.0071±0.145	0.578±1.042	0.267±0.386	0.273±0.342	0.106±0.163	0.189±0.340	0.001±0.001	0.909±1.285	0.056±0.090
NO_2^-	Surface	0.183±0.209	0.177±0.183	0.196±0.222	0.246±0.341	0.201±0.223	0.193±0.189	0.215±0.296	0.006±0.002	0.144±0.231
	Bottom	0.098±0.130	0.166±0.219	0.176±0.206	0.139±0.185	0.230±0.218	0.111±0.090	0.079±0.105	2.327±3.279	0.071±0.037
PO_4^{3-}	Surface	0.283±0.337	0.459±0.524	0.327±0.259	0.304±0.162	0.247±0.169	0.418±0.249	0.067±0.110	0.027±0.038	0.307±0.528
	Bottom	0.996±0.517	0.414±0.389	0.309±0.238	0.250±0.121	0.227±0.144	0.472±0.512	0.359±0.474	0.191±0.131	0.146±0.203

Values are Mean±SD

ammonium in surface waters are slightly different from those determined in the bottom (Table 3). This profile could be the consequence of the hydrodynamics in these bays located near Vridi channel therefore influenced by the tide. Ammonium is the reduced form of nitrogen and generally dominant at the bottom, in correlation with the vertical profile of dissolved oxygen in estuaries and coastal areas. The opposite profile was often observed here, that might reflect the input of nutrients in lagoon waters through rainy waters and domestic effluent. Apart from Bay Milliardaires, most of ammonium levels were higher than the recommended limit of 0.2 mg L^{-1} (WHO, 2004) (Table 3).

At surface, the highest mean value for nitrite was recorded at CARENA (0.353±0.364 mg L^{-1}), while the least (0.006±0.002 mg L^{-1}) was recorded at S2. In the bottom waters, the highest mean value for nitrite was recorded at S2 (2.327±3.279 mg L^{-1}), while the least (0.037±0.024 mg L^{-1}) was recorded at CARENA. Stations were not significantly different in surface waters ($p>0.05$), but, at the bottom, significant differences were observed ($p<0.05$). The highest content of nitrites observed in bottom waters at S2 (Bay Milliardaires) is the consequence of increased urbanization of the watershed during the period of the present study. The mineralization of high organic matter contents introduced may be responsible of the peak of nitrite observed at this station.

The highest mean value for ortho-phosphate was recorded at Stade FHB (0.926±0.831 mg L^{-1}), while the least (0.027±0.038 mg L^{-1}) was recorded at S2 in surface waters. At the bottom, the highest mean value for ortho-phosphate was recorded at SIR (0.996±0.517 mg L^{-1}), while the least (0.146±0.203 mg L^{-1}) was recorded at S3. A non-significant spatial variation was observed for ortho-phosphate in surface waters. In the bottom waters, the difference for ortho-phosphate between locations was significant ($p<0.05$). The highest levels of the ortho-phosphate were observed at sites located in Bays of Cocody and Bietri, due to massive domestic and industrial inputs. The Bay Milhardaires was distinguished from the urban bays with very low levels for ortho-phosphate. The significant fraction of ortho-phosphate in the Ebrie lagoon might be due to domestic effluents, introduced into the lagoon without prior treatment. We have reasons to be very concerned because these levels were similar to those observed in eutrophic waters, therefore unsuitable for aquatic life (WHO, 2004).

Seasonal variations: Results of seasonal variations of nutrients are presented in Table 4. The highest mean values for ammonium were recorded during the Long Rainy Season (LRS) (1.65±1.14 and 1.41±1.00 mg L^{-1}) in surface and bottom waters, respectively. The lowest mean values were

Table 4: Results of seasonal variations of nutrients in waters of the Ebrie lagoon (mg L^{-1}, n=8)

Nutrient		LDS	LRS	SDS	SRS
NH_4^+	Surface	0.54±1.14	1.65±1.14	1.12±0.83	0.43±0.48
	Bottom	0.23±0.35	1.41±1.00	0.55±0.28	0.34±0.36
NO_2^-	Surface	0.05±0.14	0.17±0.19	0.35±0.28	0.16±0.28
	Bottom	0.06±0.08	0.11±0.12	0.16±0.18	0.10±0.14
PO_4^{3-}	Surface	0.21±0.23	0.44±0.43	0.49±0.61	0.13±0.18
	Bottom	0.26±0.33	0.42±0.47	0.31±0.33	0.19±0.39

LDS: Long dry season, LRS: Long rainy season, SDS: Short dry season, SRS: Short rainy season, Values are Mean±SD

recorded during the short rainy season (0.43±0.48 mg L^{-1}) in surface and during the long one (0.23±0.35 mg L^{-1}) in bottom waters. For nitrite, the highest mean values were recorded during the Short Dry Season (SDS) in the whole depth (0.35±0.28 and 0.16±0.18 mg L^{-1} in surface and in the bottom, respectively). Lowest values for nitrite were recorded during the Long Dry Season (LDS), with respective levels of 0.05±0.14 and 0.06±0.08 mg L^{-1} in surface and in bottom waters.

In surface waters, the highest mean value for ortho-phosphate was recorded during the short dry season (0.49±0.61 mg L^{-1}), while the least (0.13±0.18 mg L^{-1}) was recorded during the short rainy season (SRS). In bottom waters, the highest mean value for ortho-phosphate was recorded during the Long Rainy Season (LRS) (0.42±0.47 mg L^{-1}), while the least (0.19±0.39 mg L^{-1}) was recorded during the short rainy one. Apart from the ortho-phosphate levels in the bottom waters, significant differences ($p<0.05$) for nitrite in bottom waters, $p<0.001$ elsewhere) were observed between seasons, due to runoff loads added which varied seasonally.

In general, the highest nutrients concentrations were observed during the Long Rainy Season (LRS) and Little Dry Season (LDS). During the long dry season, nitrite levels were found highest in the bottom waters. This could be explained by the lowest concentrations of dissolved oxygen often observed in those bottom waters, unfavorable condition for the completion of the nitrification process. In fact, in oxygenated water, nitrite ions are finally oxidized to nitrate ions.

Indeed, each station has its own characteristics (location, depth, fluxes of the domestic and industrial effluents, nature of the watershed, etc.). For example, the waters were enriched with nutrients during the Long Rainy Season (LRS) compared with the Long Dry Season (LDS) and the short rainy one. This could be explained by the fact that during the long rainy season, runoff waters from watersheds often contain high organic and inorganic loads, finally introduced into the lagoon. It is well known that the mineralization of organic matter is an important source of nutrients in areas with low hydrodynamics, as it's observed in the closed bays into the Ebrie lagoon. Finally, the seasonal patterns of nutrients depend on several processes (effluent nature, mineralization rate of organic matter, intensity of photosynthesis, dissolved oxygen profile, rate of water renewal, etc.). In addition, a significant proportion of nutrients in the lagoon Ebrie had anthropogenic sources (Arfi and Guiral, 1994; Yao *et al*., 2009).

Heavy metals: Knowledge about heavy metals concentrations in water body is very important both with respect to environment management and human consumption. In the present study, the levels of heavy metals (Pb, Cd, Ni, Mn and Zn) of eighteen different locations are presented in Table 5.

The highest value of Pb (670.0±5.0 μg L^{-1}) was recorded in S2 and the least (75.2±1.7 μg L^{-1}) in R. Cd has the highest value (47.5±37.5 μg L^{-1}) in S3 and the least (3.0±1.6 μg L^{-1}) in R. Ni has the highest value (262.5±57.5 μg L^{-1}) in S3 and the least (21.5±2.38 μg L^{-1}) in R. The maximum for Mn (130.0±25.0 μg L^{-1}) was observed in S3 and the minimum value (38.0±2.5 μg L^{-1}) in R,

Table 5: Levels of heavy metals in the different locations of Ebrie lagoon (μg L^{-1}, n = 8)

Site	Pb	Cd	Ni	Mn	Zn
CARENA	575.0±95.0	22.5±2.50	197.5±87.5	112.5±7.50	26390.0±30.00
Sebroko	575.0±45.0	12.5±2.50	137.5±47.5	110.0±10.0	28947.5±6947.5
Bolibana	547.5±47.5	12.5±2.50	165.0±75.0	102.5±7.50	28002.5±3792.5
Hotel-Ivoire	590.0±15.0	12.5±2.50	157.5±7.50	100.0±25.0	14662.5±2757.5
BNETD	477.5±52.5	12.5±2.50	110.0±60.0	80.0±5.00	25785.0±4195.0
Stade FHB	485.0±80.0	15.0±5.00	112.5±67.5	85.0±20.0	12705.0±2735.0
Grand Caniveau	510.0±65.0	15.0±5.00	120.0±40.0	115.0±15.0	21252.5±14522.5
Biafra	535.0±90.0	40.0±20.0	135.0±65.0	92.5±22.5	39315.0±7765.0
SIR	625.0±50.0	32.5±12.5	230.0±15.0	127.5±22.5	23187.5±1342.5
Bidet	620.0±55.0	10.00±0.02	122.5±47.5	97.5±22.5	21940.0±6095.0
Abattoir	480.0±10.0	12.5±2.50	117.5±2.50	80.0±25.0	30895.0±1254.0
SIVOA	492.5±27.5	12.5±2.50	130.0±30.0	82.5±17.5	18005.0±2650.0
Marina	545.0±10.0	12.5±2.50	145.0±35.0	75.0±15.0	6405.0±4865.0
Unilever	512.5±17.5	12.5±2.50	97.5±27.5	77.5±2.50	20512.5±5717.5
S1	607.5±32.5	20.0±10.0	170.0±5.00	65.0±15.0	9210.0±3165.0
S2	670.0±5.00	40.0±10.0	260.0±30.0	100.0±20.0	13217.5±4982.5
S3	637.5±57.5	47.5±37.5	262.5±57.5	130.0±25.0	6205.0±6050.0
R	75.2±1.70	3.0±1.60	21.5±2.38	38.0±2.50	1415.0±85.0

Values are Mean±SD

Table 6: Two-way ANOVA of heavy metals in different locations and seasons

	Pb		Cd		Ni		Mn		Zn	
Heavy metals	F	p-value	F	p-value	F	p-value	F	p-value	F	p-value
Locations	10.2940	0.0000	1.4421	0.1774	5.5979	0.0000	1.1256	0.3694	3.6437	0.0005
seasons	3.3370	0.0760	2.5503	0.1195	19.8361	0.0000	0.0913	0.7642	1.8193	0.1858

while Zn has highest value (39315.0±7765.0 μg L^{-1}) recorded in Biafra and the lowest value (1415.0±85.1 μg L^{-1}) in R. In general, heavy metals concentrations (Pb, Cd, Ni, Mn and Zn) were lower in R, close to the city of Bingerville. The heavy metals concentrations for Cd, Ni and Mn were higher in S3, nearby the boats cemetery and located in Bay Milliardaires. In Bay Bietri, highest levels for Pb, Cd, Ni and Mn were observed in SIR. Highest values of these elements observed at SIR could come from the refining of petroleum products. The lowest values of all heavy metals observed at R were due to its location farther from Abidjan. Also, the highest values of heavy metals observed in Bay Milliardaires may be the consequence of many construction jobs made in recent years, without any sanitation system. In Bay Marcory, the highest levels for Pb, Zn, Ni and Cd were recorded at Biafra. These highest values observed for these metals were the result of many activities effluents (car repair shops, car wash, etc.) conducted without control over the watershed at the station. Highest levels of Pb and Zn were observed at S2 and at Biafra respectively. Highest concentrations of zinc observed could affect reproductive capacity of some organisms such as fishes, oysters and larval growth (Osman *et al*., 2009).

Two-way ANOVA variance analysis was used to capture the main effects and possible interactions between locations and seasons. Results were presented in Table 6.

Significant variations were found between locations for heavy metals ($p<0.001$) apart from Mn. This is due to the fact that the effluents discharged into the water depend on the position of each station.

Table 7: Values of the concentrations of heavy metals compared with the limits of WHO and those determined by other authors (μg L^{-1})

References	Pb	Cd	Ni	Mn	Zn
WHO (2004)	10	3.0	20	400	3000
Burrel (1974) (TC)	100	10	NL	NL	100
Chan (1995)	40-440	8-109	NL	NL	24-403
Oguzie (2003)	82	NL	244	417	127
Obasohan (2007)	70	NL	141	195	24
Ochieng (2007)	25-563	2-43	nd-288	49-282	40-235
Range of this study	75.2-670.0	3.0-47.5	21.5-262.5	38.5-130	1415-39315

NL: Not in literature cited, nd: Not determined, TC: Threshold concentration for aquatic life tolerance (safe for most fishes)

Seasonal variations for heavy metals were found significant for Ni only ($p<0.001$). This is perhaps due to the fact that industrialization, fertilizers usage in agricultural could cause Ni to be leached into estuaries through runoff.

Levels of heavy metals observed in this study were compared to those observed in other waters and with the WHO recommended limits (Table 7). On the basis of our data, waters around Bingerville were suitable according to WHO recommended limits (WHO, 2004). For this study, according to WHO, only levels for Mn were save for aquatic life. The levels of Pb in waters of the Ebrie lagoon were higher than the guideline value (10 μg L^{-1}) (WHO, 2004). Our values were six times higher than those determined by Oguzie (2003) in Ikpoba River in Niger. They were against comparable with values found in the waters of Victoria Harbor in Hong Kong (Chan, 1995) and some lakes of Kenya (Ochieng *et al*., 2007). Lead is particularly toxic since no beneficial effect is noted in the literature regarding the metabolism of living.

For Cd, most levels were higher than those found in lakes of Kenya and the WHO guideline value of 3.0 μg L^{-1} (NPC and UNICEF, 2001; WHO, 2004; Ochieng *et al*., 2007). However, the values determined by Chan (1995) in the waters of Victoria Harbor (Hong Kong) were twice elevated than the values of this study. The waters of the Bay Milliardaires (nearby boats cemetery) were most contaminated for nickel (Table 5). Organic forms of nickel ($Ni(CO)_4$, etc.) are the most toxic and cause respiratory, digestive and skin irritation. Indeed, Cd, Pb and Ni are among heavy metals that are carcinogenic to human or considered to be carcinogenic to human by International Agency for Research on Cancer (Beyersmann and Hartwig, 2008; Sarma, 2011).

Mn levels (38.5-130.0) observed in this study were lower than those determined in other waters (Oguzie, 2003; Ochieng *et al*., 2007; Obasohan *et al*., 2007) (Table 7).

Zinc concentrations levels were generally higher than the WHO limit value (WHO, 2004) (Table 7). Zinc is an essential element for the metabolism of living beings. However, it becomes toxic at high concentrations. Our values were found higher than those determined in other waters (Chan, 1995; Oguzie, 2003; Ochieng *et al*., 2007; Obasohan *et al*., 2007) (Table 7). According to Burrel (1974), the Ebrie lagoon waters were not save for many marine species (Table 7).

Degree of metal pollution of the different stations: The degree of metal pollution of the stations is evaluated by the determination of Contamination Index (CI) and the Mean Contamination Index (MCI). The results were presented in Fig. 1.

According to the data, apart from station R, located at Bingerville and farther from direct input of wastes waters, heavy metals contamination was effective elsewhere. Highest contamination index for lead were recorded in stations S1, S2, S3, SIR, Bidet and Hotel-Ivoire. For cadmium,

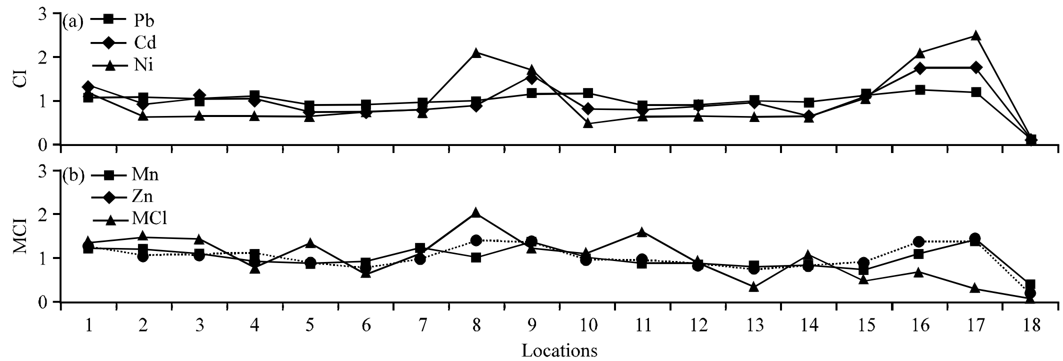

Fig. 1(a-b): Variations of (a) Contamination indexes (CI) and (b) Mean contamination index (MCI) of heavy metals

waters were most contaminated in stations S3, Biafra, S2 and SIR. Waters were more contaminated by nickel in stations S3, S2, SIR, CARENA, S1, Bolibana and Hotel-Ivoire. Highest levels of manganese contamination indexes were recorded in stations S3, SIR, Grand-caniveau, CARENA, Sebroko and Bolibana. Highest levels of zinc contamination indexes were recorded in stations Biafra, Abattoir, Sebroko, Bolibana, CARENA, BNETD, SIR, Bidet, Grand-caniveau and Unilever. Mean contamination indexes (MCI) observed were consistent with the results of the study of spatial contamination with a gradient of pollution close to that of the mold and respecting the following descending rank: S3>Biafra> SIR>S2>CARENA>Sebroko>Bolibana>Grand-caniveau>Abattoir> Bidet>Hotel-Ivoire>BNETD>S1>SIVOA>Unilever>Stade FHB>Marina>R. This ranking reveals that the waters were most contaminated in areas with high levels of domestic and industrial discharges.

CONCLUSION

Nutrients, heavy metals and some physicochemical parameters were analyzed during this study. With regards to the objectives of this research and results obtained, this current study has provides useful information and a baseline for future along with continuous studies on nutrients and heavy metals in waters in the Ebrie lagoon. According to WHO, levels of temperature, pH, salinity and conductivity were save for aquatic life. However, the values of transparency, dissolved oxygen and nutrients were comparable to the values of eutrophic waters. Waters analyzed in urban bays were found least oxygenated, with situations of hypoxia observed especially in confined areas, where the water renewal rate remains low. This situation was unsuitable for any aquatic life. For both nutrients, significant differences ($p<0.05$) were observed between locations and seasons. This reflects the contribution of various pollutants, including nutrients from different watersheds by runoff during the rainy seasons. A significant difference ($p<0.05$) was observed between locations for Pb, Cd, Ni and Zn, in contrast to Mn for which the locations were not found significantly different ($p>0.05$). Apart from Ni, no significant difference was observed between seasons ($p>0.05$). Highest levels of heavy metals found in samples collected in urban bays were mainly due to anthropogenic inputs from the city of Abidjan. Due to socio-economic and ecological roles of the Ebrie lagoon, we have reasons to be very concerned, according to the data obtained. Finally, considering the toxicity of heavy metals, traditional fishing products (fish, crustaceans, mollusks, etc.) must be controlled before their consumption, in order to protect consumers.

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