Evaluation of the Impact of Brewery Effluents on the Water Quality of the Congo River

Stéphane Mbuyamba¹, Marc klesh Maya vangua², Pascal Disa-Disa³, Odon Kupesa⁴, Crispin Mulaji⁵, Fifi Muderhwa⁶, Athanase Kusonika⁷, Sikulisimwa Céline⁸

E-mail: celine.sikulisimwa[at]unikin.ac.cd

^{1, 2, 3, 4, 5, 6, 8}Department of Chemistry, University of Kinshasa, B.P.190, Kinshasa XI, Democratic Republic of the Congo

⁷Department of the Environment, University of Kinshasa, B.P.190, Kinshasa XI, Democratic Republic of the Congo

Abstract: The overall characterization of the raw effluent and the receiving water at the discharge point, Congo River, gave the following results: $pH 12.62 \pm 0.22$ and 11.49 ± 0.61 ; $COD (mgO_2/L) 1287 \pm 51$ and 1180 ± 41 , $BOD_5 (mgO_2/L) 677 \pm 41$ and 531 ± 67 ; $PO_4^{3-} (mg/L) 14.11 \pm 1.70$ and 13.13 ± 1.91 ; $NH_4^+ (mg/L) 27.18 \pm 2.20$ and 23.48 ± 5.02 ; Electrical conductivity (at $20 \circ C$, μ S): 16166.2 \pm 7569.5 and 10292.5 \pm 3973.2; O_2 dissolved (mg/L): 0.88 ± 0.20 and 1.06 ± 0.22 ; $T(\bullet C)$: $29.4 \pm 1.3 \bullet C$ and $28.5 \pm 1.2 \bullet C$. Toxicity testing with Gambusia affinis fish revealed 4.8 mL LL50 and 13.5 mL for crude effluents and receiving waters at the point of release. These results show that crude effluents and receiving waters are toxic to the aquatic ecosystem. They must be monitored, adequately processed and regulated in order to preserve aquatic ecosystems at the point of discharge.

Keywords: freshwater, industrial discharges, Gambusia affinis, aquatic ecosystem, lethal dose

1. Introduction

The problem of industrial waste, which is becoming increasingly complex and serious, is one of the most worrying aspects that only degrades the natural environment and constitutes a real danger for the future of humanity [2], [7], [9], [16]).

The rivers, and particularly the Congo River, continually undergo pressure from industrial discharges. Rivers receive diverse inputs from their watershed, and through a multitude of processes, these inputs are metabolized, stored or processed into nutrients and other organic matter. This natural recycling can be modified by the additional inputs related to anthropogenic activities. The morphology of the rivers, the alternation of facies, the diversity of the substrate, the flow rate, the residence time are all elements that have an impact on the characteristics of the environment and on the fate of nutrients in the watercourse ([9], [13], [29]).

The evolution of discharges into a river can be summarized as deposits, organic matter dilution and organic matter transformation. [2] Living organisms (micro-organisms, plants, animals, insects, Men) derive the substances they use to nourish, develop, multiply and move in these natural environments. The physicochemical conditions generated in these environments, by external inputs, will determine whether a species can reproduce and develop ([16], [27]).

The quality of rivers, the receiving environment, is determined by parameters that play an important role in life in rivers and in public health [13]. Brewing companies, which in terms of the volume of wastewater emitted, are the 3rd place among the agro-food companies according to Valiron [10], are responsible for carbon pollution. Current investments and the modernization of the "Will lead to an increase in the volume of discharges on the Congo River. The total water consumption to produce 1 L of beer is 6.30 L of water ([10], [30])

The volume and composition of industrial effluent varies with the nature of the activity and internal measures taken to minimize the amount of discharges. Industrial effluents consist of process water, water and washing products (detergents, etc.), and sometimes non-compliant products (beverage manufacturing). The impact of releases on our environment can be assessed in the light of temperature increases, changes in pH, oxygen consumption of the environment and the specific effects inherent to each pollutant. This leads to changes in the balance of ecosystems ([27], [29]).

In the Democratic Republic of Congo; there is a law which lays down the general principles on the protection of the environment and the classification of industrial, commercial and agricultural installations according to the seriousness of the danger, inconvenience or inconvenience which may arise from its existence or exploitation [17] Put in place specific laws, services better equipped to monitor and control on the ground (companies, agricultural land, hotels, etc.) and to identify environmental problems.

Industrial waste is therefore the source of serious pollution problems. It is important to know the source, nature and composition of releases (type and concentration of pollutant) in order to predict the consequences on receiving environments. A discard monitoring policy should be developed; and the varied effects of these releases on aquatic fauna and flora at the point of discharge should also be investigated and documented.

In developed countries, the point of discharge is determined in such a way as to minimize the effects of discharges on receiving waters, to avoid obstructing the flow of water (for small rivers), preventing erosion of the bottom or banks, ensuring the clearing of deposits and limiting their formation. Companies need to take this into account ([5], [16]). In our country, there are no specific laws dealing with the characteristics of discharges or the conditions for discharging them into the Congo River.

From the ecotoxicological point of view, the overall toxicity of an effluent integrates the effects of all the contaminants present in this effluent. It represents the toxic potential of an effluent for aquatic life. Toxicity measurements are based on standardized tests carried out by exposing aquatic organisms to an effluent and predetermined dilutions of that effluent. This measure detects the presence of toxic contaminants and takes into account the combined effect of all substances present in the effluent. By comparing the environmental release limits with the technological rejection limits of the treatment systems, rejection standards can be established ([15], [20], [21], [31]).

In the Democratic Republic of the Congo, the regulation and monitoring of discharges and releases is an issue that remains complex and topical to date. This study consisted of characterizing the brewery effluents and receiving waters at the point of discharge and assessing the environmental impact of brewery discharges on the quality of the Congo River waters at the point of discharge using a biological test fishes).

2. Materials and Methods

2.1 Experimental site and sampling

We conducted our study at Lomata Harbor located at 04 $^{\circ}$ 18'34.20 South latitude and 15 $^{\circ}$ 19'52.3 East longitude on the left bank of Malebo Pool in Kinshasa. This port serves as a discharge point for brewery effluents for more than 50 years. Samples taken instantly from new and cleaned plastic bottles are packaged in a cooler at about 4 $^{\circ}$ C before being sent to the laboratory. The samples are taken twice a month during the period from October to December 2015 and 2016. The samples are taken between 7:00 and 12:00 in the morning. For metals, samples are acidified with 2 mL of concentrated HNO₃.

Gambusia affinis fish, used as test individuals for wastewater and receiving water pollution, were collected from the YOLO River and stored in a basin containing river water 24 hours before testing.



Figure 1: Mapping of experimental site

Legend

Red circle: The point of discharge of the brewery effluents located in the port on the Congo River

Blue Circle: The brewing company whose discharge management leads to a Lomata port

2.2 Physicochemical parameters

Physico-chemical parameters analyzed in situ are temperature, conductivity and salinity, pH, dissolved O_2 ; And in the laboratory: COD, BOD₅, NH₄⁺, PO₄³⁻, ([11], [13], [18]).

The methods used for this study were based on the AFNOR standards [13]. Below is the table which shows the measured parameters as well as the devices used. Pollution indicator parameters Standards Materials and methods

Paramètres indicateurs de pollution	Normes	Matériels et méthodes		
рН	NFT 90008	pH meter OHAUS / ST20 ,PH-meter water proof-hi 98130), / Potentiometry		
Conductivity	NFT 90031	Waterproof conductivity meter hi 98130 / HANNA / Resistivity		
O ₂		Oxymetry / HANNA / Electrochemical		
BOD ₅		BODTrak ™ II / HACH / Respirometry		
COD		Kit DCO / HACH		
Ammoniacal nitrogen (NH4 +)	NF T90- 015-2	Kit for NH4 + / HACH / spectrophotometry		
Phosphates (PO ₄ ³⁻)	NF EN ISO 6878	Kit for Phosphates / HACH / spectrophotometry		
Nitrites (NO ₂)		Kit for Nitrites / HACH / spectrophotometry		
Nitrates (NO_3^-)	ISO 7890-3	Kit for Nitrates / HACH / spectrophotometry		
Métaux lourds		kit for each cation / HACH / spectrophotometry		

2.3 The Biological Test

The Gambusia affinis used for assessing the toxicity of the effluent at the point of discharge was fished in the YOLO River in the Ngaba Rond Point valley at the bottom of the Mungulu Diaka Bridge, A landing net fabricated and stored in a basin containing river water. These fish are transported to the hydrobiological laboratory of the Department of Biology of the University of Kinshasa for identification and the acute toxicity test ([8], [13], [36]).

2.3.1 Identification of fish species

The identification was made using the key of Lévêque and Paygy (1999)



Figure 2: Gambusia affinis

According to the keys, these fish belong to the following Classification: Phylum: Chordes Under phylum: vertebrata Class: fish Subclass: Teleostoma Super-order: Teleosteens Order: Cyprinodontiformes Family: Poeciliidae Genre: gambusia Species: gambusia affinis(Baird &

Girard, 1853).

2.3.2 Toxicity Test

- a) Preparation of diluted solutions at different concentrations
 - Pick 100, 75, 50, 25, 1 and 0.5 mL of the crude effluent, respectively, and place in 100 mL volumetric flasks and make up to 100 mL with distilled water if necessary.
 - The different solutions are labeled as follows: T1 (100% of the raw or mixed effluent), T2 (75% of the crude effluent or mixing water), T3 (50% of the crude effluent or Mixing water), T4 (25% crude effluent or mixing water), T5 (1% crude effluent or mixing water), and T6 (0.5% crude effluent Or mixing water) for each sample taken.
 - Water from the YOLO River is used as a T control (100%).
- b) Place five specimens of Gambusia affinis in a series of vivariums or cups containing 100 mL of the diluted solutions of each sample. So we have 7 vivariums per sample, including the undiluted sample and the control. For the same concentration, we have 5 vivariums. We observe and note for each vivarium the following manifestations:
 - The taking of oxygen from the air at the surface of the vivarium;
 - Loss of mobility in swimming;
 - Fish mortality

Gambusia affinis dead are immediately removed from the solution. The duration of the test is 4 days according to the acute toxicity test.



Figure 3: The vivarium series for the biotest test

Legend

Tumbler containing test fish and different solutions. The species used in ecological tests are selected on the basis of their sensitivity to contaminants, their important role in the food chain, knowledge of their taxonomy, short breeding duration, easy laboratory breeding, the possibility of developing Biomarkers [8]. We chose Gambusia affinis.

3. Results and Discussion

3.1 Analyses physico-chimiques

We present the results of the various measurements and analyzes in the form of samples of samples marked EBrut (raw effluents) and ExmG / PR (samples taken at a distance x meters from the discharge point and in the direction G with respect to the discharge point PR:







Figure 5: Evolution of the pH in the plume

Figure 4 shows that the effluent temperature does not significantly alter the temperature of the water at or near the point of discharge. Temperature is not an unfavorable parameter for the aquatic ecosystem at the point of discharge ([23], [28]). Temperature also plays an important role in the solubility of certain CO_2 and O_2 gases present in water [13].

Figure 5 shows that the pH of the effluent and the pH of the river waters at the discharge point are very alkaline, but beyond 10 m, the pH returns to the norm (6.5-8.5). Because pH and dissolved O_2 are the key parameters of water quality for aquatic life ([21], [24]), effluents and receiving waters at the point of discharge will have a detrimental effect on aquatic life. For fish, the pH range (6.49-7.09) corresponds to the optimum breeding area for many species, but some species of fish may die at pH (> 9), and some algae are destroyed for Basic pH values (> 8.5) [27]. Aquatic life is threatened by effluent and water at the point of release.



Figure 6: Evolution of conductivity in the plume

Figure 6 shows that effluents and waters at the point of discharge have very high conductivities, conductivity> 3000 μ s / cm which are those of brackish or saline waters [13]. As a result of dilution during the rainy season, we found low conductivity values of the receiving water above 10 m from the discharge point (30 <conductivity <100 μ s / cm). As the solubility of dissolved O2 is affected by salinity, we find very low O2 values for effluents and receiving waters at the discharge point ([13], [24], [27]).



Figure 7: Evolution of the chloride content in the plume

Figure 7 shows that high chloride levels for effluent and receiving waters at the discharge point. Chlorides, present naturally in water, are toxic to plants especially at high concentrations (> 200 mg / L Cl^{-1}), especially for algae [32]. Both samples will be highly toxic to fish.



Figure 8: Evolution of organic load





Figure 8 shows, for all samples, the high COD and BOD₅ values in the effluent and in the receiving waters (at and near the discharge point). These values reveal the nature of the substances present in these effluents. Indeed, the brewery effluents contain the must, the syrup, the graze, the limestone (brewing room) and the cold (fermentation cellar), detergents, surfactants, cleaning waters, waste products As well as the beer and the yeast purged from the fermentation tanks ([6], [30]). For a shallow zone with a low flow velocity, suspended solids are deposited and sometimes resuspended by the movement of barges and pushers. Loss targets should be determined not only by the loss of profit but also the environmental impact that would result from these losses.

Figure 9 shows that the concentration of NH_4^+ ions and PO_4^{3-} is high in the crude effluent (27.18 mg / L on average) and in recipient waters at the discharge point (23.48 mg / 1 on average), And the dilution, away from the point of discharge, does not bring these concentrations back into the standard. These nutrients lead to a proliferation of algae and photosynthetic micro-organisms (eutrophication) which reduce the penetration of light into deep water layers ([11], [14], [16], [21]).

 NH_4^+ ions are normally generated by the mineralization of organic matter (proteins, amino acids, urea ...). Ammonia nitrogen usually translates into a process of incomplete degradation of organic matter. NH_4^+ is generally rapidly absorbed by aquatic organisms but may be present in large quantities in water polluted with organic matter and low in oxygen. The NH_4^+ ion is not detrimental, but under certain conditions of pH and temperature, ammonia (NH_3) is a water-soluble gas which is toxic to aquatic life [13], [16]). The high pH values of the receiving water at the point of discharge will result in the formation of NH_3 and therefore fish mortality ([8], [13]).



Figure 10: Evolution of the nitrate and nitrite content in the plume

As for PO_4^{3-} ions, they result from the degradation by bacteria of organic phosphates originating in particular from the discharge of wastewater (metabolism, washing powders, agro-food and chemical industries, etc.) and the use of fertilizers. Phosphates can be assimilated by plants and photosynthetic organisms [16].

The raw materials used in brewing also contain a great deal of organic matter which affects COD and BOD5 and, at the same time, induces an O_2 deficiency dissolved in this part of the Congo River. We find, unfortunately, that the values of

the organic load found to date are close to the values found by Kabale Ngiefu and Munginda Yong twenty-two years ago for brewery effluents: BOD5 = $690 \pm 184.32 \text{ mgO}_2 / \text{L}$ And COD = $993 \pm 188.77 \text{ mgO}_2 / \text{L}$ [22]. When organic matter is sedimented, oxygen consumption on and near the bottom can lead to anaerobic conditions (<2 mg / L) [33].

The results of FIG. 10 indicate that the concentration of the NO_3^- and NO_2^- ions in the different samples is less than 2 mg / L. Concentrations of these naturally occurring ions in surface and groundwater are generally a few milligrams per liter according to Nada [24].



Figure 11: Evolution of the nitrate and nitrite content in the plume

Figure 11 shows that the highest value of dissolved oxygen is 2.66 mg / L away from the discharge point (83 m). Raw effluents and receiving waters have a significant dissolved oxygen deficit of 0.88-1.06 mg / L, respectively.

We know that dissolved O_2 values below 1 mg O_2 per liter lead to a near-anaerobic state [11]. These values, which are close to 1 mg O_2 per liter, lead to the release of H_2S , CH_4 and NH_3 , which are foul-smelling and contribute to the greenhouse effect. It should be noted that H_2S , at certain concentrations, produces strong odors, has health effects (irritation of the eyes, lung lesions) and can lead to death in some cases [35].

It should be noted that the anaerobic state occurs when the oxidation processes of mineral waste, organic matter and nutrients consume more oxygen than the available one. The high organic charge would justify the low oxygen content in this part. A low dissolved oxygen content can cause an increase in the solubility of toxic elements that are released from sediment. Levels of 4 to 6 mg O₂ per liter are characterized by good quality water, and susceptible fish species can be disturbed by an oxygen content of less than 4 mg / 1. This discharge point is highly polluted by beer effluents ([4], [24]). Sediment analysis at this point is necessary..



Figure 12: Evolution of the content of trace elements



Figure 13: Evolution of the calcium content

FIG. 12 shows that the metallic elements are present at low concentrations (<2 mg / L). Elements such as Fe, Mn, Zn and Cu are micronutrients, the absence of which would interfere with function or prevent the development of aquatic organisms. For fish, doses of 0.5 to 5 mg.L-1 of zinc are permitted, but doses of 150 and 650 mg / L of zinc are toxic to humans [26]. The content of the various chemical elements analyzed, mostly in the standard, will not affect aquatic life at this point of the river.

The high Ca^{2+} concentration in the samples, see Figure 13 above, is beneficial to fish life [27]. Calcium is an input in the manufacture of beer ([6], [30]).



Figure 14: Evolution of the suspended matter content in the plume

Figure 14 shows very high levels of suspended solids in effluent and receiving waters at the discharge point. Concentrations> 150 mg / L suspended solids for receiving waters at the point of discharge may be considered as pollution of the receiving environment by the brewery

effluents. Suspended matter causes the formation of a large layer of deposits at the point of discharge where the flow of water is slowly increasing. Suspended materials can accumulate high amounts of toxic materials (metals, pesticides, mineral oils, polycyclic aromatic hydrocarbons, etc.). They also hinder the respiration of fish [24].

For fish, in normally populated rivers, it can be considered that from 75 mg / L the situation becomes alarming. Higher grades can prevent light penetration and thus reduce dissolved oxygen, compromise egg development, reduce the available food supply and thus limit fish development by creating imbalances between species. The asphyxiation of fish, by clogging the gills, is often the consequence of a high

content of suspended matter, especially at the time of periodic drainage of dams ([14], [27]).

3.2 Résultats du biotest

The overall toxicity of an effluent integrates the effects of all the contaminants present in this effluent. It represents the toxic potential of an effluent for aquatic life ([13], [20]).

The results of the various toxicity tests of Bralima effluents and mixing water at the point of discharge with the Congo River at the point of discharge are given in the tables and figures below:

Table II : Number and percentage of survivors of Gambusia affinis in the Bralima crude effluent

DILUTIONS	N-5	5 OBSERVATIONS				Nbre morts	04 MODIE	04 SUDVIVANTS	
E brut	IN-3	JOUR 1	JOUR 2	JOUR 3	JOUR 4		% WOR15	70 SUK VIVANIS	
T1	5	5	-	-	-	5	100	0	
T2	5	5	-	-	-	5	100	0	
T3	5	5	-	-	-	5	100	0	
T4	5	5	-	-	-	5	100	0	
T5	5	0	1	1	-	2	40	60	
T6	5	0	0	0	1	1	20	80	
	35	20	1	1	-	23	66	34	
Т	5	-	-	-	-	0	0	100	

Table 1 shows that the Bralima crude effluent is toxic in T1, T2, T3 and T4 treatments with 0% survivors observed in each of the concentrations. We then note that for the T5 sample we have 60% of survivors and for the T6 sample a rate of 80% of survivors. Note that for the control solution, the survivors' rate is 100%. For crude effluents, experience shows a death rate of 66% for a survival rate of 34%. These calculations and diagrams are done with the Origin Pro-8 software and we were able to calculate the LD50.



Figure 15 : Evolution of the number of survivors of Gambusia affinis in Bralima crude effluent dilution vivarium and determination of median lethal dose (LD50).

The graph of figure 15 allows us to find the LD50, a lethal dose that can eliminate 50% of individuals from Gambusia affinis. The LD50 of the crude effluent is about 4.8 mL, and this value shows the toxicity of the crude effluents.

Table 3: Number and percentage of survivors of Gambusia affinis in the receiving waters of the Congo River (at the discharge point)

DILUTIONS	N-5	OBSERVATIONS				Nbre morts	%	04 SUDVIVANTS
E0mPR	IN-3	JOUR 1	JOUR 2	JOUR 3	JOUR 4		MORTS	% SUKVIVANIS
T1	5	5	0	-	-	5	100	0
T2	5	3	2	0	0	5	100	0
T3	5	2	1	1	-	4	80	20
T4	5	1	1	1	0	3	60	40
T5	5	2	0	0	0	2	40	60
T6	5	1	1	0	-	2	40	60
	35	14	5	2	0	21	60	40
Т	5	-	-	-	-	0	0	100

Table 2 shows that receiving waters at the point of release are toxic in T1, T2, T3 and T4 treatments with respectively

0, 0, 20 and 40% survivors observed, followed by T5 and T6 with survival rates of 60% Gambusia survived and 100% survivors in the control solution.



Figure 16: Evolution of the number of survivors of the Gambusia affinis in the dilarium vivarium receiving waters of the Congo River (point of discharge) and determination of the median lethal dose (LD50)

The graph in Figure 16 indicates that the 50% lethal dose of Gambusia affinis (LD50) is approximately 13.5 mL; and overall, we find a death rate of 60% and a survival rate of 40%.

By comparing the toxicity of the Bralima crude effluent to the receptor waters at the point of discharge, we can say that they have almost the same toxicity. But the further away we are, this toxicity diminishes because of dilution by rainwater during periods of flood. These findings highlight the danger to receptor ecosystems and confirm the results of the work of Musibono et al [23] working on the toxicity of industrial wastewater in Kinshasa, the potential for recycling and the health impact of ecosystems, and Kusonika et al, [3] working on the digital mapping of chemical-risk zones of the environment of Kinshasa.

4. Conclusion

In light of these results, we can say that crude effluents and receiving waters at the point of release are toxic to fish; And this toxicity diminishes as one moves away from the point of discharge into the river and due to dilution. This toxicity will be greater during low water than during periods of flood. We also note that the zone of influence of the effluents is less than 10 m during the rainy season.

The key parameter, which determines the maintenance and development of aquatic fauna and flora is dissolved O2, values found at the point of release (<1 mg / L) are caused by high organic load and high salinity (Conductivity). This dissolved O2 poor environment will put the aquatic fauna and flora at this point on the Congo River in difficulty. Self-purification is a biological process that is best performed in an aerobic environment. Organic matter, in large quantities, results in organic pollution of surface water, which is often accompanied by microbiological pollution. Pollution at this point of the river may cause health problems for the populations that frequent this port and its surroundings.

This modest work reveals that, to date and in relation to other African countries such as Senegal and Morocco, the issue of standards for discharges, discharges and monitoring of discharges remains a subject of concern, And a scientific concern in the Democratic Republic of Congo. This work reveals that all discharges from brewing companies should be treated, if not a large part of them, in order to reduce the organic load emitted. Investigations in this study also reveal that this discharge point has long been used and will have to be moved to a point of the river where the flow velocity is high in order to avoid the formation of a thick deposit which causes a state anoxia. Our study is a contribution to the law n $^{\circ}$ 11/099 of July 9th which enacts the general principles from which the particular laws will be elaborated according to the different environmental sectors.



Figure 17: Low-water discharge and flood point

5. Thanks

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