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Annual Behavior of Cu, Pb, Cr and Total Hg in Superficial Waters from Dique Channel during 2006-2010, Cartagena, Colombia

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Abstract

Magdalena River is a superficial water body from Colombia, which flows into the Caribbean Sea. Dragging with it elements with diverse chemistry nature throughout the watercourse. Similarly, one of its most flowing current arm of the river, known as the Dique Channel, capture minerals, organic matter, clays and metals. Both Magdalena River and Dique Channel finally slop their water stream into the coast of Barranquilla and Cartagena bay, respectively. The presence of metallic species in dynamic aquatic structures e.g., rivers) and coasts that interact inwardly (sediments-atmosphere-water) triggers variations on the densities from heavy metals existing onto the water. Due to the heavy metal fluctuations given in estuary and marine systems, the annual behavior of Pb, Cr, Cu and Total Hg from Dique Channel was determinate during 2006-2010. The aim of this study is to complement the tracing made by the North University on 2006 and the information related to heavy metals and reports of the physical-chemistry variables given by the Dique Channel Regional Autonomous Corporation-CARDIQUE by means of its participation in the Network for the Monitoring of Environmental Quality of Marine Program-REDCAM. One of the main contributions of the present study is the purpose of control solutions to mitigate the presence of unacceptable concentrations of heavy metals that can jeopardize the flora and fauna from the impacted ecosystems. Results obtained shows that the Canal del Dique drags heavy metals in high concentrations, which can affect dramatically the intern Bay of Cartagena de Indias.

Keywords: Cartagena bay; Dique channel; Flora and fauna; Heavy metals

Introduction

Colombia is a South American country that presents several problems regarding to environmental issues related mainly to illicit activities that requires the indiscriminate use of chemical precursors, for instance, spill of serve waters and uncontrolled overuse of mercury and cyanide in mining activities, release of heavy metals from improper agricultural practices and industrial activities [1].

Dique Channel is a water body located on the Colombian Caribbean region and it is considered as an alluvial plain formed by wetland complexes, where the main environmental component is the hydric part, generator engine of a nourished terrestrial and aquatic biodiversity. Its history dates back to the XVI century, epoch in which Cartagena de Indias was interest to find one fluvial way to communicate the Magdalena River and the network of overflow swamps from the region, in this way, it would not be necessary to use land transportation, impassable in rainy season [2].

The channel and its micro basin are nowadays an important part of economic exchange, as well as the financial support of several surrounding population, facilitating numerous activities, for instance agriculture, cattle rising and artisanal fishing [3]. Despite of the massive nature wealth, its surrounding communities presents serious problems related to socio-economic issues, such as high levels of poverty, low educational level, deficient coverage of basic sanitation services and low incomes [4].

Added to the problems mentioned above, this ecosystem also faces issues generated by heavy metals and other persistent elements present into the water, which tend to accrue into the animal and aquatic tissues chronically, These elements are considered not only as one of the most dangerous for several ecosystems and its living organisms [1] but also as conservative xenobiotics presents in the water column and sediments with a potential risk to ecosystems [5], triggering bioconcentration, biomagnification and bioaccumulation processes. Such phenomenon has been reported previously in endemic fish species of massive consumption exposed to polluted waters from Cartagena de Indias Bay, Ciénaga Grande of Santa Martha and Ciénaga de la Virgen. Such fish included arenca (*Triportheus magdalenae*) and bocachico (*Prochilodus magdalenae*) [6-8]. Owing to the presence of environmental pollutants into the hydric resource, affecting the aquatic ecosystem and the public health in general negatively [9]. Tejeda-Benitez et al. [10] have been reported several damages on fauna exposed. *C. elegans* specimens were exposed to polluted sediments of water and sediments from Magdalena River, presenting problems of locomotion and reproduction, as well as the induction of changes on gene expression in mtl-2, sod-4 and gst-1, related to inflammation and endocrine disruption; Olivero-Verbel et al. [11] showed in a study made on eggs of snowy egret (*Egretta thula*) obtained from Cartagena Bay and Totumo marsh, that heavy metal pollution causes gonadal atrophy and inflammation processes.

This study had as a main purpose to identify the annual behavior of some heavy metals reported as highly dangerous: Pb, Cr, Cr and total Hg, from superficial waters of the Canal del Dique during 2006-

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2010, by means of the annual monitoring of its concentrations and the possible relationship between such concentrations and variations on physical-chemical conditions: pH, temperature and conductivity; the obtained results allowed posit manage strategies directed to the minimization of the negative impact caused by the evaluated pollutants on the ecosystems and the native species present in this environment, including humans.

Materials and Methods

Study area

The Canal del Dique is located into the Colombian Caribbean region and bifurcates from the Magdalena River, in the municipally named Calamar (Bolívar), 110 Km up from the river mouth in Bocas de Ceniza. It presents a length of 113 km [12].

In its route, the channel goes through nineteen municipalities with a total extension of 700 Ha; seven belongs to the department of Altlántico (Campo de la Cruz, Manatí, Repelón, Santa Lucía, Sabana larga, Luruaco and Suan), covering a 31.3% of the area, followed by Bolívar with a coverage of 12.2% distributed on eleven municipalities (Cartagena, Arjona, Arroyo Hondo, Calamar, Mahates, María abaja, San Cristóbal, San Estanislao, Santa Rosa del Lima, Soplaviento and Turbana) and finally the department of Sucre with one municipality (San Onofre) covering 10% from the area [8]. At the end of the path, the Dique Channel reach into Cartagena Bay. Additionally, it possesses three outlets, one by Caño Correa, offshore, another by Caño Lequerica and one last by Caño Matunilla, to the Barbacoas Bay.

Sampling and water analysis

Data obtained from this study were originate from the analysis applied to water obtained from two stations employed to the monitoring made by The Dique Channel Regional Autonomous Corporation (CARDIQUE), which presents field code C13003030 (Canal del Dique 1 Km adentro–1; con coordenadas X=842379 and Y=1628545) and C13003031 (Desembocadura C. Dique-2; con coordenadas X=841509, and Y=1630868) (Figure 1), the last one is used to monitor the flow, finally extended to the inter bay in south-west direction, with the coastal dynamics of this water body from Cartagena City, in which prevails industrial, agroindustrial, urban and port activities. Each of the stations was used to made in situ measurements of physic-chemical variables: pH and temperature (pH meter WTW, model pH315i, serial Nº 06511100), conductivity (µS/cm, Conductimeter WTW, Cond 315i model, serial N° 04070125) and dissolved oxygen (WTW oximeter, Oxi315i model, serial N° 06090329).

Likewise, superficial waters were collected to the purpose of quantify the concentrations of Cr and Cu in concentrations of mg/L, and well as total Hg and Pb expressed in µg/L, by means of the laboratory analysis made by Cardique, employing atomic absorption spectrometry (SPECTRAA 220 FS, Serial Nº EL01095075). Every water analysis was made following the Standard Methods [13] recommendations.

Processing and data analysis

Results were analyzed after samples treatment and simplification of the obtained data, employing dispersion and central tendency measurements, arithmetic average and standard deviation to every year and sampling site [14]. Subsequently, similarity grade between the sampling years was verified throughout the nearest neighbor multivariable method [15].

Moreover, an existing relationship between variables was identified by using the Spearman non-parametric correlation analysis, given that the assumption was not accomplish [16]. Besides, the average value of the heavy metals behavior in function on time and electric conductivity was verified, due to the last one normally presents a close relationship to salinity; which can be related inversely to the heavy metal concentrations.

The behavior of the average value of the heavy metals as a function of time and the electrical conductivity was also verified, since the latter normally has a close relationship with the salinity; Which in turn is usually inversely related to the concentration of heavy metals [17].

The obtained data was tabulated by Microsoft Excel and subsequently processed through Statgraphics Centurión XV. II.

Results and Discussion

Space-Temporal behavior of the variables

To determinate the parameters that contributed to the system variability, it was necessary to reduce the dimension of the problem by fixing afterwards the existing relation between every one of such parameters. The values summary, average and standard deviation of the different evaluated variables shown high concentrations of lead (158.8 µg/L) on 2006, being the station located into the Canal del Dique, 1 Km to the outfall, the one that registered the highest concentration. It is important to mention that the other evaluated variables presented little variation, except for conductivity, which oscillated slightly because of the space-temporal changes.

High concentration values of lead, mercury and copper into the intern part of the Canal del Dique indicate solid and liquid residue contributions from the high basin. Heavy metals usually affect in directly and indirectly way the survival of aquatic species, owing to the interference they make to the biochemical and physiological processes, e.g., reproduction [18]. Reports made by Mansour et al. [19] concluded that fresh water bodies could present serious pollution damages related to high concentrations of heavy metal such as iron, copper, cadmium, nickel, chromium, lead and tin, among others. Although they described that water concentrations could below the permissible limits proposed by EPA or other legislations, and even so, generate mean concentrations on living creatures from the stressed ecosystem above the permissible limits given by FAO, due to bioaccumulation in fish organs like flesh, head and viscera. This bioaccumulation varies among species. The presence of heavy metals into fish and other organisms is, related to endocrine disruption, associated to oxidative stress and overexpression of carcinogenic genes and other health illnesses [10,20,21], as well as reproduction issues and teratogen and genetic abnormalities not only on fauna, but also on flora and microorganisms [22,23].

High concentrations of heavy metals generate negative impact not only on the native species from the Channel, but also on the surrounding organisms from the Intern Bay of Cartagena. This intern bay suffers because it is the receptor of about 7.5 Ton of shedding sediments per day as well, that have themselves variable concentrations of heavy metals [11,24-26].

The association between years respecting to its affinity, calculated by the nearest neighbor Eucladian distance method, using the values from the different variables evaluated, shown in the Figure 2 cluster, indicates the division among every one of the variables, in two groups. The first one, confirmed by the years 2006, 2008 and 2009; the second one, integrated by the 2007 and 2010.

The difference of 2007 and 2010 respecting to the rest of the studied years, takes order to the low values of cupper and oxygen, which could

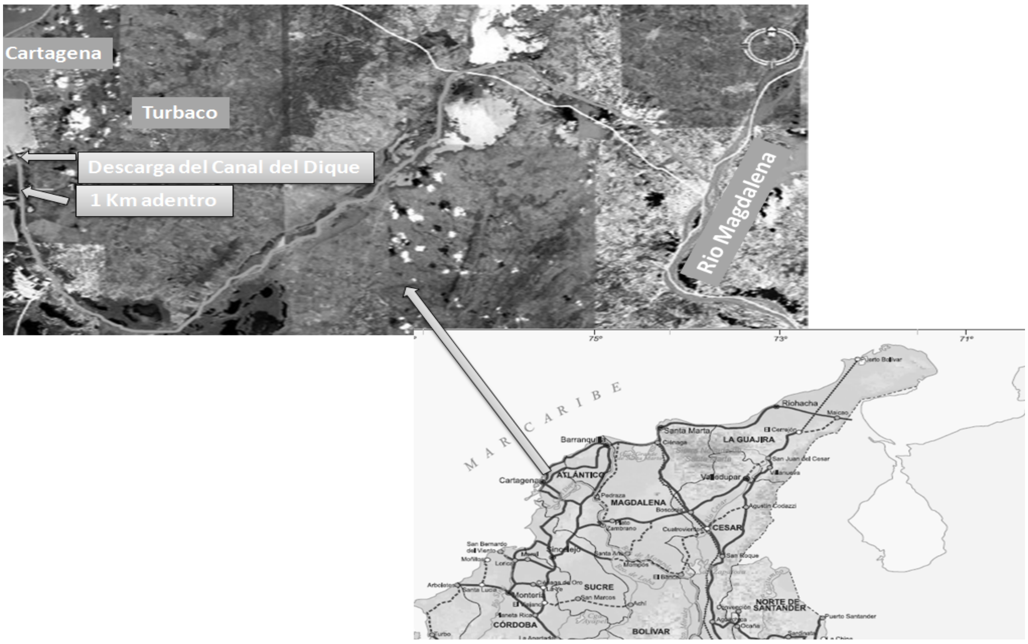

Figure 1: Study area and location of the sampling stations. Source: CARDIQUE, 2010.

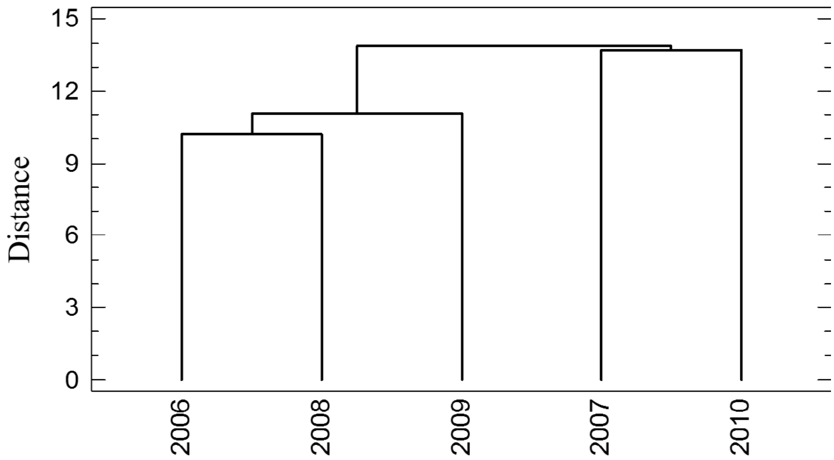

Figure 2: Similarity cluster between years, through the nearest neighbour Eucladian distance method.

be related to the sampling point (C13003030-Canal del Dique 1 Km adentro-1: Sample point 1; and Outfall C. Dique: Sample point 2), due to the difference found on the temperature, slightly higher into the superficial water layer, which decreases dissolved oxygen. In addition, it is possible that this behavior is owing to an increase of the organic matter in the sampling period, because it also suffered chelation and precipitation processes, as described by Chowdhury et al. [22].

Relation between variables

After the application of Spearman nonparametric rank correlation coefficient analysis, it was found that, from all of the analyzed variables, only Cr-DO and Pb-Temp combinations presented slight correlations, characterized by being significant and reverse (Tables 1 and 2). This situation is commonly related to industrial sewage discharge, as well as the emission of solid residues with high amounts of organic matter (domestic discharges) and the thermic dynamics in the metal transport, probably affected by the pH stability, which would be tending to dissolve it, turning such metals into trace elements. Demirak et al. [21,22] sustain the former affirmation.

Behavior of the heavy metal concentrations function of time and conductivity

The graphic analysis of the heavy metals behavior, function of year, sampling site and conductivity, reveals that, in the case of chromium, the highest concentration achieved was during 2007, coinciding to high conductivity values (Figure 3).

The behavior described on Figure 3 could be explained if compare salinity and total suspended solids (0 and 91.6 mg/L respectively) obtained from the sampling site. In addition, Chowdhury et al. [22] relates this behavior to the natural levels of inorganic ions in the natural water evaluated can receive high amounts of such ions and some metals

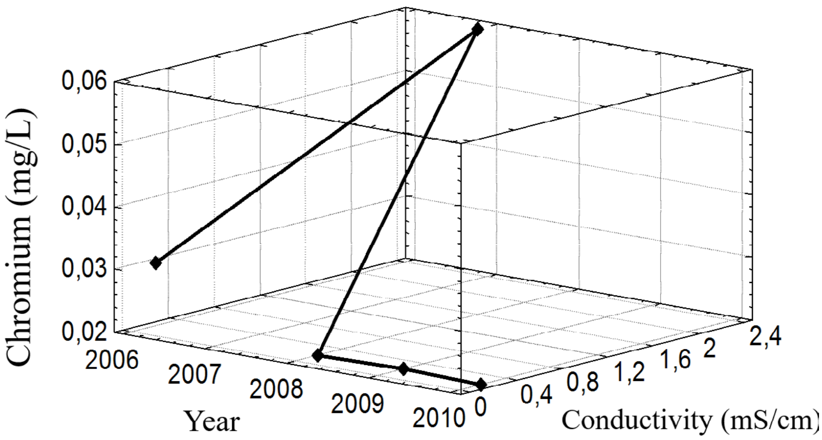

Figure 3: Behaviour of the average values of Chromium, in function of time and conductivity.

		Year					Site	
		2006	**2007**	**2008**	**2009**	**2010**	**DQ**	**KS**
Cr (mg/L)	**Media**	0.03	0.06	0.02	0.02	0.02	0.03	0.04
	SD	0.02	0.01	0.01	0.01	0.02	0.01	0.01
Hg (µg/L)	**Media**	2.4	2.4	-	2.18	2.67	2.65	2.17
	SD	0.63	0.45	-	0.45	0.63	0.37	0.37
Pb (µg/L)	**Media**	158.8	17.5	26.3	17.5	24.5	33.12	64.68
	SD	42.82	30.3	30.3	30.28	42.8	22.04	22.04
Cu (mg/L)	**Media**	0.03	0.01	0.02	0.07	0.01	0.01	0.04
	SD	0.04	0.03	0.03	0.0.3	0.04	0.02	0.02
OD (mg/L)	**Media**	6.23	5.92	7.25	6.75	5.3	6.36	6.21
	SD	1.03	0.73	0.73	0.73	1.03	0.53	0.53
pH	**Media**	7.28	7.64	7.1	7.55	7.6	7.42	7.44
	SD	0.21	0.15	0.21	0.15	0.21	0.12	0.12
Temp (°C)	**Media**	28.5	30.3	30	30.95	29.9	29.93	29.9
	SD	0.17	0.12	0.17	0.12	0.17	0.1	0.1
Cond (mS/Cm)	**Media**	-	2.3	0.19	0.22	0.19	1.18	0.27
	SD	-	1	1.41	1	1.41	0.84	0.84

Media: Arithmetic average; SD: Standard Deviation; OD: Optical Density; DQ: Canal del Dique Outfall; KS: Station located into the Canal del Dique from the outfall

Table 1: Average values of the heavy metals concentrations and physic-chemical variables from the Canal del Dique during 2006-2010.

	Variables							
	Correlation	**DO (mg/L)**	**pH**	**Temp (°C)**	**Cond (mS/cm)**	**Cr (mg/L)**	**Hg (µg/L)**	**Pb (µg/L)**
pH	R^2	0.27						
	P-value	0.33						
Temp (°C)	R^2	0.11	0.52					
	P-value	0.69	0.06					
Cond (mS/cm	R^2	0.29	0.35	-0.21				
	P-value	0.33	0.24	0.48				
Cr (mg/L)	R^2	-0.67	-0.31	0.18	-0.10			
	P-value	0.01	0.26	0.51	0.75			
Hg (µg/L)	R^2	-0.11	-0.05	-0.10	-0.07	-0.11		
	P-value	0.70	0.88	0.75	0.84	0.72		
Pb (µg/L)	R^2	-0.37	-0.28	-0.57	-0.18	-0.09	0.22	
	P-value	0.15	0.31	0.04	0.56	0.74	0.46	
Cu (mg/L)	R^2	-0.20	-0.48	-0.10	-0.16	0.48	-0.30	-0.22
	P-value	0.43	0.08	0.71	0.59	0.06	0.32	0.93

Table 2: Spearman Correlations between physic-chemical variables and metal traces from de Canal del Dique.

like Cr from anthropogenic activities. It is noticed that the Colombian policy (Decree 159/84) consider the presence of Cr^6 in superficial waters as a threat based on bioassays as 0.01 CL_{50}^{96} (Lethal concentration at 96 hours, 50% mortality). It has been described the toxicity of Cr^{6+} over Cr^{3+} and the damage on tissues from living organisms in the order of at environmental relevant concentrations ranging from 5.2 µg L^{-1} to 260 µg

L^{-1} [27]. Nevertheless, Cr^{3+} can change to Cr^{6+} in aquatic ecosystems by microbiological action [28,29].

Data of mercury levels was treated to the same analysis, showing a contrary behavior if compare to chromium, its higher levels were present when conductivity was low (Figure 4), confirming the results presented in one recent report of Invemar, by Cogua et al. [30].

The highest concentration of total mercury (3.68 µg/L) indicates that this heavy metal has a resuspension behavior. This conduct could be explained when compare to the values of Total suspended solids (728 mg/L) from the mix zone (outfall). It is possible that different forms of mercury have a briefer activity period into the atmosphere and molecules can deposit in earth or water mass over 100 to 1000 km away from its source [31,32].

In addition, Colombian normativity contemplates the toxicity of total mercury in marine and estuary waters, based on reported bioassays, as 0.01 CL_{50}^{96} (lethal concentration at 96 hours, 50% mortality). Moreover, it is necessary to evaluate some organic compounds that could constitute phases with high capacity to capture metallic cations, for instance, mercury, generating adducts [10] or Hg transformations into more toxic forms, such as methyl mercury [7,8].

Otherwise, measurement of the former parameters from lead showed this heavy metal to behave similarly to mercury with regard to conductivity (inverse relationship shown in Figure 5).

The highest level of lead detected was 300 µg/L from one Km into the Channel; this result suggest that lead sources could be generated by anthropogenic activities. The zone is directly impacted by effluents from manufacture of artisanal fishing networks, fishing by using molten lead and metallurgical industries, according to Garay et al. [26,30]. International parameters to environmental control suggest that no concentration should be accepted as safe for lead, due to its known to generate cardiovascular, nephrotoxic and neurological effects in adults, and it is not well described its capacity to alter early development in trace concentrations [17,33]. Nonetheless, Colombian normative contemplates the toxicity of lead in sweet and warm water, based on reported bioassays, as 0.01 CL_{50}^{96} (lethal concentration at 96 hours, 50% mortality). It was also evidenced for cupper, an inverse relationship between high concentrations (0.236 mg/L) and low conductivity values (Figure 6).

Cupper has a toxic behavior according to the Colombian regulation, according to bioassays made in sweet waters as 0.01 CL_{50}^{96} (lethal

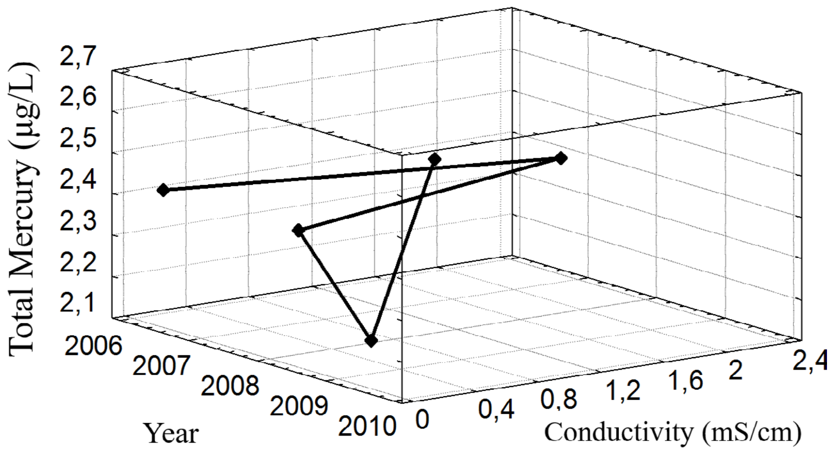

Figure 4: Behaviour of the average values of total mercury, in function of time and conductivity.

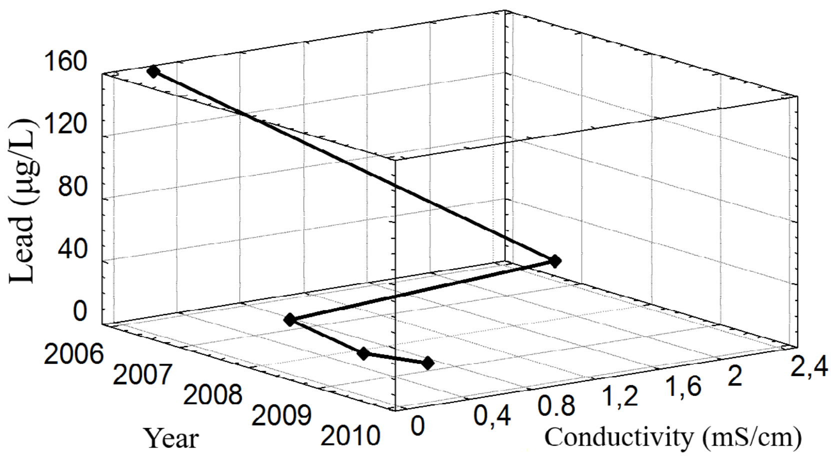

Figure 5: Behaviour of the average values of lead, in function of time and conductivity.

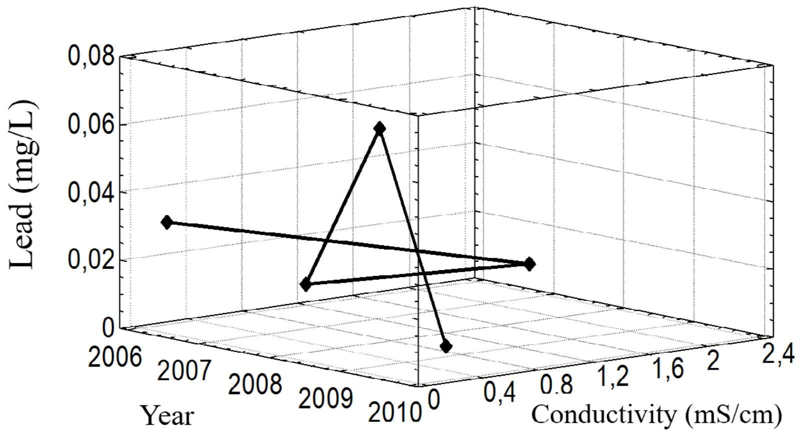

Figure 6: Behaviour of the average values of cupper, in function of time and conductivity.

concentration at 96 hours, 50% mortality). The presence of this metal in the studied ecosystem can be related to the type of sediments from the Dique; such soils are mainly clayey [26,30], capable to sorption of metallic oxides and organic particulate matter, whence, studies of the presence of heavy metals in sediments has to be done.

Conclusion

The Canal del Dique presents high concentrations of some heavy metals into the superficial waters, especially chromium. When compare the amounts of these metals to conductivity, the relationship is directly proportional. This can explain to a possible interaction between metallic molecules and the presence of calcium, potassium, sodium, carbonates, sulphates and chlorates.

Furthermore, there is an inverse association between lead, total mercury and cupper if compare to conductivity, which suggest that in the upper basin exists effluents of wastewater that would be responsible to changes on heavy metals in the studied years.

In addition, the deposit of 7.5 Ton of sediment per day [26,30] discharges from the dam to the Cartagena Bay, contain variable concentrations of heavy metals that represents a negative factor of environmental press [34,35]. Furthermore, the chemical dynamic in the water regulates the adsorption-absorption rate into the sediment-water system. The adsorption activity removes metals from the water column, desorption incorporates them into the mentioned column through the parameters that regulate the system, for instance, salinity, redox potential (Eh) and pH. The increase of salinity not only defines the competition between metals from Groups I and II, but also improves the molecule freedom from the clayey sediments to the water. Nevertheless, when pH lows, immediately generates the promotion of metal-carbonated dissolution (e.g., $PbCO_3$) and enhance solubility of the dissolved metals [36]. According to the baseline of the Environmental Protection Agency (EPA), acceptable ranges of total mercury averages 0.012 µg/L, with a mean concentration for four days, if compare this data to the results from the mean obtain in the present study (2.46 µg/L), the Canal del Dique present an alarming breach of the international policy.

The intern Cartagena bay is affect by effluents from the Canal del Dique, industrial and urban activities, agro industrial and port activities, amply studied by Olivero-Verbel et al. [3,6,7,10-12,17]. The former authors have reported the bioaccumulation problems associated to high levels of heavy metals in Cartagena de Indias and surrounding areas, finding alarming concentrations of mercury in *Prochilodus magdalenae, Triportheus magdalenae, Rhamdiasebae* and *Pseudoplatystoma fasciatum*. One of the most affected species is *T. magdalenae*, which is a high-consumed organism, characterized for its detritivore zoo planktonic habits. This situation can be explained due to the metal transportation until the Dique Canal. However, according to Olivero et al. [17], although *T. magdalenae* presents the higher concentration of total mercury, it does not achieve the limit internationally accepted to consider these organisms as not able to human consumption. Nonetheless, recent studies suggest that the use of these fish as a human nutriment source is, in fact, a real and increasing problem, due to the consequences on health that the constant consumption entails [10].

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