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BASELINE METALS CONCENTRATIONS IN WATERS FROM A TROPICAL BINATIONAL RIVER: THE CATATUMBO RIVER, VENEZUELA

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The Catatumbo river is a binational basin shared by both Venezuela and Colombia approximately 30% and 70%, respectively. It is one of the main contributors of nutrients, organic matter and metals to Lake Maracaibo, due to the natural runoff of the river basin, and to domestic, industrial, agricultural and oil activities in the basin. This work is the first study of metals in waters of the Catatumbo River, including the zones within Venezuelan and Colombian territory, and the metal load to Lake Maracaibo. Metal concentrations in the Catatumbo river water were in the following order: Na > Al > Mg > Fe > K > Ca > Cu > Zn = Pb > Mn > Cr (30.582, 9.386, 8.313, 5.137, 4.617, 1.863, 0.192, 0.157, 0.157, 0.141, and 0.0005 mg/l respectively). With the exception of Cr, these values exceed reported values by other authors for natural waters. The molar ratio metal/phosphorus found in river waters was high, suggesting complex formation. The annual metal load from the Catatumbo river to Lake Maracaibo is the following: Na > Mg> K > Ca > Al > Fe > Pb > Cu > Zn > Mn > Cr (966.74, 219.60, 49.80, 18.12, 7.56, 5.27, 0.95, 0.82, 0.57, 0.33, and 0.0015 x 10^4 kg/yr respectively). These results indicate that the Catatumbo River is an important contributor of metals to Lake Maracaibo.

INTRODUCTION

A river basin is the area drained by itself and its tributaries. The characteristics of each river are unique due to many factors in its basin. Physical variables include size, climatology, topography, geology, vegetation and land use. These characteristics are further affected by the river gradient, flow rate and depth, as well as basin biota which have influence on the physical and chemical environment.

Clearly a most important factor of the river is transport in both the vertical and horizontal planes. The water erodes, suspends and transports materials in the river bed. Where the river flow is turbulent, solid particles remain in suspension while at lower flow velocities sedimentation occurs.

These mechanisms are important for the transport of materials retained on sediment particle surfaces such as organic matter, phosphorus, and many other elements (Margalef, 1981; Martinova, 1993; Rivas, 1995). The transported material is considered an indicator of the degree of land surface erosion because it provides most of these materials to lakes and rivers (ECOPETROL et al., 1996; Margalef, 1981), and the accumulation of these elements on surficial sediments can indicate geographic sources of pollution (Moyano et al., 1993).

The presence of toxic metals such as Pb and Cd in the environment has been a source of worry to environmentalists, government agencies and health practitioners. This is mainly due to their health implications since they are nonessential metals of no benefit to humans.

Some trace elements or micronutrients such as magnesium, iron, zinc, manganese and copper are essential for living organisms in small amounts since they play a role in important physiological processes (Mg in the formation of chlorophyll and Fe and Cu as part of the citochrome and ferrodoxine respectively in the respiratory chain). On the other hand, Pb and Cr do not have a known biological role and are toxic to a variety of organisms (Estevez, 1988; Wetzel, 1981).

In continental aquatic ecosystems these metals can be present as ions (forming complexes mainly with organic molecules and free radicals) and in particulate form (as components of detritus and biomass). With the increase of industrialization and the demand of mineral resources, the concentration of these elements has caused severe environmental problems in some regions of the planet. Since lakes act as reservoirs they can present high pollution levels in certain areas, posing a risk for the ecosystem and the population using their resources (Estevez, 1988; Wetzel, 1981).

Vaithiyanathan found that agricultural soils contain mostly inorganic phosphorus (close to 75% of total phosphorus)(Vaithiyanathan et al., 1992). Inorganic phosphate makes up 95% in forests and 98% in agricultural soils. Aluminum and calcium phosphates are 1.6 and 4.5% respectively of the total inorganic phosphate. Chemistry of phosphorus is closely related to pH and Fe concentration, since these properties control the capacity for holding phosphorus in the soils (Harrison, 1988; IGAC, 1989). Insoluble iron phosphate is quickly precipitated or adsorbed on the surface of highly acidic soils. Therefore, iron phosphate is accumulated in agricultural and forest soils .

Most bodies of water have the capacity to assimilate contaminants in an amount that depends on its dynamic character. For rivers and lakes this ability is lower during the dry season (ECOPETROL et al., 1996; Rivas, 1995). In most cases, rivers which discharge to lakes can contribute an increase of these elements to the ecosystem such as in Lake Ijsselmeer in Holland which receives a higher amount of cadmium, chromium, copper, nickel and zinc from the fluvial system (Estevez, 1988).

The major contribution of fresh water to Lake Maracaibo comes from the Catatumbo river (70% approximately). This fact shows the importance of determining the levels of metals in the river water in order to know the amounts transported into the lake and pollution impacts to this body of water.

Several studies have been conducted on the conditions of the Catatumbo river bed and basin (Romero, 1996; ECOPETROL et al., 1996). Neither evaluated metals content in water. This work establishes a baseline and presents an evaluation of the metals input from the river to Lake Maracaibo.

STUDY AREA

Catatumbo River

The hydrographic system of the Catatumbo River is such that it is a binational basin shared by both Venezuela and Colombia in approximately 30% and 70% proportions, respectively. It is located between the coordinates 72° 4' 00" and 73° 26' 19" east longitude and 7° 46' 30" and 9° 31' 05" north latitude. Its area is 25,563 km^2 and it has a mean yearly flow of 1.147 m^3/s. It is one of the main tributaries to Lake Maracaibo, contributing 70% of the fresh water discharged to the lake.

Venezuela is one of the world's top oil producers and an OPEC member. Frequently, the dynamiting of the Caño Limones pipeline in Colombia has set off alarms in Venezuela. These events cause many barrels of crude oil to be spilled into the Catatumbo and Tarra rivers that flow into Venezuela. Lake Maracaibo itself is the central location of Venezuela's oil production.

There is no similar study in this zone, especially in the higher elevations and upper basin of the river, because of the previously described situation. This greatly limits any data collection effort, and the present study is the only information available at this time.

Lake Maracaibo System

Lake Maracaibo, the largest lake in Latin America, is a large hypereutrophic estuarine lake in northwestern Venezuela which has suffered severe pollution problems caused by inputs of excessive nutrients, petroleum products from a major petrochemical industrial park and other contaminants. The lake is considered to be naturally eutrophic; however, the current state of hypereutrophy is mostly caused by excessive inputs of nutrients from treated and untreated sewage water and industrial wastes, riverine and agricultural sources, as well as air pollution. A large petroleum activity is developed in the Colombian part of the river, and environmental impacts are aggravated by sabotage to the oil pipelines (guerrilla activity) which are numerous during the year, affecting mainly the river and the Lake Maracaibo basin. The Catatumbo river brings approximately 70% of the fresh water to the lake, which indicates that it could be a significant contributor to eutrophication (Rivas et al., 2000). Frequently these problems have reoccurred, creating alarm in the population when the accumulation of algae in shallow areas increases problems of foul odors (Ledo et al., 2004).

MATERIALS AND METHODS

A total of 17 sampling stations were located along the Catatumbo River, taken close to the shore from the Colombian to the Venezuelan side to the outlet in the lake. Figure 1 and Table 1 show the sampling sites and the location of the Catatumbo River in the Lake Maracaibo system. The dotted line is the boundary between countries, and the dark line shows the main bed of the Catatumbo River. From each location a sample of water was collected giving a total of 51 samples during three periods: Oct-Nov 1993 (rainy season); Feb-March 1994 (dry season) and August-Sept 1994 (transition season). All stations could not be sampled in all three seasons, since during the dry season some stations were completely dry, and in the rainy season flooding impeded sampling activities.

Sample concentrations were analyzed using 5 ml of river water and 2 ml of concentrated nitric acid which was digested for 4 hours at 130 ºC in a Parr type bomb. The final solution was analyzed with a flame atomic absorption spectrometer (Perkin Elmer 3100 instrument). Three replicates were conducted for each analysis.

DATA ANALYSIS

For data analysis, graphics and tables were processed with all the information available to visualize the general aspects of the distribution of metals, by sampling event and stations. Also, comparisons were carried out with previous studies to determine the relation between metals concentrations in river water using correlation analysis.

A simple cluster analysis was used in order to clarify the differences between sampling sites, sampling period and metal contents in the river water of the area. Classification was performed using the Pearson coefficient as the measure of dissimilarity. The UPGMA (Unweighted Pair-Group Method with Arithmetic mean) clustering method was used.

Analysis of variance (ANOVA) was carried out to compare the levels of metals on different cluster sites. Linear regression was carried out between all elements in the study with $p < 0.05$.

Figure 1. Location of sampling sites on the Catatumbo River.

Table 1. Location of sampling sites along the Catatumbo River.

Sampling Sites	COLOMBIA	Distance to Lake Maracaibo (km)
1	Población de San Pablo	355
2	Población Filogringo	345
3	Población Aserrío	303
4	Conf-Caño Brandy	254
5	Conf-Río San Miguel	247
6	200m abajo población La Gabarra	241
7	Puerto Barco	234
8	Las Delicias	229
9	La Trinidad	221
10	La Gran Colombia	210
	VENEZUELA	
11	Conf-Río Oro	209
12	Puente Ecuador (El Cruce)	194
13	Conf-Río Tarra	153
14	Río Bravo	138
15	Conf-Río Zulia	120
16	Encontrados	114
17	Conf-Caño Limones	64
18	Desembocadura al Lago de Maracaibo	0

RESULTS AND DISCUSSION

The results of the analysis of metals in Catatumbo river water samples are presented in a discriminated form during the sample periods; rainy, dry and transition.

It can be seen that for all periods, metals form characteristic groups such as Na, K, Ca, Mg, Al, and Fe with highest values. Cu, Zn, Mn, and Pb showed intermediate values, with Cr at the lowest value (Figure 2).

Highest concentrations were found during the dry season while the rainy season had the lowest. This was due to the effect of dilution of elements by rain in the river basin. In the transition period, intermediate concentration levels were observed. This general behavior pattern is highly variable along the river, showing the influence of tributaries and other natural and anthropogenic sources such as runoff and domestic and industrial discharges.

Figure 2A shows an increase in the concentration of Al, Fe, K, and Mg (Stations 7 and 9, Puerto Barco and Gran Colombia) during the rainy season. Gutierrez (1995) found total suspended solids (TSS) at these stations to be 216 and 400 mg/l respectively, which could indicate that these metals are entering the river bed in suspension due to a strong soil wash. In addition, there are several farms in the area which could be partially responsible for the concentration of these metals. The rainy season has a dilution effect on Ca, Mn, Cu, Zn, and Cr since the river shows the highest volume flow (411 m^3/s) (ECOPETROL et al., 1996).

At the confluence of the Tarra and Zulia rivers (sampling points 13 and 15) the majority of the metals(Al, Fe, K, Mg, Cu, Zn, and Cr) increased their concentrations because of the suspension of sediments. Gutierrez (1995) earlier reported values for total suspended solids in both stations as 230 and 240 mg/l respectively which agrees with values found here for sediment transport of 5.84×10^3 and 22.97×10^3 ton/day, respectively (ECOPETROL et al., 1996). Ca and Mg were lowered in their concentrations due to dilution. The flow in this location is approximately 250 and

215 m^3/s, respectively (ECOPETROL et al., 1996). The Bravo and Tivi rivers are effluents of the Catatumbo that cause a decrease of the flow.

At Stations 6, 8, and 12, Gabarra (Las Delicias) and Ecuador bridge (El Cruce) a decrease of Al, Fe, K, Mg, Cu, and Zn was found caused by domestic disposal and a decrease in sediment suspension at Station 12 compared to earlier values (1.25 x 10^3 ton/day). Gutierrez (1995) found the values of total suspended solids for these three stations to be 66.150 and 70.000 mg/l respectively, which proves the earlier reasoning. Meanwhile, the opposite behavior is shown by Ca and Mn (increase in concentration) mainly due to disposal from farms and houses located in the vicinity.

Na and Pb maintained their concentrations along the river bed. Oil industry activities and spills could be responsible for the presence of Pb in water.

The pH values showed small variations during the 24 hr period at all sampling stations (6.5-7.1). The same behavior was observed for conductivity values while dissolved oxygen was stable and close to 100% saturation during the day (ECOPETROL et al., 1996).

Figure 2B shows that during the dry season (Feb-March) the concentrations of Al, Fe, K, Mg, Cu, Zn, Pb, and Ca decreased at the confluence of the Brandy and Gabarra rivers. The same occurred at the Oro and Bravo rivers (Stations 4, 6, 11, and 14) due to dilution. Ca increases in La Gabarra and at the confluence of the Brandy river (Stations 4 and 6) which suggests suspension of calcareous materials by the tributary rivers. The pH values in La Gabarra were constant (7.29-7.58) suggesting that metal concentration is independent of pH (ECOPETROL et al., 1996).

Due to the natural characteristics of the area, an increase in the concentration of Na, K, Ca, and Mg was found in the outlet to Lake Maracaibo (Station 18). This can be explained by the effect of sea water from the Gulf of Venezuela entering Lake Maracaibo. The other elements (Al, Fe, Cu, and Zn) showed a decrease in concentration due to dilution caused by water from the lake on the water of the Catatumbo river. The pH and electrical conductivity were constant during this sampling period.

During the transition period (Aug-Sept 1994) the behavior of metal concentrations varies as illustrated in Figure 2C. However, this variation is less sharp than in earlier periods. The majority of metals concentrations have a slight increase at the confluence of the Brandy, San Miguel, Tarra (Venezuelan side) and Zulia rivers and small dilutions at other stations. This behavior can be explained by the start of the rainy season which causes a suspension of sediments. Gutiérrez reported values of TSS of 110, 72.5 and 180 mg/l for these stations which supports the earlier arguments (Gutierrez, 1995). At the outlet to Lake Maracaibo (Station 18) an increase of the major constituents is observed (Na, K, Ca, and Mg) due to the influence of waters from the Gulf of Venezuela mixing with the lake. The other metals decreased in concentration due to dilution by the lake.

The pH values were close to neutral with a mean value of 6.78. Dissolved oxygen remained slightly above 100% saturation. A decrease of this value is observed closer to the river bed which is explained by the laminar flow characteristics of the area (ECOPETROL et al., 1996).

Venezuela does not have water quality criteria for natural waters. This study used Canadian standards to support our conclusions. Results indicate that the Catatumbo river is polluted by metals from autochthonous and anthropogenic sources. When comparing concentration values for Cr, Cu, Pb, Mn, and Zn found in the Danube river (Table 2) it is seen that they are lower. The same is true when comparing with Tigris river in Samana (1993) for concentrations of Cu, Fe, Zn, Mn,

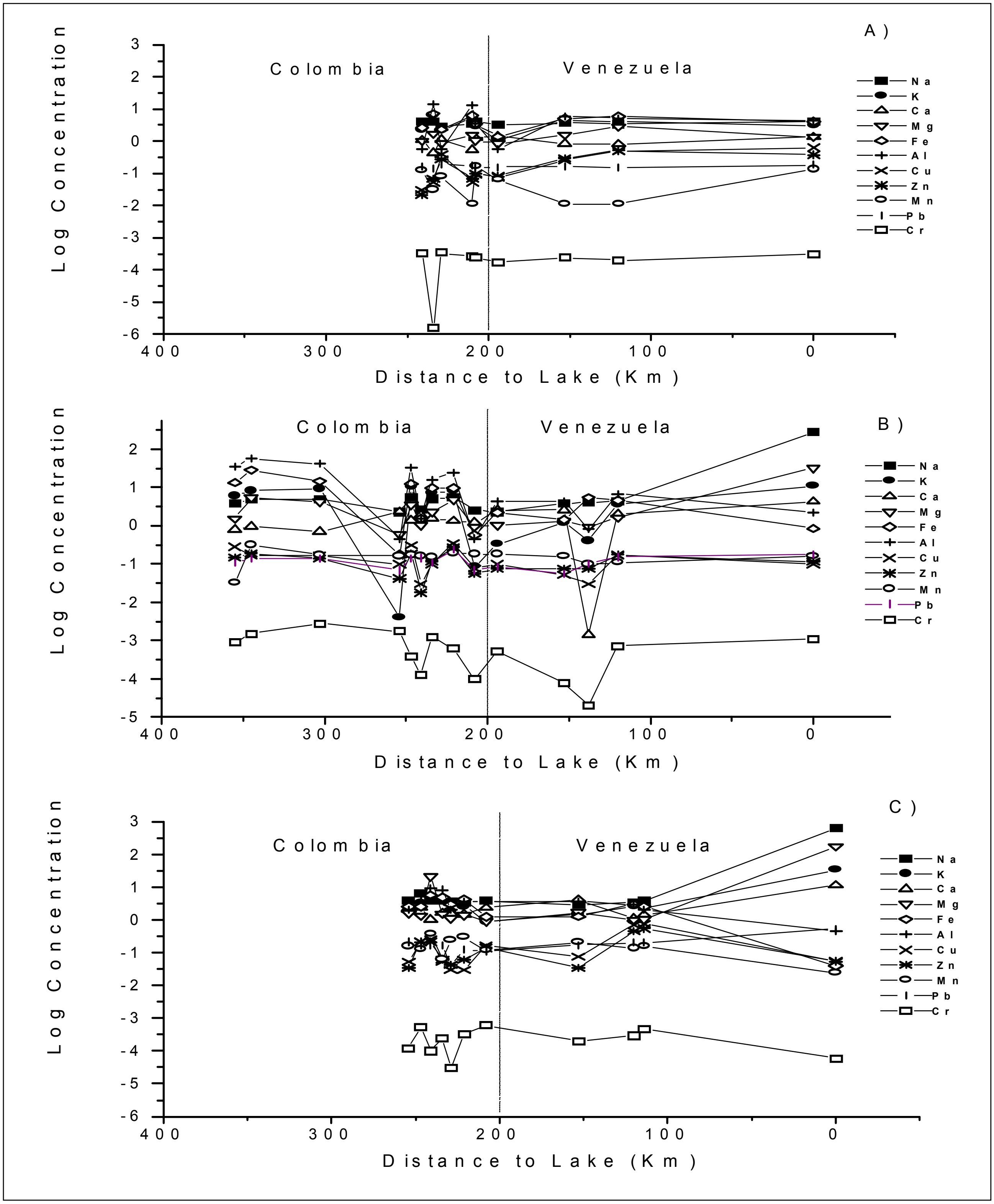

Figure 2. Metals concentrations in Catatumbo River water. A) October-November; B) February-March; C) August-September.

and Pb. The Langat river, in Malaysia, showed values for Cu and Pb lower than the Catatumbo. Values for Zn were at about similar levels (Sarmani, 1989).

The concentration of metals found along the Catatumbo river have the following order: Na > Al > Mg > Fe > K > Ca > Cu > Zn = Pb > Mn > Cr ((30.582, 9.386, 8.313, 5.137, 4.617, 1.863, 0.192,

Table 2. Metal concentrations in different water bodies (mg./L)

Element	Seawater	Freshwater	Canada Water Quality Criteria (Hebron, 1996)	Catatumbo (This Study)	Danube (Forstner et al., 1981)	Tigris (Sabri, 1993)	Langat (Sarmani, 1989)
Aluminum	0.001	< 0.003	0.1	9.386	-	-	-
Chromium	0.00008	0.0005	0.002	0.00049	0.4-1	-	-
Copper	0.00001	0.0018	0.002	0.192	3-7	0.019	0.034
Iron	0.0013	< 0.003	0.3	5.136	-	0.025	-
Lead	$5x10^{-6}$ – $1.5x10^{-5}$	0.0002	0.001	0.156	2-4	0.039	0.058
Manganese	0.0002	< 0.005	-	0.140	2-9	ND	-
Zinc	0.00001	0.0005	0.03	0.157	7-28	0.19	0.176

0.157, 0.157, 0.141, and 0.0005 mg/L respectively). It can be seen that major constituents (K, Na, Ca, and Mg) as well as Al and Fe show the higher concentrations along the river bed.

Table 3 shows that major constituents are very correlated amongst themselves. There is also an important positive correlation of these elements with Pb. According to Zhou et al., (1995), Na, K, Ca, and Mg, when present in high concentrations, compete with Pb for adsorption on suspended particles. Ca has a negative correlation with Fe which suggests that one of them is present in water in higher concentration as compared with the other. It is shown in Figure 2 that concentrations of Fe are above Ca concentrations in the majority of the sampling stations. This could indicate that Fe has higher concentrations in water than sediments, while calcium has the tendency to precipitate on the sediment.

A positive correlation for Fe, Al and Cr indicates the common source of these metals. High concentrations of Fe and Al found in the river bed, and their tendency to increase when sediment transport is greater seem to show that they are soil constituents in the area, and that probably the source for Cr is also the suspended soil because of the small concentrations found along the river bed.

Cu and Zn also showed a positive correlation which could indicate a fixed and continuous common pollution source. Paulson et al., (1989) and Muller (1994) stated that the increase in Cu and Zn concentrations was due to construction activities and ship transport (anthropogenic sources). Sarmani et al., (1992) found Cu in the Linggi river came from pig farms where copper sulfate was used as additive for pig feeding. Sources for Cu and Zn are not identified as yet. However, these elements are typical pollutants of human activities and come from domestic and industrial residues. Mn does not show significant correlation with the other elements.

According to values of total phosphorus and orthophosphate in waters found by Gutierrez (1995) it was found that total phosphorus is correlated negatively with Ca which could suggest competition for a common site in the formation of complexes. Mn has a wide adsorption surface, retaining phosphorus. This could be the reason for the positive correlation between orthophosphate and this element.

Table 3. Summary of linear correlation coefficients between elements from Catatumbo river water n=33; p<0.05; r = 0.349).

	Na	K	Ca	Mg	Fe	Al	Cu	Zn	Mn	Pb	Cr
Na	1.00										
K	.88 *	1.00									
Ca	.91 *	.74 *	1.00								
Mg	.96 *	.90 *	.90 *	1.00							
Fe	- .20	.19	- .34 *	- .15	1.00						
Al	- .14	.26	- .25	- .10	.95 *	1.00					
Cu	- .15	- .06	- .20	- .13	.09	.06	1.00				
Zn	- .14	- .04	- .23	- .12	.13	.06	.95 *	1.00			
Mn	- .21	- .18	- .11	- .17	.23	.20	- .06	- .11	1.00		
Pb	.79 *	.80 *	.73 *	.84 *	- .12	- .09	.16	.16	- .28	1.00	
Cr	- .05	.12	- .09	- .10	.50 *	.59 *	.02	.01	.19	- .17	1.00

The load of metals from the Catatumbo river to Lake Maracaibo is as follows: Na > Mg > K > Ca > Al > Fe > Pb > Cu > Zn > Mn > Cr (966.74, 219.60, 49.80, 18.12, 7.56, 5.27, 0.95, 0.82, 0.57, 0.33, and 0.0015 x 10^4 kg/yr). Major constituents (Na, K, Ca, and Mg) have higher values due to the influence of the lake waters on the river in the dry season. The load of Al and Fe to the lake is high (7.6 x 10^4 and 5.3 x 10^4 kg/yr respectively) which suggests high concentration of both elements in the soils of the region (M.E.M., 1995). The load of the other elements is lower.

The load of Mn and Cu (0.82 x 10^4 and 0.33 x 10^4 kg/yr) from the Catatumbo river to the lake is similar to the load of both elements from the Brazos river to the Gulf of Mexico (0.33 x 10^4 and 0.11 x 10^4 kg/yr). The load of Pb from the same river (0.0066 x 10^4 kg/yr) and from the Loire river (0.0055 x 10^4 kg/yr) compared with the load from Catatumbo to the lake (0.95 x 10^4 kg/yr) showed that the Catatumbo is approximately two orders of magnitude higher. These results seem to indicate that the Catatumbo is a significant contributor of Pb, due probably to the oil activities in the basin.

By means of statistical cluster analysis the unsimilarity amongst stations was tested for metals concentration. To obtain successive partitions (clusterings) organized in different priority levels, each partition was formed by clusters in which the elements of the same class should be reasonably homogeneous. The result is represented in a dendrogram (Cuadras, 1991)

Figure 3 shows the dendrogram obtained for the sampling period October-November. It separates the stations into three groups, and Fe, Al, K and Mg are the cations which limit this separation. Puerto Barco and Gran Colombia (Stations 7 and 10) are separated since they have the highest values for these metals. Stations 11, 13, 15, and 18 (confluence of the Oro, Tarra, and Zulia rivers and the outlet to Lake Maracaibo) are grouped to present intermediate values of these elements. The flow of these rivers is lower and therefore the sediment transport must be lower. Stations 6, 8, and 12 (La Gabarra, Las Delicias and Puente Ecuador) are separated from the others and show the lowest values for Fe, Al, K and Mg, due to less transport. This finding agrees with the values found by Gutierrez for total suspended solids, (Gutierrez, 1995).

The dendrogram for the sampling period of February-March (Figure 4) shows three groups of stations with two stations clearly separated. Station 18 (outlet to Lake Maracaibo) is very different from the others and shows the highest values of Na, K, Ca and Mg. This could be due to the influence of waters of the lake on the Catatumbo during the dry season. Station 14 (confluence with the Bravo river) had the lowest values of Al, Ca, and Cr due to the outflow of waters from the Catatumbo to the Bravo river. The other three groups in the dendrogram are separated for Fe and Al concentrations: Stations 4 and 11 (confluence with Brandy creek and the Oro river) are separated from the rest of the stations since they have the lowest values of Fe and Al, caused by the dilution effect due to the inflow of these rivers. Stations 6, 12, 13, and 15 (Gabarra, Puente Ecuador, confluence with the Tarra river and Zulia river) form a group in the intermediate Venezuelan zone showing intermediate values for Fe and Al caused by a decrease in the transport of sediments and the discharge of neighboring cities to the Catatumbo. This was supported by Gutierrez when determining total suspended solids for these stations as 70, 75, 76, and 140 mg/l respectively (Gutierrez, 1995). On the other hand, Stations 1, 2, 3, 5, 7, and 9 (San Pablo, Aserrio, Filogringo, confluence of the San Miguel river, Puerto Barco and Trinidad) form a group in the Colombian zone with the highest values of Al and Fe due to the transport of sediments and domestic disposal. This is supported by the values of total suspended solids, found by Gutierrez (420, 255, 360, 130, 125 and 100 mg/l, respectively). This is due to the mountainous characteristics of the Colombian area as compared with the Venezuelan flatlands (ECOPETROL et al., 1996).

During the sampling period of August-September (Figure 5), the dendrogram depicts a ladder which groups two sets of stations and four separated stations. This is due to the peculiarities of this sampling which occurred in both dry and rainy seasons. Station 18 (outlet to Lake Maracaibo) had the highest values of Na, K, Ca, and Mg due to the effect of the lake waters (with a similar behavior

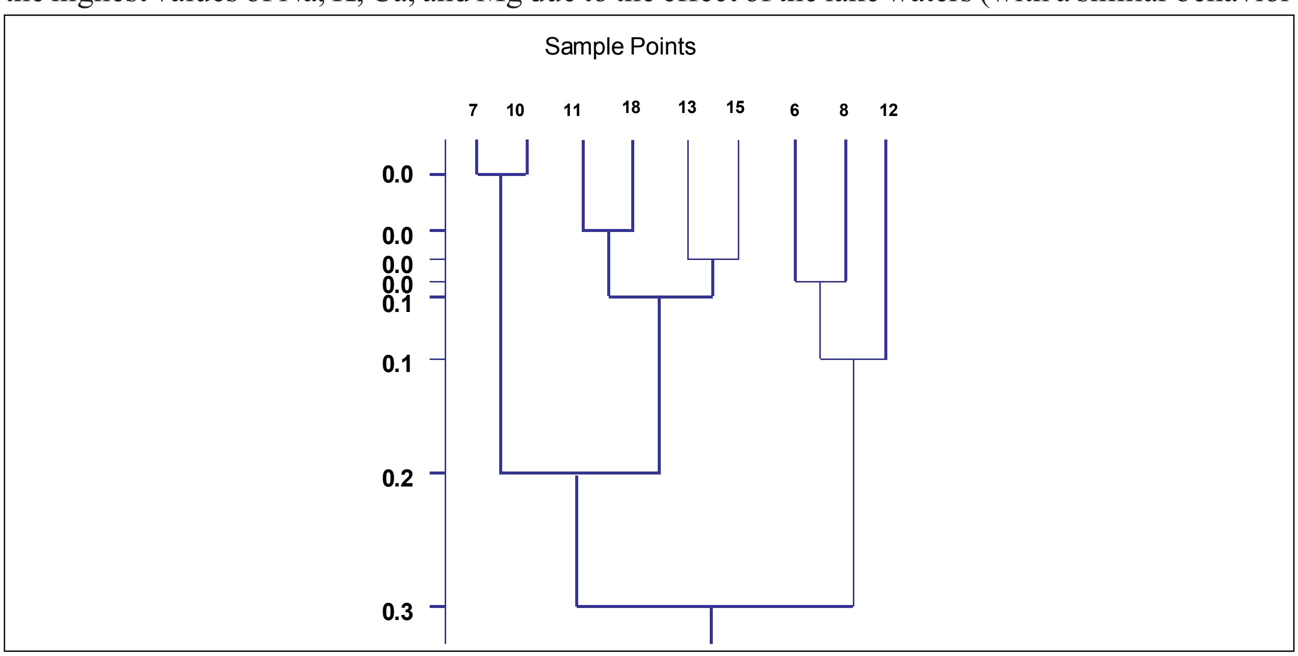

Figure 3. Unsimilarity of sampling sites (October-November).

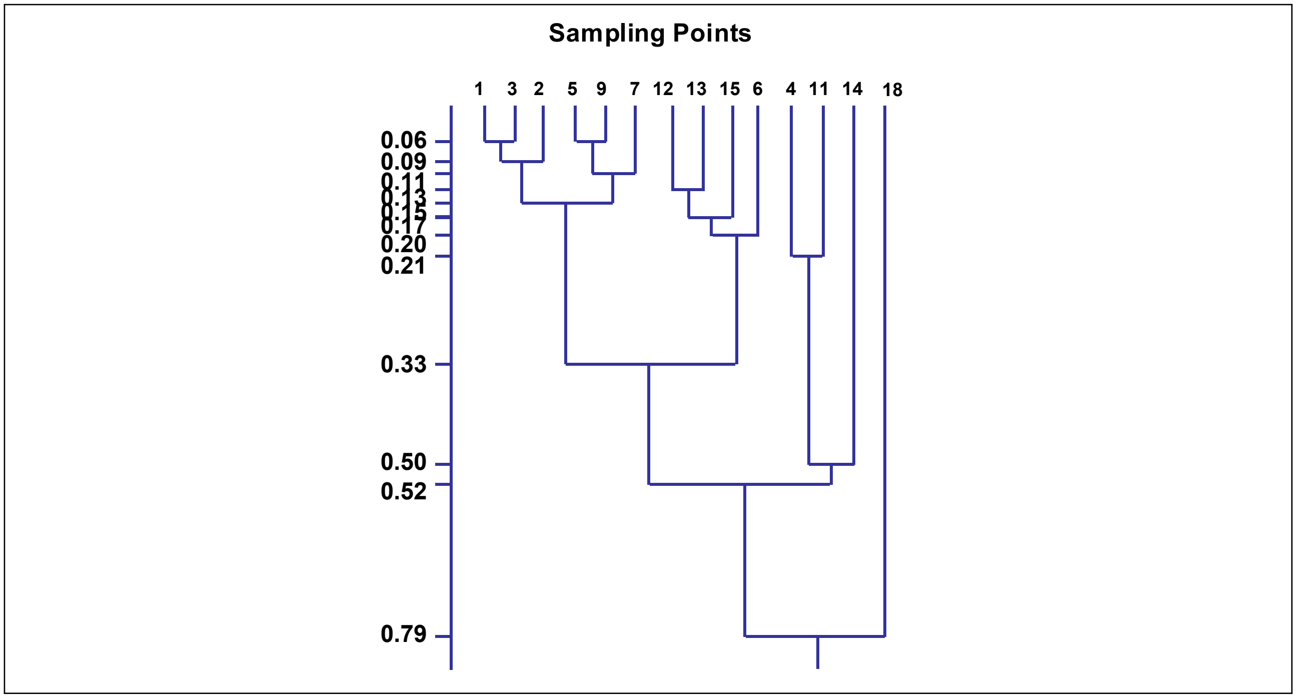

Figure 4. Unsimilarity of sampling sites (February-March).

for the dry season) and low values of Al, Fe, and Mn due to dilution. Station 6 (La Gabarra) presents the highest values of Al, Fe, and Mn due to domestic discharges and the increase in the transport of sediments. The value of TSS found by Gutierrez for this station was 320 mg/l (Gutierrez, 1995). The other stations showed intermediate values for the three elements. Station 13 (confluence of the Venezuelan Tarra river) had the lowest value of Na. Station 7 (Puerto Barco) is separated of the rest of stations showing the highest values of Al and Fe and the lowest value of Mn due probably to the influence of domestic discharges. Stations 5 and 11 (confluence of San Miguel and Oro rivers) had the highest levels of Ca and Cr, while Stations 4, 8, 9, 15, and 16 (confluence with Brandy creek, Las Delicias, La Trinidad, confluence with Zulia river, Encontrados) had the lowest concentrations of Ca and Cr.

The important influence of the rainy season on the rivers can be seen in the differences between stations. For the dry season, the station differences are due to the influence of the tributaries, domestic discharges and the mixing of lake waters with the Catatumbo. In this particular season a number of groups are shown; one in the Colombian side, a second in the intermediate Venezuelan area and a third at the outlet to Lake Maracaibo. During the transition season, the influence of the rivers, the domestic discharges and the mixing of waters from the Lake are again present, showing characteristics of both dry and rainy seasons.

CONCLUSIONS

This work represents the first metal content evaluation in water samples from the Catatumbo river and establishes a reference for future studies.

Na, K, Ca, Mg, Fe, and Al had the highest concentrations in the samples. This could be due to the effect of mixing of waters from Lake Maracaibo, mainly during the dry season, whereas Fe and Al showed high values due to runoff and transport of soils from the region.

There is good correlation amongst the metals which shows their common origin. Na, K, Ca, and Mg are present due to the action of Lake Maracaibo in the river. Al, Fe, and Ca come from the strong

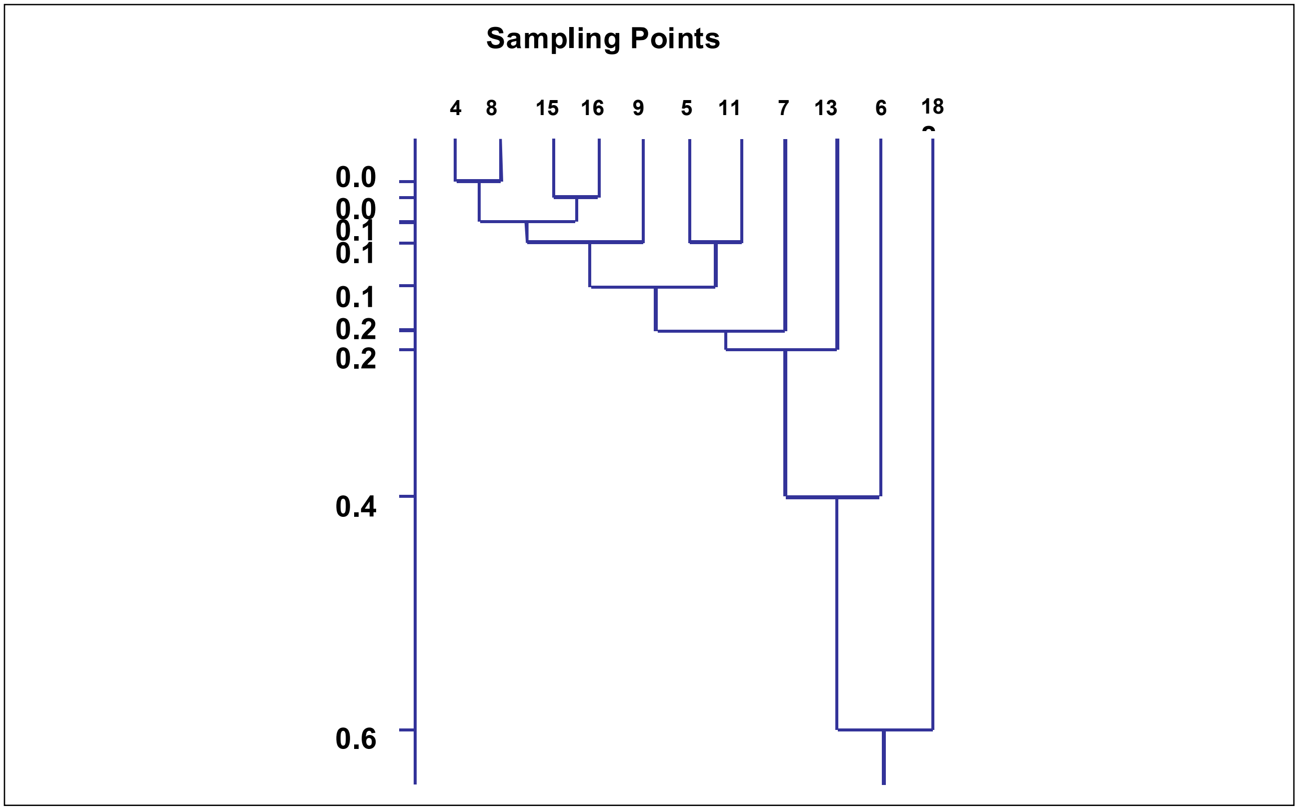

Figure 5. Unsimilarity of sampling sites (August-September).

process of soil erosion and transport. Finally Cu and Zn appear to come from a fixed source.

The high yearly load of metals to Lake Maracaibo indicates that the Catatumbo river is a major contributor of metals to the lake.

The statistical analysis determined that the separation of elements with highest concentrations (Fe, Al, Na, K, Ca, and Mg) is controlled by the seasons. During the dry season both populations can be observed by the formation of groups in different geographical areas: one in the mountainous Colombian zone, a second one in the Venezuela intermediate flatland zone and a third at the outlet to Lake Maracaibo. The first is likely due to sediment transport, the second is caused by sediment accumulation and the third is the mixing with Lake Maracaibo waters. During rainy and transition seasons, these differences are muted.

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