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CONTENIDO

Página

DÍAZ, O. & I. LIÑERO-ARANA. Poliquetos asociados a substratos artificiales sumergidos en la costa nororiental de Venezuela. III: Eunicida (Annelida: Polychaeta). 3

MÁRQUEZ, A., W. SENIOR., G. MARTÍNEZ & J. CASTAÑEDA. Environmental conditions of the waters of the Manzanares river, eastern Venezuela. 15

Díaz, O. & I. LIÑERO-ARANA. Poliquetos asociados a substratos artificiales sumergidos en la costa nororiental de Venezuela. IV: Orden Phyllodocida. 25

SANT, S., A. PRIETO & E. DE ELGUEZABAL. Composición y estructura de la comunidad de corales en dos localidades del Golfo de Cariaco, Estado Sucre, Venezuela. 39

AMARO, M. & I. LIÑERO-ARANA. Demospongiae (Porifera) de Isla Larga, Bahía de Mochima, Venezuela. 45

JIMÉNEZ, M. & I. LIÑERO-ARANA. Moluscos en praderas de *Thalassia testudinum* en Isla Larga, Bahía de Mochima, Edo. Sucre, Venezuela. 55

GUTIÉRREZ, M., M. BALZA & B. MARÍN. Efecto de la temperatura en el desarrollo embrionario de la sardina, *Sardinella aurita* (Valenciennes, 1847) (Pisces: Clupeidae) en condiciones controladas de laboratorio. 67

MARCANO, J., A. LÁREZ., X. GUTIÉRREZ., H. SALAZAR., M. MÁRQUEZ & J. SAYEGH. Pesquería de túnidos por pequeños palangreros en el Mar Caribe y el Océano Atlántico durante el período 1986-2000. 73

MARTÍNEZ, G. Metales pesados en sedimentos superficiales del Golfo de Cariaco, Venezuela. 83

Indice acumulativo del Boletín del Instituto Oceanográfico de Venezuela desde 1961 hasta 2002. 97

Bol. Inst. Oceanogr. Venezuela, Univ. Oriente 41 (1&2): 15-24 (2002); 7 Figs., 2Tabs.

ENVIRONMENTAL CONDITIONS OF THE WATERS OF THE MANZANARES RIVER, CUMANA-SUCRE, VENEZUELA.

A. MÁRQUEZ, W. SENIOR, G. MARTÍNEZ, AND J. CASTAÑEDA

Instituto Oceanográfico de Venezuela, Universidad de Oriente, Cumaná, Venezuela.
aristide@sucre.udo.edu.ve.; wsenior@sucre.udo.edu.ve.; gmartine@sucre.udo.edu.ve.

ABSTRACT: The Manzanares River is one of the more important rivers of Venezuela inasmuch as it is used to supply drinking water to a large part of the northeastern zone of Venezuela. For this reason a study was undertaken of the surface waters of the estuarine zone of the river, following the saline gradient from zero to salinities greater than 30. The following properties were measured: river volume flow, rainfall, pH, temperature, suspended materials, dissolved oxygen and ammonium, and heavy metals (Fe, Mn, Cu, Zn, Ni, Cr, Pb and Cd) in particulate and dissolved phases. River volume flow varied with seasonal rainfall throughout the year, as expected, while temperature varied between 24.5 and30.4 °C and pH ranged from 6.65 and 8.9. From the dry to the wet season, suspended material increased from 23 to 880 mg/l at low salinity, and always decreased progressively as salinity increased. Concentrations of total ammonium, 14.5 to 14.3 mmol/l, were high, while those of dissolved oxygen, 3.57 to 5.27 ml/l, were low, and these levels were even more accentuated at salinities under 5 during the dry season. The highest concentrations found for heavy metals were: Fe 406.02; Mn 5.57; Zn 2.18; Cu 0.72; Cr 0.19; Ni 0.72; Pb 0.12; Cd 0.03 mmol/l. These surpass Venezuelan legal limits for water intended for human consumption as well as for waters to be discharged in coastal areas. Concentrations decreased at increased salinity because of the dilution effect, flocculation and/or precipitation in the form of oxyhydroxides. The results obtained in this study reveal a serious deterioration of the state of the waters of the lower Manzanares river.

Key words: Contamination, surface water, estuarine zone, Venezuela.

RESUMEN: El río Manzanares es uno de los ríos más importantes de Venezuela ya que sus aguas se usan para abastecer de agua potable a la zona nororiental de Venezuela. En vista de la importancia de este río, se emprendió un estudio de las propiedades siguientes: el flujo de volumen del río, lluvia, pH, temperatura, material en suspensión, oxígeno disuelto, amonio y metales pesados (Fe, Mn, Cu, Zn, Ni, Cr, Pb y Cd) en las fases disuelta y particulada de sus aguas, siguiendo el gradiente salina desde cero hasta salinidades mayores a 30 en las aguas superficiales de la pluma que forma. El flujo de volumen del río siguió la intensidad de lluvia, la temperatura y pH variaron respectivamente entre 30,4 y 24,5 °C y 6,65 y 8,9 unidades. De la estación seca a la lluviosa, el material suspendido aumentó de 23 a 880 mg/l, disminuyendo progresivamente a lo largo de la pluma con el aumento de la salinidad. Las concentraciones de amonio total, 14,5 a 14,3 μmol/l eran altas, mientras que el oxígeno disuelto, 3,57 a 5,27 ml/l, era bajo, y sus niveles se disminuyeron más aun a salinidades inferiores a 5 unidades durante la estación seca. Las concentraciones más altas encontradas para los metales pesados eran: Fe 406,02; Mn 5,57; Zn 2,18; Cu 0,72; Cr 0,19; Ni 0,72; Pb 0,12; Cd 0,03 μmol/l. Éstos superan los límites legales venezolanos para agua de consumo humano así como para las aguas a ser servidas en las áreas costeras. Estas concentraciones disminuyeron a medida que aumentaba la salinidad debido a efectos de dilución, floculación y/o precipitación en la forma de oxihidróxidos. Los resultados obtenidos en este estudio revelan un deterioro del estado de las aguas de la cuenca baja y la pluma del río Manzanares.

Palabras clave: Agua superficial, zona estuarina, Venezuela.

INTRODUCTION

The deterioration of the environment has been, during recent years, a subject of primary importance for the countries of the first world. Ironically, in Venezuela, which has been classified as one of the six "mega-diverse" countries of Latin America and is considered to be among the ten most important places of the world for the conservation of biodiversity, the debate concerning environmental problems has not been accorded the importance which it merits. After the United Nations Conference on the Environment and Development, Rio 92, there remain no doubts concerning the scientific, economic and social importance of rivers, estuaries and coastal zones (CINCIN-SAIN, 1993).

Environmental problems are of such diverse natures that generally it is necessary to order them by some means in order to systematize their study. The deterioration of a hydro-resource may be a process of various phases, such that in the initial phases the causative agents of the deterioration may perhaps be detectable through appropriate analyses. If corrective action is not taken as soon as the symptoms are detected, they may grow rapidly to an alarming level and be capable of impacting the ecosystem. The development of such a hydro-resource following the application of the corrective measures will depend upon their efficacy (EMILIANI, 1997). In general, any refuse which is discharged into a body of water changes the ecological equilibrium and the capacity of the receiving current to transform such refuse (FERNÁNDEZ, 1984).

The Manzanares River is one of the more important rivers of Venezuela. In its basin, which is characterized by a dry season, from December to June, and a wet season, from July to November, is found the Turimiquire dam and reservoir, which supplies water to the entire northeast region of Venezuela. This river arises in the Turimiquire hills at an altitude of over 2000 m above sea level and discharges into Caribbean Sea at the entrance of the Gulf of Cariaco. It exerts a great influence upon the Venezuelan coast to the west of the city of Cumaná, which is situated between 10° and 10°30' latitude north and between 64°10' and 64°20' longitude west (Figure 1). The river's hydrographic basin covers about 1,652.1 km^2 and its yearly discharge is estimated at 600 million m^3. In recent years this contribution has increased by more than 20% to 771 ′ 10^6 m^3 (SENIOR & GODOY, 1991; SENIOR, 1994; LEÓN *et al.*, 1997; MÁRQUEZ, 1997; MÁRQUEZ *et al.*, 2000, MARTÍNEZ & SENIOR, 2001). Depending on the direction of the winds and currents, the water discharged by the river into the Caribbean Sea, flows from east to west (toward the entrance to the Mochima bay) or from south to north (toward the Araya peninsula) (MORA *et al.*, 1967). The greater portion of this current is aerobic and causes mucilages to be deposited on the sea bed, where the processes of fermentation are more frequent. At times when local industries discharge significant amounts of organic material, acids and caustic substances into the river, the mass of water undergoes changes in both its composition and its appearance, as well as the life which it sustains (FERNÁNDEZ, 1984).

The waters of the Manzanares River drain a vast agricultural area characterized by sugar cane plantations. Studies carried out in the decade of the nineties have shown that the quality of the waters of the Manzanares River in its lower basin, from the town of Cumanacoa toward its mouth in Cumaná, has been altered as a result of increased industrial, agricultural and anthropogenic activity in the area. This is manifested as a progressive rise in the levels of organic matter, coliform organisms and heavy metals in the coastal waters near the city of Cumaná (SENIOR & GODOY, 1991; IABICHELLA, 1993; LEÓN, 1995, MÁRQUEZ *et al.*, 2000).

Further details concerning the study area are described by MALONEY (1966), for its geology, FERNÁNDEZ (1971, 1973, 1984), IABICHELLA (1993), for bacteriological contamination, ALVARADO (1976, 1979), GODOY (1991), for organic contamination, SENIOR & GODOY (1991) for the distribution of nutritive elements, SENIOR (1994) for the environmental evaluation of the ecosystem, LEÓN *et al.* (1997), MARTÍNEZ (1999) and MÁRQUEZ *et al.* (2000) for the behavior of heavy metals in the lower basin of the Manzanares River.

The principal interest of this study is to investigate the deterioration which the waters of the Manzanares River have been experiencing. Results are presented for the superficial waters of the estuarine zone of the river during the year 1997. The regional rainfall throughout the year is reported, as well as the volume flow rate of the river, the pH and temperature of its waters, and the concentrations of suspended matter, dissolved oxygen, and total ammonium and heavy metals in suspended and dissolved phases.

MATERIALS AND METHODS

A total of 22 samples of surface water of the river were collected each month during the year 1997. The samples were taken following the saline gradient from zero to salinities greater than 30, in the direction toward the Araya peninsula (Fig.1). The salinity was measured *in situ* by means of a portable salinometer (YSI model 33) to a precision of ± 0.1, and confirmed in a separate induction unit (Kahlsico model 118 WC 200) having a precision of ± 0.001.

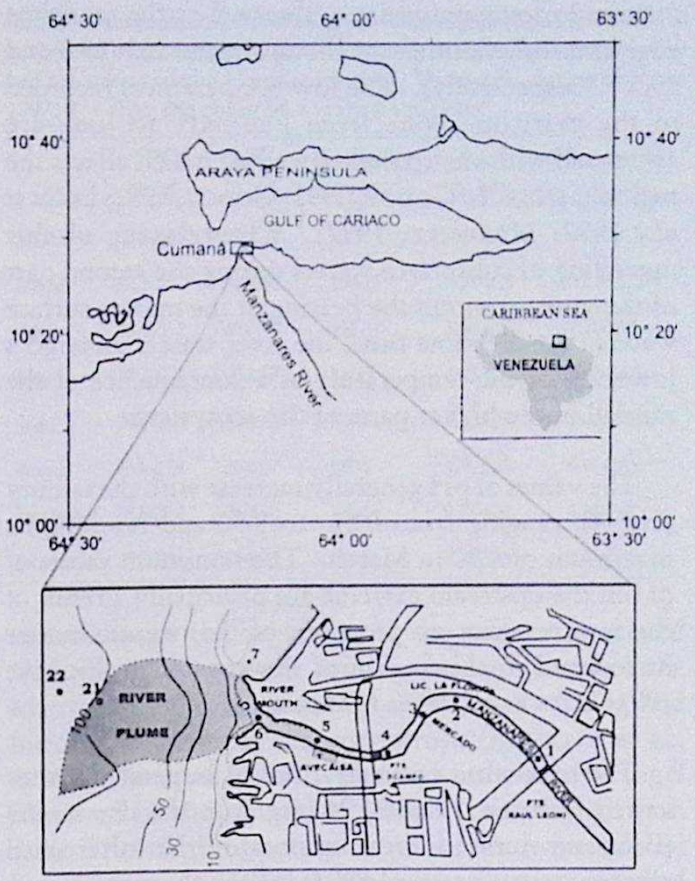


Figure 1. Sampling area, showing a section of the Manzanares river passing through the city of Cumaná

The data for the volume flow rate of the river in m^3/s and rainfall (mm) were supplied by the Departamento de Hidrología y Meteorología del Ministerio del Ambiente y de los Recursos Naturales (M.A.R.N), Caracas, Venezuela. The monthly average for the period 1980–1991 for the volume flow rate at Guaripa station and for the rainfall at Salsipuedes station of the Manzanares River were used. The pH was determined *in situ* with a pH-meter (Bantex, LCG-5) having a precision of ± 0.01 unit. The surface temperature was determined *in situ* by the use of a mercury thermometer to a precision of ± 0.1 °C. The dissolved oxygen was analyzed by the Winkler method, with a routine precision of ± 0.03 ml/l (AMINOT & CHAUSSEPIED, 1983). Ammonium was determined according to KOROLEFF (1969), which measures the total ammoniac nitrogen $N\text{-}NH_3$ + $N\text{-}NH_4^+$. Suspended material was captured on glass filters, Gelman Science type A/E 47 mm. The precision of this method is ± 0.15 mg/l and provides a limit of detection of 0.3 mg deposited on the filter (SENIOR, 1995). Heavy metals were determined in both particulate form and dissolved phases. For metals in the particulate phase, one liter of each sample was filtered in a Millipore apparatus, using filter membranes of cellulose type HA with pores of 0.45 mm in diameter. The material retained on the filter was treated with a mixture of concentrated nitric and hydrochloric acid (GREENBER *et al.*, 1992). The dissolved metals were determined from the filtrate by chelating with ammonium pirrolidine dithiocarbamate (APDC) and extracting with methyl isobutyl ketone (MIBK). The chelates in organic phase were treated with concentrated nitric and hydrochloric acid (OLSEN & SOMMERFELD, 1973; GREENBER *et al.*, 1992). The particulate and dissolved extracts were analyzed by atomic absorption spectrophotometry with an air-acetylene flame in a Perkin-Elmer model 3110 instrument with deuterium background corrector. The blanks received the same treatment. The concentrations of metals allowed by Venezuelan law, which are cited in the text, are taken from the Gaceta Oficial N° 34,829 of 29 January 1992.

RESULTS AND DISCUSSION

Monthly time evolution of the discharge behavior of the Manzanares River and the rainfall are shown in Figure 2, for the period 1980–1991. The values of temperature, pH, suspended material, dissolved ammonium and oxygen are shown in Table I. The concentrations of heavy metals are presented in Table II. The behavior of the temperature and pH are given in Figures 3 and 4, the reduction of suspended material and heavy metals with the increase of salinity in the dry season are shown in Figures 5 and 7, respectively.

A linear relation was found with positive significance ($r = 0.86$) between the volume flow of the river and the rainfall. The flow evolved parallel with the rainfall, recording lower values (8.98–15.05 m^3/s) in the months of low rainfall (January to June), increasing (23.96–42.77 m^3/s) from July through November, which corresponds to the time of greatest rainfall, and then decreasing in December as the dry season begins once more. In the decade of the seventies, the values of the river flow decreased quite significantly to 14.70 m^3/s, which is equivalent to an annual drainage of 464×10^6 m^3. This situation was made clear by AGUILERA DE LEÓN and ROJAS (1976), who reported that

in the year 1972 the average flow of the river was 11.75 m^3/s. At that time these authors pointed out the risk for the wildlife in the river. Nonetheless, in the following decades (1980-1991), according to data obtained from MARN, the waters of the river registered their greatest flow values (21.99–34.05 m^3/s), with an average of 23.17 m^3/s and an annual drainage of 731 × 10^6 m^3.

In spite of the fact that apparently there has been an increase in the flow of water in the river, it is worrisome that currently there is inadequate management and usage of this important fluvial body. Indiscriminate logging occurs in the higher basin and products of domestic and industrial discharge commonly become concentrated during the dry season. The small increase of average flow in recent years during the months of the dry season does not appear significant, inasmuch as the deterioration in quality of the waters has increased and the physical and chemical conditions continue to be strongly altered during the dry period of the year.

The temperature recorded during this study range between 30.4 and 24.5°C. During the dry season, which comprises the months from February to June. Maximum values of 30.4 °C were reached at the river upstream end in April and the minimum at the maritime edge. With the beginning of the rainy season, from August to November (Fig. 3), this situation is reversed and the maximum temperatures are observed at the maritime edge and the minimum at the upstream end (29.0 and 25.5 °C respectively). The low temperatures recorded in the maritime zone from February to June are associated with the coastal upwelling which affects the region (SENIOR & GODOY, 1991; GODOY, 1991; LEÓN *et al.*, 1997; MÁRQUEZ, 1997). The relaxing of this upwelling of subsurface waters during the second part of the year promotes the heating of the marine surface waters. At the same time, the river waters undergo a lowering of the temperature as a consequence of the rainfall in the higher parts of the ecosystem.

The values of pH generally increase with the salinity (Fig. 4), ranging from 6.65 to 8.90 and reaching its maximum of 8.90 in March. The minimum values of pH in the upstream extreme are principally a result of the remineralization processes of the organic matter introduced in this region of the ecosystem (GODOY, 1991; LEÓN *et al.*, 1997; MÁRQUEZ, 1997).

The maximum concentrations of suspended matter varied between 23 and 194 (mg/l) in the dry season (February–June), increasing notably thereafter until reaching a maximum of 880 (mg/l) in the rainy season (August) (Table I). These values was observed to decline with the salinity because of a process of flocculation (MÁRQUEZ *et al.*, 2000) (Fig. 5). The increase of this

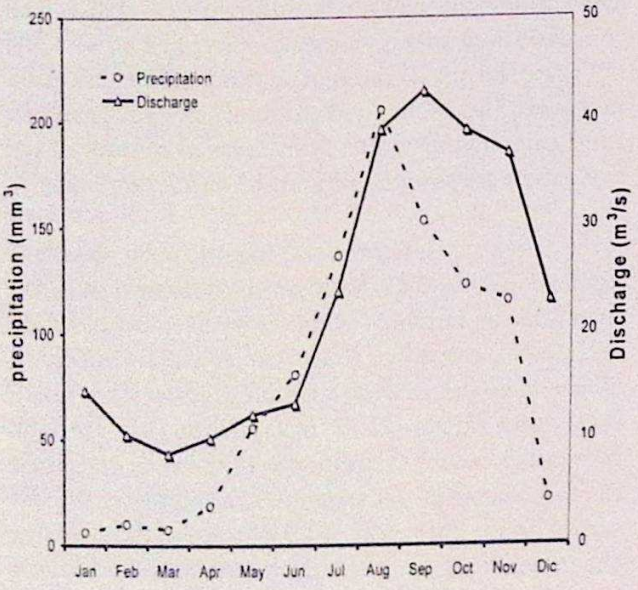


Figure. 2. Monthly averages of the annual variation of the discharge and precipitation of Manzanares River, 1980-1991.

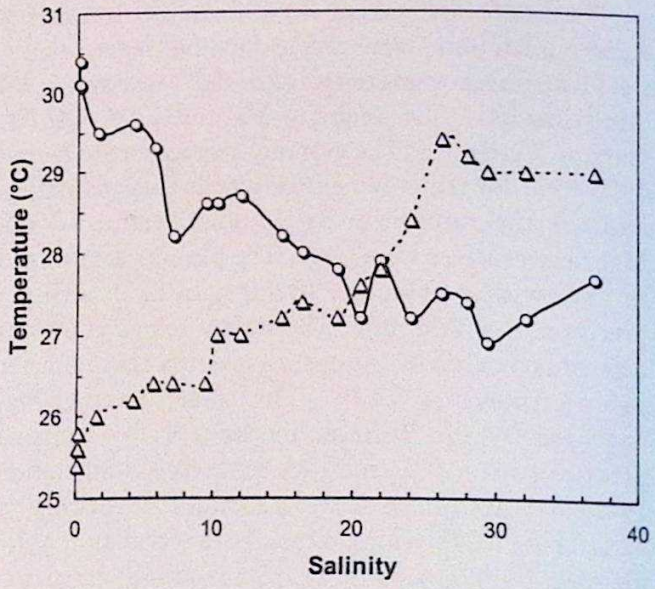


Figure 3. Behavior of the temperature in the surface waters of the Manzanares river, Venezuela, during the months of the dry season (–o–) and the wet season (–Δ–) of the year 1997.

Table I. Values of temperatura and pH and ranges of concentrations of suspended material (SM), dissólved oxygen and ammonium in the surface waters of the Manzanares river, Venezuela, during the year 1997. R = river end point; M = marine end point

	T (°C) R-M	pH R-M	SM (mg/l) R-M	O_2 (ml/l) R-M	NH_4^+ (µmol/l) R-M
February	27.8-24.5	8.23-8.22	32-2	4.33-3.90	14.50-4.14
March	27.8-27.0	7.70-8.90	194-23	4.07-4.79	12.16-3.00
April	30.4-27.2	7.47-7.91	155-21	3.57-4.53	7.70-1.91
May	28.2-26.4	7.28-8.07	83-19	4.02-4.75	6.93-2.62
June	29.6-26.0	6.65-8.87	70-13	4.10-4.54	14.30-0.67
August	25.4-29.4	7.36-8.47	880-8	4.76-5.27	4.47-0.83
September	26.8-27.1	7.04-7.90	115-14	2.17-4.34	6.78-0.40
November	25.8-27.1	7.69-8.39	112-31	6.20-7.89	2.61-0.85

material with the beginning of the rains is associated with the erosion of the soils in the high basin of the Manzanares River, caused by activities of cutting and burning of the trees and underbrush (AGUILERA *et al.*, 1985; LEÓN *et al.*, 1997). The high value of 194 mg/l observed in the month of March is associated with material of anthropogenic origin which is introduced into the river and/or with the resuspension of riverbed sediments, which accumulate in the period of reduced river flow and increased residence times of the waters (MÁRQUEZ, 1997; MÁRQUEZ *et al.*, 2000). The concentrations reported here are lower than the 1124 and 1074 mg/l reported by LEÓN (1995) and MARTÍNEZ (1999) respectively in this same sampling zone.

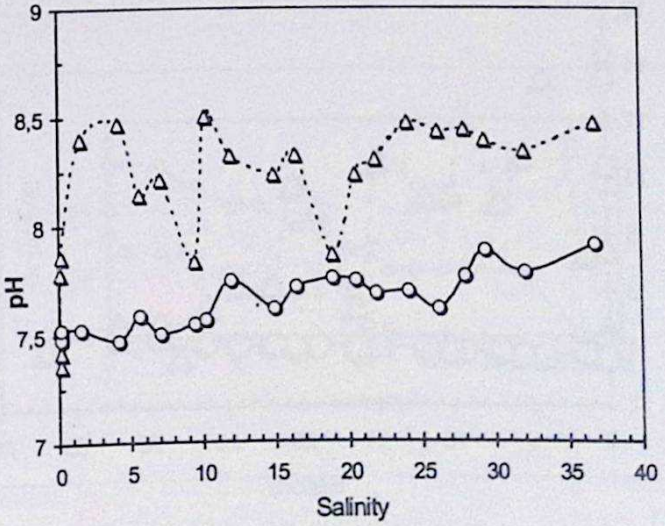


Figure 4. Behavior of the pH in the surface waters of the Manzanares river, Venezuela, during the months of the dry season (-o-) and the wet season (— Δ —) of the year 1997.

The maximum concentrations of ammonium varied between 14.5 and 14.3 mmol/l, the lower values being found always at the maritime extreme. The highest values, observed between February and June at the upstream extreme, coincide with the period of least river flow, highest water temperature and least pH and dissolved oxygen concentrations, as well as the greatest residence time of the waters. These factors promote the gradual decomposition of the organic matter introduced into the river from urban waters, the Municipal Market and food processing factories located along the riverbanks in the city of Cumaná. In the study zone the ammonium would appear to have two origins: industrial and urban discharges with posterior hydrolytic liberation and through the process of decomposition of organic matter discharged into the

Table II. Maximum concentrations (µmol/l) of heavy metals en suspension (S), dissolved (D) and total (T) in the surface waters of the Manzanares river, Venezuela, during the year 1997. S = Metals in the particulate fraction; D = Metals in the dissolved fraction; T = Total metals = S + D; nd = Not detected

		Fe	Mn	Zn	Cu	Cr	Ni	Pb	Cd
February	S	10	0.13	0.38	0.02	0.05	0.14	0.01	0.004
	D	0.53	0.03	0.05	0.01	nd	0.02	nd	nd
	T	10.53	0.16	0.43	0.03	0.05	0.16	0.01	0.004
March	S	123	1.80	0.36	0.07	0.07	0.15	0.03	0.004
	D	1.65	0.08	0.06	0.02	nd	0.02	nd	nd
	T	124.65	1.88	0.42	0.09	0.07	0.017	0.03	0.004
April	S	83	1.18	0.43	0.10	0.07	0.13	0.06	nd
	D	0.95	0.8	0.06	0.02	nd	0.01	nd	nd
	T	83.95	1.26	0.49	0.12	0.07	0.14	0.06	0.004
May	S	42	0.65	0.39	0.05	0.19	0.12	0.05	nd
	D	0.7	0.04	0.03	0.01	nd	0.01	nd	nd
	T	42.07	0.69	0.42	0.06	0.19	0.13	0.05	0.004
June	S	55	0.60	0.56	0.09	0.19	0.19	0.02	0.02
	D	0.85	0.04	0.04	0.02	nd	0.02	nd	nd
	T	55.85	0.64	0.60	0.11	0.19	0.21	0.02	0.02
August	S	405.3	5.55	2.14	0.71	0.09	0.71	0.12	0.03
	D	0.72	0.02	0.04	0.01	nd	0.01	nd	nd
	T	406.02	5.57	2.18	0.72	0.09	0.72	0.12	0.03
September	S	76.6	0.70	0.39	0.07	0.09	0.10	0.04	0.01
	D	0.82	0.04	0.04	0.02	nd	0.01	nd	nd
	T	80.42	0.74	0.43	0.09	0.09	0.11	0.04	0.01
November	S	55	0.01	0.56	0.07	0.04	0.09	0.04	0.01
	D	0.83	0.05	0.06	0.01	nd	0.01	nd	nd
	T	55.83	1.06	0.60	0.09	0.04	0.10	0.04	0.01

medium (GODOY, 1991; MÁRQUEZ, 1997). Remineralization from the decomposition of the organic matter present in the riverbed sediments is likewise not to be overlooked, inasmuch as this mechanism has been verified in the river Neckar in Germany (SONG & MÜLLER, 1995). The concentrations of ammonium of 14.5 mmol/l found in the river Manzanares are alarming since normal values vary between 0.5 y 2.9 mmol/l in rivers (MEYBECKI, 1982) and are generally less than 1 mmol/l in uncontaminated coastal waters (SENIOR, 1994).

During the entire study the concentrations of dissolved oxygen remained between 3.57 and 5.27 ml/l until reaching a maximum level of 7.89 ml/l in November. Minimum concentrations of oxygen were always found at the upstream extreme. The reduction of pH and the increase in the concentration of ammonium at the point where the mixing of fresh and salt water begins (upstream extreme) suggest that the oxygen is being consumed by heterotrophic organisms during the process of oxidation of the organic matter which is introduced in the zone (Fig. 6). SENIOR & GODOY (1991) and LEÓN (1995) indicated that the high temperatures in the first months of the year are reached in the period of least volume flow, which promotes the decomposition of the organic matter, a process which consumes much dissolved oxygen and increases the concentrations of ammonium. The concentrations of dissolved oxygen obtained in this work are below those reported for the Neckar river (Germany) (SONG & MULLER, 1995): 6.2–8.9 ml/l in the summer and 8.6–11.4 ml/l in winter. These concentrations are worrisome inasmuch as during the decade of the seventies, concentrations between 6.8 and 9.8 ml/l were reported in this river (FERNÁNDEZ, 1984). Uncontaminated waters with sufficient ventilation are generally saturated with oxygen, reaching values of 8.5 ml/l, while contaminated waters generally show an oxygen deficit, depending in large part on the content of biodegradable organic material (SENIOR, 1994). This process would appear to be occurring in the Manzanares river.

The maximum concentrations of total heavy metals were as follows: Fe 406.02; Mn 5.57; Zn 2.18; Cu 0.72; Cr 0.19; Ni 0.72; Pb 0.12 and Cd 0.03 mmol/l. In suspended solids the concentrations were: Fe 405.03; Mn 5.55; Zn 0.04; Cu 0.01; Cr 0.19; Ni 0.011; Pb 0.12 and Cd 0.03. For the dissolved phase they were: Fe 0.,72; Mn 0.,02; Zn 2.,18; Cu 0.,72; Cr 0.,19 and Ni 0.,01m mol/l, Pb and Cd not being detected in this phase. All concentrations for the suspended phase were found to diminish with increasing salinity (Fig. 7), owing to processes of dilution, flocculation and/or precipitation of the suspended particles.

The maximum concentrations of all the suspended metals increased in the rainy season, with values being greatest in the month of August (Fig. 7), with the exception of chromium, which reached its greatest values in the months of May and June (0.19 mmol/l), perhaps owing to processes of dilution attributable to the increased volume flow of the river, as has been reported in the river Rhone in France (ELBAZ-POULICHET *et al.*, 1996).

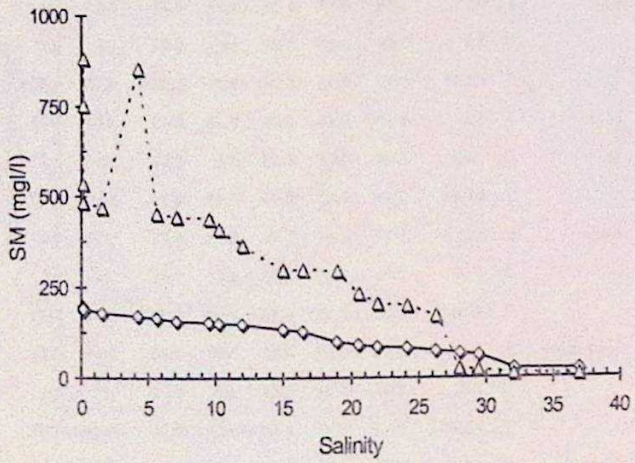


Figure 5. Reduction of suspended material (SM) with salinity in estuarine waters of the Manzanares river, Venezuela, during the months of the dry season (-o-) and the wet season (--Δ--) of the year 1997.

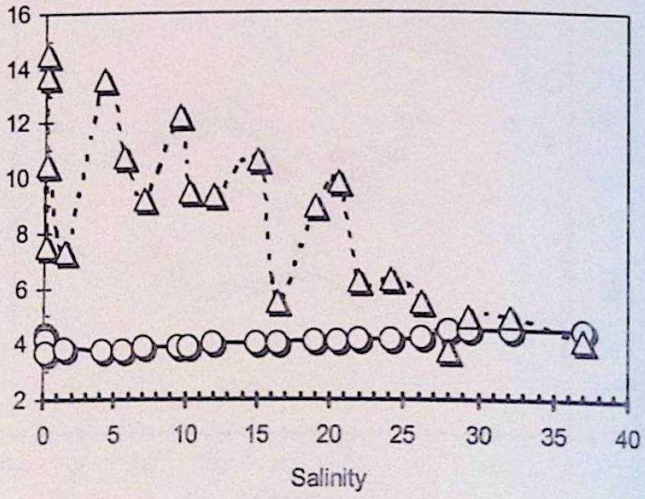


Figure 6. Simultaneous generation of ammonium (m mol/l) (--Δ--) and consumption of oxygen (ml/l) (-o-) in the surface waters of the Manzanares river, Venezuela, during the months of the dry season of the year 1997.

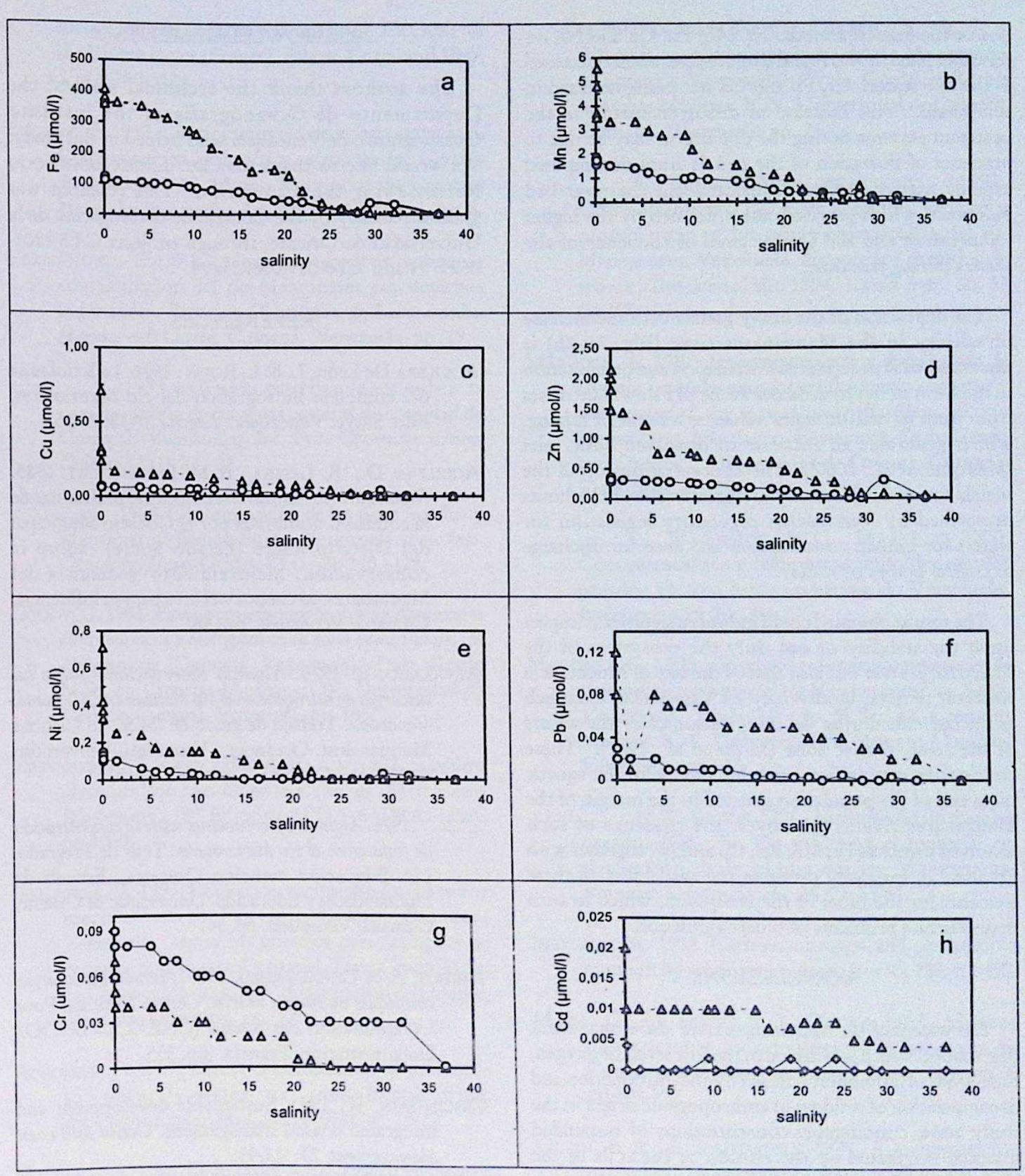


Figure 7. Diagrams of mixing of the studied metals in the suspended fraction as a function of salinity in the estuarine waters of the Manzanares river, Venezuela, during the months of low water (-o-) and of high water (August: -Δ-) of the year 1997.

For the dissolved metals Fe, Mn, Zn, Cu and Ni, on the other hand, it was found that concentrations increased in the dry season, Cr, Pb and Cd not being detected in this phase. This increase of dissolved metals in the upstream extreme during the dry season may be due to processes of liberation of the metals from decomposed organic matter and/or diffusion from the river bed sediments, which processes are promoted by the higher temperature and the greater time of residence of the waters during this time.

The deposition of the heavy metals with the increase of salinity in the Manzanares river (Fig. 7a–7h) is associated with processes of flocculation and precipitation in the form of oxyhydroxides as the pH slowly increases from fresh to marine water values as a result of mixing, which generates an increase in dissolved basic salts (MÁRQUEZ *et al.*, 2000). The concentrations of all the metals found in this study are greatly above the limits prescribed by Venezuelan regulatory legislation for waters for human consumption and even for discharge to coastal bodies of water.

The results obtained could indicate a significant impact upon the stability of not only the ecosystem of the Manzanares river but also that of the bay of Mochima (a reservoir of great biodiversity en Venezuela), inasmuch as the currents during the rainy season carry the waters of the river to that zone (MORA *et al.*, 1967). These conclusions may indicate risk for the life of the aquatic biota and of the population situated in the margin of the Manzanares river. Moreover, the presence of such dissolved metals as Fe, Mn, Zn, Cu and Ni, together with Pb and Cd, may well promote the availability of these elements for the biota of the ecosystem, which in turn may generate problems of bioaccumulation.

CONCLUSIONS

The waters of the Manzanares river show an evident degradation which is reflected in the low levels of oxygen, high levels of ammonium caused by the introduction and decomposition of residues of anthropogenic origin in the study zone, considerable concentrations of suspended material originated by the erosion of the soils in the higher drainage basin and levels of heavy metals which are above the values permitted by Venezuelan legislation for consumable waters and even for waters discharged into coastal bodies of water.

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