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## Assessment of heavy metal's in Atlantic sea fish sold in Benin

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### ABSTRACT

Marine space is constantly threatened by various sources of pollution that may reduce its economic potential and have negative repercussions on human health. This study aims to assess heavy metals contamination of eight fish species and their impact on human health. Heavy metals such as cadmium, lead, copper and zinc were determined by atomic absorption spectrophotometry in fresh, cooked and fried fish. The results found in fresh fish (cadmium: 0.002 to 0.005 mg / kg, lead: 0 to 0.031 mg / kg, copper: 0.0045 to 0.305 mg / kg, zinc: 0.1245 to 0.6195 mg / kg), in cooked fish (cadmium: 0.0035 to 0.005 mg / kg, lead: 0 to 0.01 mg / kg, copper: 0 to 0.021 mg / kg, zinc: 0.171 to 0.327 mg / kg) and in fried fish (cadmium: 0.004 mg / kg, lead: 0 to 0.007 mg / kg, copper: 0 to 0.016 mg / kg, zinc: 0.0875 to 0.5065 mg / kg) showed that heavy metal levels are all below the standard values accepted by FAO / WHO. The consumption of these fish could therefore have no negative effect on the population's health. Both types of cooking have both positive and negative effects on the heavy metal reduction in fish species. Although the concentrations of heavy metals are not worrying, the vigilance of the populations and a variation of the diet are important to guarantee a better health.

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**Keywords:** Heavy metals, health impact, Atlantic see fish, Cotonou.

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### INTRODUCTION

Marine space is an immense reserve of biological resources which constitutes a major part of the world's population diet. However; this space continues to be threatened by various sources of pollution that may reduce its economic potential and have adverse repercussions on human health (Machouri, 1999). Due to human activity thousands of chemical substances end up in the ocean via the atmosphere or continental waters. Some of

those substances, such as heavy metals, pesticides and artificial radioelements, are foreign to the marine environment (Nakhlé, 2003).

Among the major consequences of pollution, the chemical pollution has now become a serious concern affecting the hydrosphere. The impact of these substances on the environment is complex, their toxic actions can be direct or indirect on individuals, populations and ecosystems (Devauchelles,

2002). The consumption of contaminated seafood represents a potential danger to human health.

Benin's coastal area covers 8692 km<sup>2</sup> about 7.7% of the national territory and composed of thirty (30) administrative districts. Along this coastal area there are many ecosystems and infrastructures such as the port, the airport, sales parks for second-hand vehicles, and industries. More than 80% of Benin's industrial companies such as SOBEBRA, SONICOG, SOBETEX, SOBEPEC, SCB, and CIMBENIN are located in the area between Cotonou and Porto-Novo district (CEDA, 2007). These industrial companies generate liquid waste that is directly dumped into the Atlantic sea.

The occupation of the maritime area by fishermen is the main cause of vegetation cover disappearance and the pollution of beaches by garbage. To this solid household waste are added direct discharges of domestic and industrial waters drained into the sea causing a disturbing pollution for biological resources and for the health of marine products consumers. Thus human health protection and normal functioning of the marine environment requires continuous control of the quality of this ecosystem. With this in mind, this article aims to assess the level of seafood contamination by heavy metals, as well as their impact on human health.

## MATERIALS AND METHODS

### Study area

This study took place in the Beninese coastal area at Cotonou fishing (Figure 1) port.

### Methods

#### *Fish sampling*

Early in the morning, fish were sampled directly from marine fishermen. The fish collected were rinsed with distilled water and were immediately kept cold in coolers until they were put to the laboratory for analysis.

#### *Choice of fish species and heavy metals*

Fish choice criteria are: their availability during the study period and their appreciation by the population. The species sampled are: *Albula vulpes*, *Galeoides decadactylus*, *Scomber scombrus*, *Brachydeuterus auritus*, *Sardinella mederensis*, *Sphyraena barracuda*, *Trichius lepturus* and *Cephalopholis taeniops*. Ten fish were collected per species. Fish flesh was dissected, freeze-dried and lyophilised, and were ground to fine powder with a mixer for heavy metal's analysis. Heavy metals such as lead and cadmium are chosen in this study because they are the most toxic to humans and the most frequently found in the environment (Viala and Grimaldi, 2005). Copper and zinc are also associated because there are toxic at high thresholds.

#### *Analysis method*

In order to better assess the risks incurred by consumers, it was agreed to analyze the flesh which is the portion consumed by the population. 10 fish per species having approximately the same length and weight were dissected, mixed, weighted and divided into 3 parts: the first was analyzed fresh, the second part was boiled with demineralized water with laboratory flasks and the third was fried with sunflower oil before analysis. They were freeze-dried and lyophilized, and were ground to fine powder. 5 g of each sample were weighed in a quartz crucible. 5 g of distilled water in another crucible to serve as blank. The crucibles containing samples and water as blank were put in a programmable oven. Initial temperature was lower than 100°C. The temperature increased to 450°C at a rate of 50°C/hour. After this calcinations step, crucibles were removed and allowed to cool down. 1 to 3 ml of water was added and was evaporated in a water bath. 5 ml of hydrochloric acid were added to each crucible and were evaporated. Residue were dissolved in a volume of 10 to 30 ml of nitric acid 0.1 mol / L. Crucibles were stirred

thoroughly to dissolve the ashes for 1 to 2 hours then filtered in a 50 ml flask. The resulting solution was then analyzed by atomic spectrophotometer absorption with a Spectr AA110

### Statistical analysis

Heavy metal content data were subjected to a linear mixed effect model to evaluate their variation according to the cooking methods and the species of fish products. The forms of the fish (fresh, cooked and fried) and the species factor were considered fixed and the repetition as random.

The mixed-effect linear model was made possible by the lmer function of the lmerTest package (Kuznetsova, et al., 2017). Adjusted averages were obtained by the lsmeans function of the lsmeans package (Russell, 2016). The ggplot2 package (Wickham, 2016) presented these averages graphically. In order to evaluate the two-to-two correlation between the various heavy metals analyzed, the corrplot function of the corrplot package (Taiyun and Viliam, 2017) was used with the Pearson method. All analyzes and graphs were performed in the R 3.5.1 software.

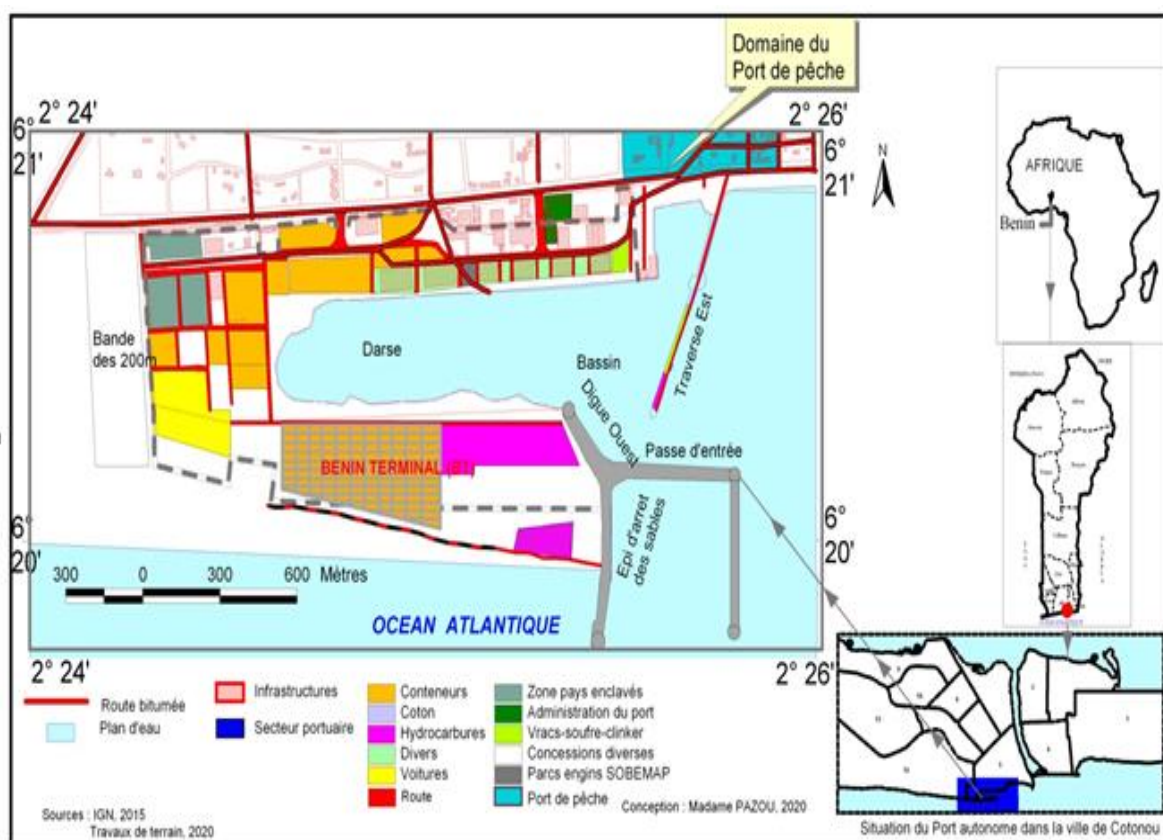


Figure 1: Beninese coastal area at Cotonou fishing.

## RESULTS

### Heavy metal content in fresh fish, cooked and fried

Heavy metal content in the different species of fish obtained varied from species depending on the cooking methods as shown in Figure 2. Figure 2 shows the presence of cadmium, lead, copper and zinc in almost all species caught (fresh) from the Atlantic Ocean along the Beninese coast. *Scomber scombrus* is the species that accumulated the most cadmium with 5 µg / kg against *Sphyraena barracuda* which accumulated the least with 2 µg / kg. The species that accumulates the most lead, copper and zinc is *Trichius lepturus* with 31 µg / kg, 305 µg / kg and 619.5 µg / kg, respectively. The species that accumulated the least copper and zinc is *Brachydeuterus auritus* with 4.5 µg / kg and 124.5 µg / kg, respectively. None of these concentrations exceeded the FAO / WHO standards for fresh fish (50 µg Cd / kg, 500 µg Pb / kg, 3000 µg Cu / kg and 4000 µg Zn / kg)

In all the cooked species analyzed, the presence of cadmium and zinc is noted. On the other hand, the presence of lead and copper was recorded only in a few species. In fish, the levels of cadmium, lead, copper and zinc varied between 3.5 and 5 µg / kg, 0 and 2 µg / kg, 0 and 21 µg / kg, 171 and 327 µg / kg, respectively. *Sphyraena barracuda*, *Albula vulpes* and *Sardinella mederensis* are the species that accumulated the most cadmium, lead, copper and zinc respectively. None of these concentrations exceeded the FAO / WHO standards for cooked fish. The consumption of these fish would therefore have no negative effect on the population's health.

As for fried fish, the presence of cadmium, lead, copper and zinc has been recorded in most species. Cadmium content is 4 µg / kg in all fish species. For lead, copper and zinc, levels range from 0 to 7 µg / kg, 0 to 16 µg / kg, and 87.5 to 506.5 µg / kg, respectively. *Sphyraena barracuda* and *Trichius lepturus* are the species that accumulated the most lead. *Scomber scombrus*

and *Trichius lepturus* are the species that accumulated the most copper and zinc respectively. None of these concentrations exceeded the FAO / WHO standards for fried fish either. The consumption of these fried fish would therefore have no negative effect on the population's health.

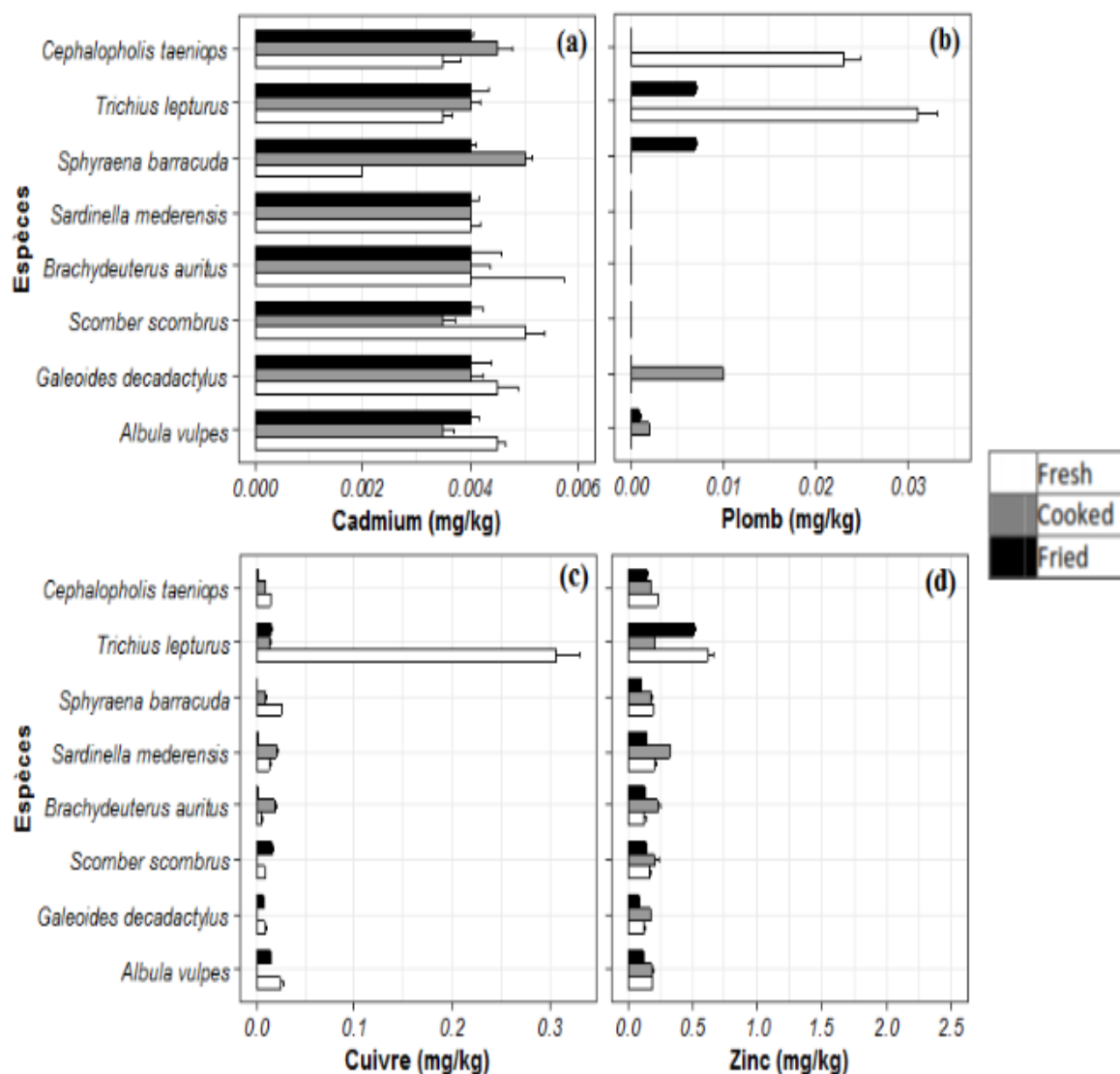
Statistical analysis of these results showed that, with the exception of cadmium, the presence of other heavy metals such as lead, copper and zinc varied significantly depending on the cooking methods and the species. The interaction of these two factors with  $p < 0.05$  (Table 1). This variation of heavy metal concentration in fish caught in the Atlantic sea may be due to absorption phenomenon, diffusion and excretion at the time they were caught.

### Effects of cooking methods on heavy metal concentration in fish

Heavy metal determination has focused on three forms of fish namely: fresh, cooked and fried. Table 2 shows the comparison of the presence of heavy metals in the different forms of fish.

From this table it can be seen that the trend in the contents of the different metals varies from one species to another depending on the fish. Indeed, depending on the fish species, it was observed a decrease or increase of cadmium, lead, copper and zinc content from the fresh form to the fried form through the cooked form. It can therefore be deduced that both cooking modes have a positive effect on the reduction of heavy metal levels in fish species. In other fish, the effect was negative. This behavior could be attributed to several parameters such as fish size, oil absorption, water loss and metal evaporation during cooking (Bassey et al., 2014).

Statistical analysis revealed a strong correlation between copper and zinc in fresh and cooked fish. For fried fish, the correlation is strong and positive between lead and zinc (Figure 3).



**Figure 2:** Variation in Heavy Metal Levels in Atlantic Ocean Fishes by Cooking Mode.

**Table 1:** Results of the linear model on the variation of the contents of heavy metals.

		Cadmium		lead		copper		Zinc	
	ddl	F	Prob	F	Prob	F	Prob	F	Prob
<b>MC</b>	2	0,91	0,411	22,33	<0,001	15,03	<0,001	3,78	0,029
<b>E</b>	9	0,40	0,929	18,06	<0,001	102,51	<0,001	312,96	<0,001
<b>MC : E</b>	15	1,24	0,358	17,42	<0,001	10,91	<0,001	6,51	<0,001
<b>ICC Répétition</b>			0,00		0,00		0,00		0,00

MC: Cooking mode; E: Species; ddl: degree of freedom; F: Fischer statistic; Prob: Probability of significance; ICC: Intra class correlation

**Table 2:** Comparison of Heavy Metal Levels in Different Forms of Fish.

Fish species	Cadmium (µg/kg)			Lead (µg/kg)			Copper (µg/kg)			Zinc (µg/kg)		
	Fresh	Cooked	Fried	Fresh	Cooked	Fried	Fresh	Cooked	Fried	Fresh	Cooked	Fried
<i>Albula vulpes</i>	4.5	3.5	4	<1	2	1	25	<1	14	183	19	117
<i>Galeoides decadactylus</i>	4.5	4	4	<1	0,01	<1	9	<1	7	125.5	171	87.5
<i>Scomber scombrus</i>	5	3.5	4	<1	<1	<1	9	<1	16	167.5	212	140.5
<i>Brachydeuterus auritus</i>	4	4	4	<1	<1	<1	4.5	19.5	2	124.5	229	128
<i>Sardinella mederensis</i>	4	4	4	<1	<1	<1	13.5	21	2	210.5	327	139
<i>Sphyaena barracuda</i>	2	5	4	<1	<1	7	25.5	9.5	<1	193.5	171.5	1045
<i>Trichius lepturus</i>	3.5	4	4	31	<1	7	305	13.5	15	619.5	203.5	506.5
<i>Cephalopholis taeniops</i>	3.5	4.5	4	23	<1	1	14	8.5	2	224.5	170.5	148.5



**Figure 3:** Correlation between heavy metals found in fish in the Atlantic Ocean.

## DISCUSSION

In this study, heavy metal values obtained in analyzed fresh fish are lower than those obtained by El-Moselhy and al., (2014) in fourteen species of fish collected in the Red Sea in Egypt. They were also below the concentrations of cadmium (1.17- 4.25  $\mu\text{g} / \text{g}$ ), lead (3.24-9.17  $\mu\text{g} / \text{g}$ ), copper (2.3-12.05  $\mu\text{g} / \text{g}$ ) and zinc (16.79-49.43  $\mu\text{g} / \text{g}$ ), recorded by Alturiqi and Albedair (2012) in some fish taken from Saudi Arabia markets. However, our results are slightly higher than the concentrations of cadmium (4.9  $\mu\text{g} / \text{kg}$ ) and lead (29  $\mu\text{g} / \text{kg}$ ) obtained by Al-Busaidi and al. (2011) in Oman sea fish. The lead levels recorded in *Trichius lepturus* and *Cephalopholis taeniops* in this study are higher than those recorded by Tawfik (2013) in the *Oreochromis niloticus* fish (0.002  $\mu\text{g} / \text{g}$ ), *Mugil cephalus* (0.002  $\mu\text{g} / \text{g}$ ) and *Sardinops sagax* (0.005  $\mu\text{g} / \text{g}$ ). The dissimilarity between these results and those recorded in this study may be due to the difference in many factors such as: feeding habits of fish species, their habitats, their ecological needs, their metabolism, their biology and their physiology (Arellano and al., 1999).

Regarding cooked fish, the results of this work are smaller to those obtained by Huque and al. (2014) in *Pampus argenteus* boiled fish sampled along Bengal Bay in Bengal. They recorded mean concentrations of 6.03 mg / kg, 15.34 mg / kg, 3.55 mg / kg and 24.82 mg / kg respectively for cadmium, lead, copper and zinc. Obodai and al. (2011) at Ghana obtained in boiled *Sarotherodon melanotheron* mean concentrations of cadmium (0.364 mg / kg) and lead (12.154 mg / kg) which were higher than those obtained for all fish analyzed in this study. However, high levels of lead in food cause kidney failure and damage human liver. Also, fatal ingestions of cadmium exceeding 350 mg/kg could produce a shock and an acute renal failure (Alturiqi and Albedair, 2012).

Concerning fried fish, results of this study are significantly lower than those obtained by Tawfik (2013) in fried *Oreochromis niloticus*, *Mugil cephalus* and *Sardinops sagax* where he recorded for

cadmium respectively 0.021  $\mu\text{g} / \text{g}$ , 0.360  $\mu\text{g} / \text{g}$  and 0.821  $\mu\text{g} / \text{g}$ , for lead respectively 0.011  $\mu\text{g} / \text{g}$ , 0.011  $\mu\text{g} / \text{g}$  and 0.022  $\mu\text{g} / \text{g}$ , for copper respectively 0.48  $\mu\text{g} / \text{g}$ , 0, 89  $\mu\text{g} / \text{g}$  and 1.13  $\mu\text{g} / \text{g}$ , for zinc respectively 6.45  $\mu\text{g} / \text{g}$ , 8.97  $\mu\text{g} / \text{g}$  and 13.86  $\mu\text{g} / \text{g}$ . They are also below the concentrations recorded by Devi and Sarojnalini (2012) in *Amblypharyngodon mola* for copper (0.023  $\mu\text{g} / \text{g}$ ) and zinc (0.96  $\mu\text{g} / \text{g}$ ). Copper is an integral part of many enzymes and is needed for hemoglobin synthesis (Huque et al., 2014). Zinc is an essential trace element that is a component of more than 300 enzymes needed to play a role in many biological functions of the human body. However, they become toxic when they exceed maximum limits (Das and Das, 2012).

The results of the cooking method effects on heavy metal levels obtained in fish are similar to those recorded by Ersoy et al. (2006) on *Dicentrarchus labrax* fish where a positive and negative effect on the heavy metal reduction was recorded according to the cooking methods. On the same fish species, frying and microwave cooking methods showed cadmium and arsenic increase while grilling and boiling methods showed lead decrease. These results are also similar to those obtained by Basseyy et al. (2014) in three species of fish from coastal waters of Nigeria. The cooking methods had a significant impact on cadmium concentrations in *Cynoglossus senegalensis*. In *Polydactylus quadratifilis*, boiling and frying led to an increase of 100% of cadmium concentration, while grilling resulted in seven times the cadmium concentration in fresh fish. In addition, cadmium levels in *Chrysichthys nigrodigitatus* increased. Cadmium increasing during grilling and frying was obviously the result of water loss (Kalogeropoulos et al., 2012). As for lead, its concentration in *Polydactylus quadratifilis* increased by 5.9% for boiling, 70.6% for grilling and 41.2% for frying. Boiling caused 32.6% of lead decrease in *Chrysichthys nigrodigitatus*, while frying and grilling showed 2.2% and 4.2% lead increasing respectively. However, the different cooking methods caused 20.8%, 22.6% and 20.8%,

respectively of lead level decrease in boiled, grilled and fried *Cynoglossus senegalensis*

### Conclusion

This study evaluated heavy metal contamination in fish caught in southern coastal waters of Benin. It shows that the heavy metal concentrations obtained from the analysis of eight fresh, cooked and fried fish species are all below the standard values accepted by FAO and WHO. The consumption of those fish would therefore have no negative effect on the population's health. However, frequent consumption of a lot of fish per meal can increase the concentration of heavy metals in the consumer's body. Both types of cooking have both positive and negative effects on the reduction of heavy metal levels per fish species. People's vigilance and dietary variation are important to ensure better health even if heavy metal concentrations are not worrying.

### COMPETING INTERESTS

The authors declare that they have no competing interests.

### AUTHORS' CONTRIBUTIONS

This work is the fruit of the contributions of all the authors: EYAP, JAP and MRA.

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