Bull. Environ. Contam. Toxicol. (2004) 73:762–769

DOI: 10.1007/s00128-004-0491-0

Bulletin of Environmental Contamination and Toxicology

Heavy Metals and Hydrocarbons in Sediments from Three Lakes from San Miguel, Chiapas, Mexico

A. Pascual-Barrera, G. Gold-Bouchot, V. Ceja-Moreno, M. del Río-García

Marine Resources Department, CINVESTAV Unidad Merida, Km 6 Antigua Carretera a Progreso, Merida, Yucatan 97310, Mexico

Received: 5 January 2004/Accepted: 15 July 2004

North of the Chiapas state, in a zone of petroleum extraction and processing, there is a system of three seasonally connected lakes called Laguna Limón, Laguna Enmedio and Laguna del Río (SEMARNAP, 1999; Fig. 1). During the rainy season these lakes connect with each other as the water level rises. The Mexican petroleum company, PEMEX, exploits 111 oil wells around the lake system, and also processes natural gas in the Cactus Gas Petrochemical Compund (GPCC). Previous studies in the system revealed the presence, in water and sediment, of high concentrations of hydrocarbons and metals (COMIMSA, 1999; SEMARNAP 1999; PROFEPA, 1998). Even though substances have been discharged to Laguna Limón from the GPCC, and also by PEMEX Production and Exploration (PEP), the absence in previous studies of a spatial analysis of the pollutants did not allow to evaluate the relative importance of this discharge as a source of the reported pollutants to the system.

In 1999, a culture of Nile Tilapia, *Oreochromis niloticus*, was initiated in Río, one of the lakes in the system. After a few weeks all the tilapia died. It was later determined that the culture design was severely flawed. In an attempt to evaluate the environmental health of these lakes, petroleum hydrocarbons and metals were determined in sediments during the extreme climactic seasons in this region: rain and dry seasons, and, by means of a spatial analysis, to determine the possible sources of contaminants to the system.

MATERIALS AND METHODS

Fifteen stations were sampled in the lake system, during the two extreme climatic seasons in this area, rainy season in September 2000 and dry season in June 2002 (Fig. 1). In each station two water samples were taken at the surface and 1 sediment sample was taken using a 0.1 m^2 Van Veen grab, for the determination of hydrocarbons and metals. A sediment core was extracted at the central portion of each lake using a 1 m PVC corer, to determine the concentration of hydrocarbons at different depths. The distance, "as the fish swims", amongst the stations with respect to the mixed discharge in the GPCC was calculated with a 1:50,000 topographical chart (Reforma E15 C19, Chiapas

Correspondence to: G. Gold-Bouchot

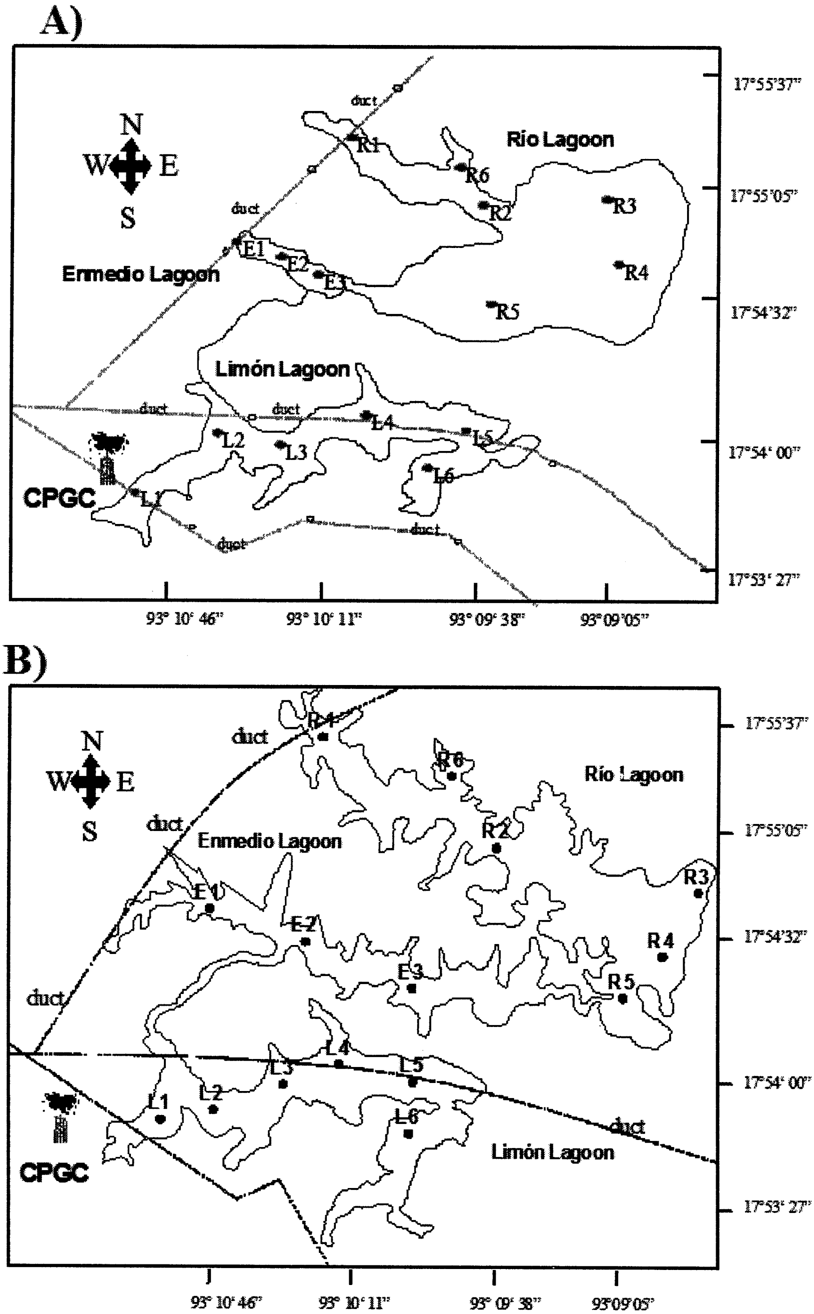

Figure 1. The lake system at San Miguel, Mexico, during the rainy (A) and dry (B) seasons, and the location of the sampling stations.

and Tabasco; INEGI, 1999).

Hydrocarbons in sediments were determined following the technique proposed by Wade and Sericano (1993), extracting in a reflux with hexane, and fractionating by alumina/silica gel column chromatography. Quantification and identification of hydrocarbons was carried out by gas chromatography using a Hewlett Packard 5890 Series II gas chromatograph. Metals in sediments were determined following the technique proposed by APHA (1985), with an acid extraction during 24 hrs. Metal concentrations were quantified using a Perkin Elmer Spectrum Emission Plasma 400 ICP.

To model the variability of hydrocarbon and metal concentrations as a function of the distance with respect to the mixed discharge, a monotonically decreasing or increasing exponencial function of the form $Y = ae^{bX}$, where the concentrations are "Y", "X" is the distance and "a" and "b" are adjustable parameters, with respect to the mixed discharged, was fitted. This model was linearized and adjusted by minimum squares using the program Statistica 5.5 (StatSoft, 1991). Spatial distribution maps of hydrocarbons and metals were generated by kriging interpolation using the software Surfer (Golden Software, 1999).

RESULTS AND DISCUSSION

Median concentrations for metals in sediments for the three lakes and seasons, and three other lagoons in the same hydrological basin are presented in Table 1. Nickel concentrations in the dry season in all three lakes, and zinc in lake Limon, were above the Probable Effects Level (PEL), which means that it is likely that these metals are producing toxic effects. Cadmium levels were close to the PEL in Rio and Enmedio in the rainy season. The surface strata in the sediment cores presented, in both seasons, the highest concentrations of hydrocarbons which decreased with depth of the stratum analyzed (Table 2). A horizontal concentration gradient was also observed when the three cores were compared; the thickness of the sediment layer with hydrocarbons decreases with increasing distance from the mixed discharge, in both climatic seasons.

Hydrocarbons in sediment concentrations presented a significant negative lineal correlation as a function of the distance with respect to the mixed discharge in the two climatic seasons (Fig. 2). The highest concentrations were located in the western side of L. Limon where the discharge is located, and decrease as the distance with respect to the source of emission increases. These values found in L. Límon (approximately 10,000 μg/g) were higher than those observed in other coastal systems in Mexico (Botello y Macko, 1982; Toledo *et. al.*, 1989; Botello *et. al.*, 1986; Botello, 1991), and much higher than the criterion of 70 μg/g reported by UNESCO (1976) for pristine areas. There were no significant differences in the mean concentration of hydrocarbons in sediments between the two climatic seasons ($F= 1.325$; $p= 0.259$), suggesting the hydrocarbons are not affected by seasonal changes, and are not transported by runoff into the

Table 1. Median concentrations (in µg/g dry weight) of metals in sediments in the lake system in Chiapas, Mexico, in the dry and rainy seasons.

Lake	Ba	Cd	Cr	Cu	Fe	Pb	Zn	Ni	HCs	PAHs
Mecoacán†	NR	1.22	3.01	1,15	1756	1.63	12.5	NR	9	0.03
Carmen†	NR	1.26	1.66	1.28	671	0.58	14.1	NR	12	0.04
Machona†	NR	1.25	1.12	1.02	487	0.83	12.5	NR	11	0.06
Limón (Dry)	54.4	ND	54.5	40.9	14.254	ND	942.3	79.7	1992	5.9
Río (Dry)	121.2	ND	1.61	9.6	26.580	ND	24.1	148	46.7	2.2
Enmedio (Dry)	70.0	ND	1.72	16.4	25.010	ND	63.6	157	152	6.1
Limón (Rain)	89.3	2.48	48.8	33.0	6.255	25.6	545.6	NR	5353	1.3
Río (Rain)	155.3	2.66	11.6	28.6	6.333	25.0	22.3	NR	226	1.1
Enmedio (Rain)	50.3	2.72	10.6	28.3	6.318	25.5	42.2	NR	213	1.1
PEL§	NR	3.5	90	197	NR	91	315	35.9	NR	12

†Gold-Bouchot *et al.*, 1997. § Probable Effects Level, NOAA 1999. NR= Not Reported. ND= Not Detected.

Table 2. Hydrocarbon concentrations (in µg/g dry weight) in sediment cores, in the dry and rainy seasons.

Stratum	Total hydrocarbon concentration	
	Rainy season	Dry season
Limón Surface	14899.94	1021.68
Limón Bottom	128.80	5.91
Enmedio Surface	979.71	107.19
Enmedio Bottom	205.60	82.24
Río Surface	357.46	85.42
Río Bottom	180.85	26.54

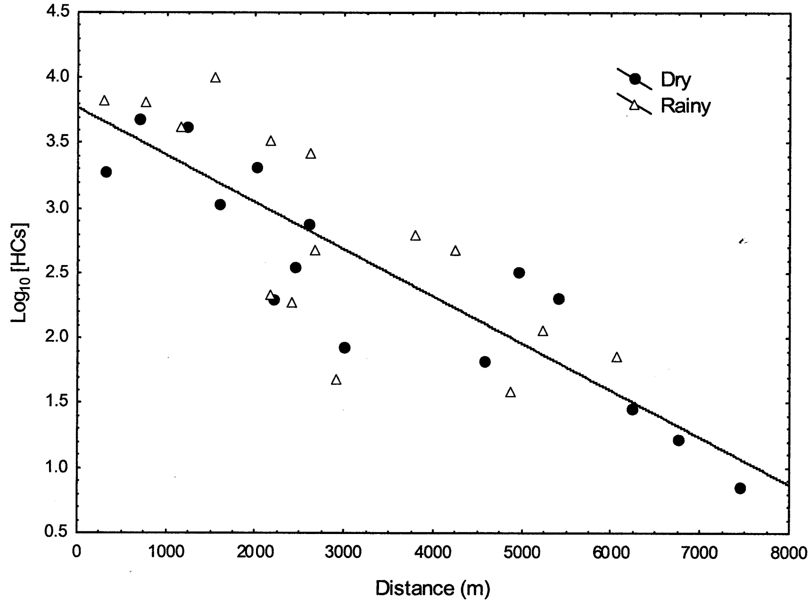

Figure 2. Total hydrocarbon concentrations (Log X_i) in sediments from the lake system in San Miguel, Mexico, as a function of distance to the mixed discharge, in the rainy and dry seasons.

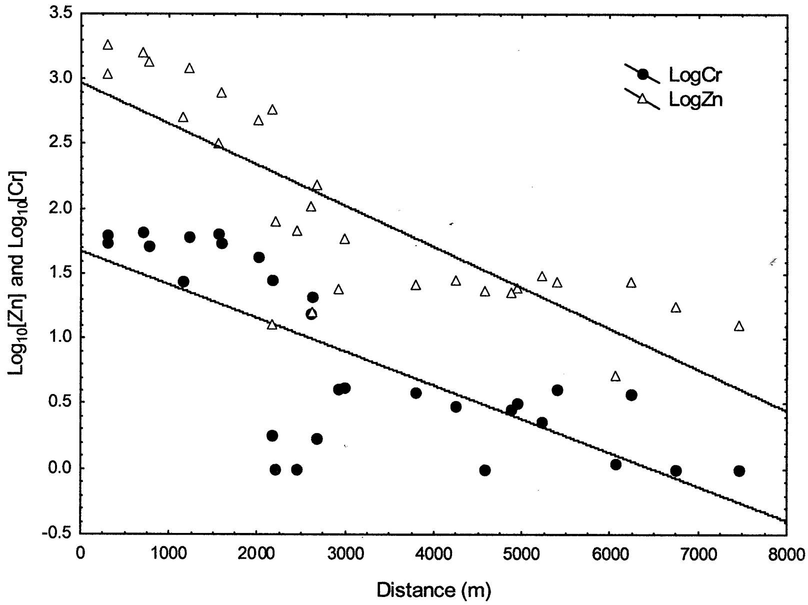

Figure 3. Chromium and zinc concentrations (Log X_i) in sediments from the lake system in San Miguel, Mexico, as a function of distance to the mixed discharge, in the rainy and dry seasons.

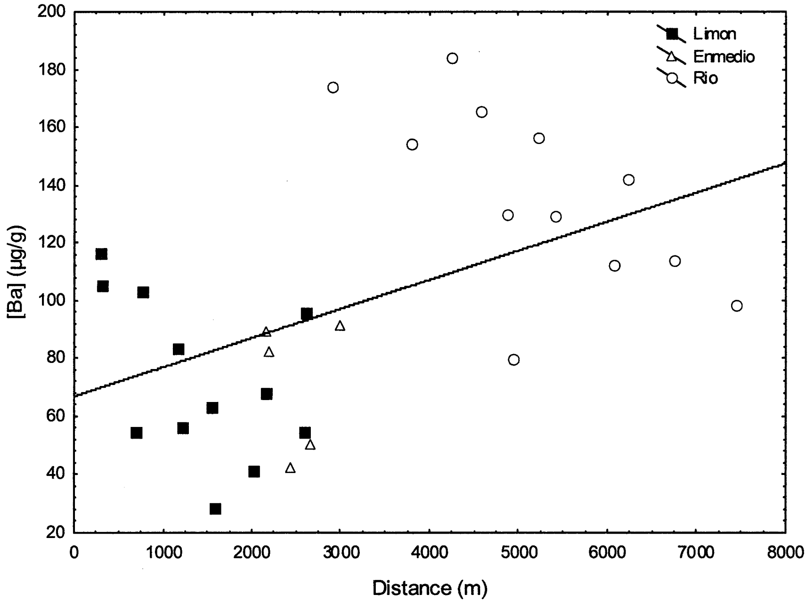

Figure 4. Barium concentrations in sediments from the three lakes in the system in San Miguel, Mexico.

lakes.

The values of Cu, Cr and Zn in the sediments presented, in both seasons, a significant negative lineal relation as a function of the distance from the mixed discharge. Their spatial distributions were similar to those of hydrocarbons (Fig. 3). The concentrations of Ba increased with increasing distance from the mixed discharge, suggesting a different origin (Fig. 4). The highest concentrations of Ba were obtained in L. Rio, and it is clearly separated form the concentrations from the other two lakes. Rio is the lake with the highest density of oil wells in the system, indicating that its distribution might have been the result of its use in the drilling muds used during oil well perforation (Warnheim and Sjoblom, 1986).

As shown by this work, an analysis of the spatial distribution of contaminants can be a useful approach to evaluate the relative contribution of substances to a system by a specific source.

The results obtained revealed that the main source of hydrocarbons and metals to the lake system has been the mixed discharge from GPCC, since the presence of a negative concentration gradient with increasing distance from the mixed discharge, was in general found. Exceptions were Fe and Ba concentrations, which were higher at Lake Del Rio, probably as a result of oil well drilling activities. As a result, median Ni and Zn concentrations exceed the Probable Effects Limit (PEL) for freshwater sediments (Buchman, 1999).

An interesting point is that the effluents from GPCC comply with the Mexican regulations for effluent quality. However, the river flowing through the lake system was diverted about 40 years ago, to stop floods in the cities, and thus the contaminants enter a closed system and accumulate over time. This has important consequences for the sustainable environmental management of this lake system.

Acknowledgments. This work was funded by Petróleos Mexicanos Producción Exploración (PEP) and Petróleos Mexicanos Refinación y Petroquímica.

REFERENCES

American Public Health Association (1985) Standard Methods for the Analysis of Water and Wastewater. City Press, Baltimore, USA.

Botello AV, Macko SA (1982) Presencia de hidrocarburos fósiles (n-parafinas) en sedimentos recientes de lagunas costeras en el Pacífico de México. An. Cien. Mar y Lim., Universidad Nacional Autónoma de México, México, D.F.

Botello AV, Mendelewicz M, Villanueva S (1986) Impacto ambiental de los hidrocarburos fosiles en dos sistemas costeros del caribe occidental (México Costa Rica). Primer Informe Anual Proyecto OEA-CONACYT. Inst. Cien. Mar y Lim. Univ. Nac. Aut. de México. p. 73.

Botello AV, Pica Y, Villanueva S (1991) Evaluación geoquímica del puerto de Salina Cruz y áreas adyacentes al puerto. Informe final a PEMEX-CECODES-ICMYL-UNAM. Noviembre, 1991. pp. 57-88.

Buchman MF (1999) NOAA Screening Quick Referente Tables. NOAA HazMat report 99-1. Seattle, WA. Coastal Protection and restoration Division, Nacional Oceanic and Atmospheric Administration. 12 p.

COMIMSA Corporación Mexicana de Investigación de Materiales S.A. (1999) Muestreo Prospectivo en las Lagunas Limón, Enmedio y Río del ejido de San Miguel en Reforma, Chiapas. Tuxtla Gutiérrez, Chiapas, 31 p.

Gold-Bouchot G, Zavala-Coral M, Zapata-Pérez O, Ceja-Moreno V (1997) Hydrocarbon Concentrations in Oysters (Crassostrea virginica) and Recent Sediments from Three Coastal Lagoons in Tabasco, Mexico. Bull Environ Contam Toxicol 59: 430-437.

Golden Software (1999) Contouring and 3D surface mapping for scientists and engineers. Golden Software, Inc. Golden, Colorado, USA.

INEGI Instituto Nacional de Estadística Geografía e Informática (1999) Carta Topográfica 1:50000 Reforma E15 C19 Chiapas y Tabasco, México.

Procuraduría Federal de Protección al Ambiente, Delegación Chiapas (1998) Resultados de la visita al sistema lagunar de Reforma, Chiapas. Tuxtla Gutiérrez, Chiapas. 20 p.

Secretaría de Ecología, Medio Ambiente, Recursos Naturales y Pesca (1999) Mortandad de peces en Laguna del Río, Municipio de Reforma. Tuxtla Gutiérrez, Chiapas. p. 20.

StatSoft, Inc. (1991) CSS:STATISTICA. Tulsa, Oklahoma, United States of America.

Toledo A, Botello AV, Herzing M, Paez M, Bozada L, Contreras F, Chazaro M, Baez A (1989) La contaminación en la región del Río Coatzacoalcos. Ciencia y Desarrollo. Consejo nacional de Ciencia y Tecnología. XV: 27-46.

UNESCO (1976) Guide to operational procedures for the IGOSS pilot project on marine pollution (petroleum). Monitoring Manual and Guides No. 7. UNESCO, Paris. 50 p.

Wade TL, Brooks JM, Kennicutt MC, McDonald TJ, Sericano JL, Jackson TJ (1993) GERG trace organics contaminant analytical techniques. NOAA Tech Memo NOS ORCA 71, pp. 1-182.

Warnheim T, Sjoblom A (1986) A theoretical study of surfactants and surfactant systems suitable for washing of drill cutting contaminated by oily mud. In: Proceedings of the conference: oil based drilling fluids-cleaning and environmental effects of oil contaminated drill cuttings, pp. 49-54. Trondheim, Norway. February 1986.