COMUNICACIONES
REPORTS
COMUNICAÇÕES

DETERMINATION OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHs) IN SUPERFICIAL WATER AND SEDIMENT OF LAKE TECOCOMULCO, MEXICO

Claudia Romo-Gómez, Scott Monks, Griselda Pulido-Flores and Alberto José Gordillo-Martínez

SUMMARY

To evaluate the environmental quality of bodies of water it is essential to know the risk that using it represents to human health, as well as to the floral and fauna present. This information is derived from knowledge of the concentrations of any toxic substances present in the water body under study. The objective of the present work was to evaluate the presence and concentrations of 16 US EPA priority polycyclic aromatic hydrocarbons (PAHs) in abiotic environmental matrices of Tecocomulco Lake, Hidalgo, Mexico. Samples from six localities were selected according to accessibility. From each locality, three samples of water and of sediment were taken from three different points, and samples from each point were combined to make three compound samples from each locality. Extraction of PAHs from water was carried out by solid phase extraction with C18; extraction from sediments following the EPA 3550C method. Analyses were made using a gas chromatograph connected to a mass spectrophotometer (CG-MS). The highest concentration of PAH in water was for acenaphthylene (2.400mg·l^{-1}*), anthracene (1.770mg·l*$^{-1}$*), and phenanthrene (1,500mg·l*$^{-1}$*); in sediment the highest concentrations corresponded to naphthalene (2.155mg·l*$^{-1}$*), benzo[g,h,i]perylene (4.940mg·l*$^{-1}$*), and fluoranthene (2.240mg·l*$^{-1}$*). The ∑PAHs showed a noticeable difference between matrices, a concentration of 6.658mg·l*$^{-1}$* in water and 10.927mg·kg*$^{-1}$* in sediment, with a total ∑PAHs of 17.585mg·kg*$^{-1}$*. Details of the methodology are included to facilitate similar studies.*

Introduction

Polycyclic aromatic hydrocarbons (PAHs), a class of diverse organic compounds containing two or more fused aromatic rings of carbon and hydrogen atoms, are organic compounds widely distributed in the environment (Chen *et al*., 2007). Naturally existing PAHs have been suggested as the chemical building blocks that participated in the origin of life (Allamandola *et al*., 1999). Normally low concentration levels of PAHs, formed by the incomplete combustion of organic materials during natural processes, have been supplemented by industrialization processes and the synthesis of new chemical compounds liberated mainly through an atmospheric route in vapor phase and particle form or soot (Walker, 2001). Other sources are spills and direct discharges of petroleum and its derivatives to the soil or aquatic systems (Mastandrea *et al*., 2005).

PAHs are strongly hydrophobic and difficult to biodegrade. They are adsorbed readily onto sludge particles in

KEYWORDS / Pollution / Polycyclic Aromatic Hydrocarbon / Sediment / Water /
Received: 06/29/2009. Modified: 10/20/2010. Accepted: 10/22/2010.

Claudia Romo-Gómez. Chemist, specialist in gas and liquid chromatography, Universidad Autónoma del Estado de Hidalgo (UAEH), México. Academic Technician, UAEH, México. e-mail: clauro_2001@yahoo.com.mx.

Scott Monks. PhD in Ecology and Evolutionary Biology, University of Toronto, Canada. Professor Investigator, UAEH, Centro de Investigaciones Biológicas, Ciudad Universitaria, Apdo. Postal 1-69, Pachuca, C.P. 42001, Hidalgo, México. e-mail: smonks@uaeh.edu.mx.

Griselda Pulido-Flores. Doctorate in Ciencias in Ecology and Sustainable Development, El Colegio de la Frontera Sur, México. Professor Investigator, UAEH, México. e-mail: gpulido@uaeh.edu.mx.

Alberto José Gordillo-Martínez. Doctorate in Ciencias Químicas, Universidad Politécnica de Madrid, Spain. Professor Investigator, UAEH, México. e-mail: gordillo@uaeh.edu.mx.

DETERMINACIÓN DE HIDROCARBUROS AROMÁTICOS POLICÍCLICOS (PAHS) EN AGUAS SUPERFICIALES Y SEDIMENTOS DEL LAGO TECOCOMULCO, MÉXICO

Claudia Romo-Gómez, Scott Monks, Griselda Pulido-Flores y Alberto José Gordillo-Martínez

RESUMEN

La evaluación de la calidad ambiental de los cuerpos de agua es esencial para conocer el riesgo que representan a la salud humana y a la diversidad florística y faunística presentes en ellos. Tal calidad dependerá de la dispersión de sustancias tóxicas presentes en el cuerpo de agua en estudio. El objetivo del presente trabajo fue analizar 16 hidrocarburos aromáticos policíclicos (PAHs) de prioridad para el US EPA en agua y sedimento superficial del Lago de Tecocomulco, Hidalgo, México. La toma de muestras se efectuó en seis sitios seleccionados con base a su accesibilidad. De cada sitio se tomaron tres muestras en diferentes puntos de agua y de sedimento, de las cuales se obtuvieron tres muestras compuestas. La extracción de los PAHs en agua se llevó a cabo por extracción en fase sólida con C18. Para la extracción de los PAHs en sedimento se utilizó el método EPA 3550C, el cual es un proceso ultrasónico. Los análisis se realizaron en un cromatógrafo de gases acoplado a masas (CG-MS) por impacto electrónico. La concentración más alta de PAH en agua fue para acenaftileno (2.400mg·l^{-1}), antraceno (1,770mg·l^{-1}) y fenantreno (1,500mg·l^{-1}); en cuanto al sedimento las concentraciones más altas correspondieron a naftaleno (2,155mg·l^{-1}), benzo[g,h,i]perileno (4,940mg·l^{-1}), y fluoranteno (2,240mg·l^{-1}). La $\sum$PAH mostró marcada diferencia entre matrices; la concentración en agua fue 6,658mg·l^{-1} y 10,927mg·kg^{-1} en sedimentos, con un $\sum$PAHs total de 17,585mg·kg^{-1}. Se incluye detalles de la metodología para facilitar estudios similares.

DETERMINAÇÃO DE HIDROCARBONETOS AROMÁTICOS POLICÍCLICOS (PAHS) EM ÀGUAS SUPERFICIAIS E SEDIMENTOS DO LAGO TECOCOMULCO, MÉXICO

Claudia Romo-Gómez, Scott Monks, Griselda Pulido-Flores e Alberto José Gordillo-Martínez

RESUMO

A avaliação da qualidade ambiental dos corpos de água é essencial para conhecer o risco que representam à saude humana e à diversidade florística e faunística presentes neles. Tal qualidade dependerá da dispersão de substâncias tóxicas presentes no corpo de água em estudo. O objetivo do presente trabalho foi analisar 16 hidrocarbonetos aromáticos policíclicos (PAHs) de prioridade para o US EPA na água e sedimento superficial del Lago de Tecocomulco, Hidalgo, México. A coleta de amostras foi efetuada em seis locais selecionados com base em sua acesibilidade. De cada local foram coletadas em diferentes pontos, três amostras de água e de sedimento, das quais se obtiveram três amostras compostas. A extração dos PAHs em água se realizou por extração em fase sólida com C18. Para a extração dos PAHs em sedimento foi utilizado o método EPA 3550C, o qual é um processo ultrassônico. As análises se realizaram em um cromatógrafo de gases acoplado a massas (CG-MS) por impacto eletrônico. A concentração mais alta de PAH em água foi para acenaftileno (2,400mg·l^{-1}), antraceno (1,770mg·l^{-1}) e fenantreno (1,500mg·l^{-1}); quanto ao sedimento as concentrações mais altas corresponderam a naftaleno (2,155mg·l^{-1}), benzo[g,h,i]perileno (4,940mg·l^{-1}), e fluoranteno (2,240mg·l^{-1}). A $\sum$PAH mostrou marcada diferença entre matrizes; a concentração em água foi 6.658mg·l^{-1} e 10,927mg·kg^{-1} em sedimentos, com um $\sum$PAHs total de 17,585mg·kg^{-1}. Se inclui detalhes da metodologia para facilitar estudos similares.

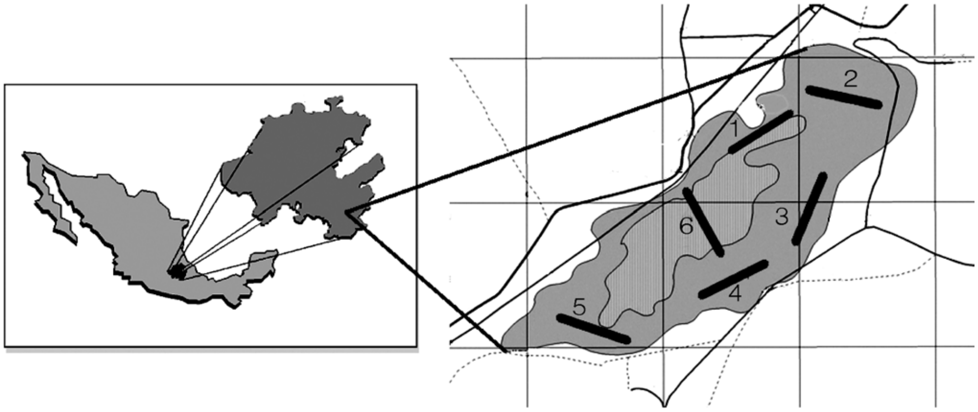

Figure 1. Location of the study area and the six sample localities in Tecocomulco Lake.

wastewater treatment plants (Sánchez-Brunete *et al*., 2007) and adhere chemically to the organic matter of soil and sediments rather than staying in the solution (Zhu *et al*., 2008). PAHs may exhibit a wide range of hazardous effects on aquatic organisms, including acute toxicity, developmental and reproductive toxicity, photo-induced toxicity, mutagenicity and carcinogenicity (Delistraty, 1997). Sediment-associated PAHs are known to exhibit narcotic effects in benthic organisms (Di Toro *et al*., 2000) and also have been implicated in the development of tumors in bottom feeding fish and in the induction of malformations (Barron *et al*., 2004), as well as in loss of fertility and immune deficiency in many organisms, including oysters (Reynaud and Deschaux, 2006), which, when contaminated, can in turn be the cause of lung cancer in humans (Law *et al*., 2002). Because of these known and potential risks, PAHs have been classified as priority pollutants by both the U.S. Environmental Protection Agency and the European Community (Zhou *et al*., 1998).

TABLE I
LOCALITIES SAMPLED FOR POLYCYCLIC AROMATIC HYDROCARBON AT TECOCOMULCO LAKE

Area	Sampling points	Local names	Geographic location
1	A	El Cañón	19°52'47.6"N, 98°23'0.4"W
	B	La Isleta	19°52'57.5"N, 98°22'53.4"W
	C	La Isleta	19°52'59.6"N, 98°22'47.6"W
2	A	El Recodo	19°52'30.9"N, 98°22'57.7"W
	B	El Recodo	19°52'28.8"N, 98°23'00.1"W
	C	El Recodo	19°52'28.4"N, 98°22'53.6"W
3	A	Mata de los Boludos	19°51'59.5"N, 98°22'36.8"W
	B	Derramadero del Colorado	19°51'41.9"N, 98°22'45.4"W
	C	Derramadero de alcantarilla	19°51'13.8"N, 98°23'32.2"W
4	A	Propiedad de Martín Alvarado	19°50'57.5"N, 98°23'52.8"W
	B	Vista Hermosa	19°50'34.3"N, 98°24'18.3"W
	C	San José or El Maguey	19°50'18.6"N, 98°24'57.3"W
5	A	Entrada de Isleta al Espejuelo	19°51'58.6"N, 98°23'54.7"W
	B	Entrada de Isleta al Espejuelo	19°52'08.0"N, 98°23'50.5"W
	C	Entrada de Isleta al Espejuelo	19°50'18.6"N, 98°24'57.3"W
6	A	Muelle	19°52'07.9"N, 98°23'53.7"W

The Tecocomulco Lake (2514masl), covering 1769ha, is located in the southwest part of the state of Hidalgo, Mexico (Figure 1), between 19º50'00" and 19º74'00"N and between 98º21'00" and 98º26'00"W. The lake, also known as Laguna de Tecocomulco, is the last relatively uncontaminated relic of the historic lake that existed in the area that now is covered by Mexico City. It was part of the Great Basin of the Valley of Mexico that served both to protect the pre-Spanish-Mexican city that later became Mexico City, and as a source of food for the inhabitants. The present lake, at the northeastern edge of the ancient basin, is still an important habitat for fish, amphibians and birds, many of them endemic to the Anáhuac Basin (Bautista-Hernández *et al.*, 2008; Miranda *et al.*, 2008). The principal economic activity in the area surrounding the lake is agriculture, but recently the lake has become an important tourist attraction that draws visitors from around the state as well as from the greater Mexico City area (Huízar-Álvarez *et al.*, 2005). To provide for these tourists, local residents have developed boating services that offer lake tours, fishing, and duck hunting in season. They also have developed several areas with restaurants that offer local dishes, fish and duck, and some small hotels. Restaurants depend on local fishermen who capture fish, principally *Cyprinus carpio* L, 1758, from the lake.

Local residents are exceptional in that they have promoted the use of lake resources in a sustainable fashion (NOM, 2005), and were the driving force behind a government-funded research project designed to evaluate the environmental quality of the lake and the surrounding region (Monks *et al.*, 2008) and to offer options for sustainable development for increased tourism. The present paper gives a first overview on the PAH pollution of superficial water and sediment of Lake Tecocomulco. Contamination of water and lake sediments as a potential hazard to local residents and to the aquatic community of the lake is discussed.

Materials and Methods

Samples were collected from July 2006 to July 2007 during four sampling periods, two during the dry season and two during the rainy season, from designated points of the lake. Much of the central area of the lake is irregularly covered by dense growth of cattails (*Schoenoplectus californicus*) and random sampling was not possible; thus, collection points in six areas (Figure 1) were chosen for accessibility. In areas 1-5, triplicate samples were taken from three different points within each area and these samples (nine from each area) were combined and then subsampled. Area 6 is a channel that extends from a small dock on the northern side of the lake, and it divides the two major stands of cattails so that local fishermen can cross the center of the lake; because of the constant passage of small boats that stir up sediment only a single point near the dock was sampled. The local names of collection points are given in Table I.

Sample collection

Samples of water were taken using a 1.2 liter Kemmerer non-metallic sampler for trace metals (Wildco Instruments, 1520-C22). One liter of the sampler's contents were used to fill narrow-mouth amber glass bottles that had been washed with water and a mixture of HNO$_3$ (1:1) and then rinsed with abundant distilled water; 80mg of sodium thiosulfate was added to each bottle. At Tecocomulco lake the bottom has only a superficial layer of sediment bounded below by a hard layer of rock, so samples of superficial sediment were taken using an Ogeechee Corer sampler (Wildco Instruments, 2427-B20). Sediment samples were placed in 1 liter amber glass bottles previously acid washed as above. Samples of water and sediment were placed in an ice chest with ice for transportation to the laboratory and thereafter kept under refrigeration and protected from light until analysis.

Extraction of PAHs

Water. Water was filtered in a Büchner funnel using Whatman 42 paper. A solid phase extraction (SPE C18 disk) system (Supelco; Sigma-Aldrich Corp.) was used to extract PAHs. The extraction disk was placed in a vacuum filtration system and pre-washed with 10ml of dichloromethane (DCM)/acetate ethyl chloride (1:1), vacuum dried, allowed to stabilize for 1min, and then vacuum was reapplied and the disk washed with 10ml of methanol, rinsed with 10ml of organic compound-free water and allowed to dry without vacuum. A 1 l sample of water to be analyzed was run through the disk, and the vacuum was suspended when a layer of ~1mm of water remained. To extract PAHs from the SPE disk, a test tube of 50ml was placed within a Büchner side-arm flask to catch the filtered sample. Ethyl acetate (5ml) was added to the sample, which was transferred to the extraction funnel. Vacuum was applied until the first drops appeared, and then suspended to allow the penetration of the solvent into the disc. After 1min, the vacuum was reapplied slowly. The container where the sample had been kept was washed with 5ml DCM, and the solvent transferred to the extraction funnel with the vacuum applied until all solvent passed through. The elutant was dried using anhydrous sodium sulphate; once dry, the supernatant was transferred to a conical-base graduated tube, a small amount of dry N$_2$ gas was applied, and the extract was stored at -4ºC until analysis.

Sediment. In the laboratory, sediment samples were dried at ambient temperature in open containers covered lightly with clean paper and then stored in clean bottles. The samples were ground with an agate mortar and then passed through a series of graduated strainers to remove stones and vegetable matter. Material that passed through a 1mm mesh was used for the extraction of PAHs. The extraction was based on EPA method 3550C (EPA, 1996), an ultrasonic process recommended for solid samples such as dirt or sludge and assures intimate contact of the matrix of the sample with the solvent of the extract. Three extractions, each using 30ml of solvent, were performed using 10g of subsamples of dry sediment. Extracts were filtered, recovered in round-bottomed flasks, and then concentrated in a Büchi rotary evaporator to yield a 1ml liquid subsample that was stored in a vial wrapped in aluminum foil and kept at -4ºC until post-extraction cleanup.

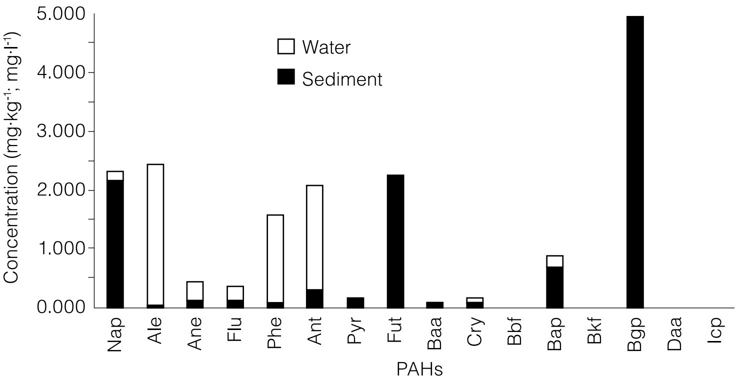

Figure 2. Total concentration of 16 priority polycyclic aromatic hydrocarbons in water and sediment; Nap: naphthalene, Ale: acenaphthylene, Anc: acenaphthene, Flu: fluorene, Phe: phenanthrene, Ant: anthracene, Pyr: pyrene, Fut: fluoranthene, Baa: benzo[*a*]anthracene, Cry: chrysene, Bbf: benzo[*b*]fluoranthene, Bap: benzo[*a*]pyrene, Bkf: benzo[*k*]fluoranthene, Bgp: benzo[*g,h,i*] perylene, Daa: dibenzo[*a,h*]anthracene, Icp: indeno[1,2,3-*cd*]pyrene (concentrations of Bbf, Bkf, Daa, and Icp were below minimum level of detection).

For post-extraction cleanup, a silica gel column was prepared by loading activated gel onto a 5cm long chromatographic column (1cm internal diameter). An additional 1cm of anhydrous Na_2SO_4 was added to the column, which was then conditioned by running DCM through the column. Concentrated subsamples (1ml) were loaded onto the column and eluted with 10ml DCM. The extract was again concentrated to about 2ml by gently passing a stream of dry N_2 over the liquid.

Analyses

A Hewlett-Packard 5890 SERIES II GC (fused-silica HP-5 capillary column; 30m×0.25mm i.d.; 5% phenyl-95% dimethylpolysiloxane; film thickness 0.25µm) coupled to a mass spectrometer Hewlett-Packard 5989A with an MS Chemstation G1034C software was used. Oven temperatures were 100ºC at start, 2min to 200ºC (at 10ºC/min), held at 200ºC for 5min; 200ºC to 250ºC (at 8ºC/min), held at 250ºC for 7min; 250ºC to 310ºC (5ºC/min), 310ºC for 5min. Splitless injections of 1µl sample were carried out with the split valve closed for 1min. Ultra high purity (99.999%) helium was used as a carrier gas at a flow of 1ml·min^{-1} with an injector temperature of 250ºC; equilibration time of 2min, and total analysis time of 43min. The GC system was operated in an electron impact ionization mode with an ionizing energy of 70eV, scanning from 50 to 400 m/z (mass-to-charge ratio), 1.9s per scan, with an ion source temperature 200ºC, quadruple temperature 180ºC. Electron multiplier voltage was maintained 1819V above auto tune with a solvent delay of 3min. Before each analysis, the relevant standards (16 PAHs-target compounds from Supelco PAH Kit 610-N; lot LB44087) were run to check column performance, peak height and resolution. Calibration curves were linear, with correlation coefficients from the linear regression ranging from 0.9928 to 1.000. Analyses were performed with selected ion monitoring (SIM), using one target and two qualifier ions determined by injection of standards under the same chromatographic conditions as for the analyses. Results of the analyses are shown in Figure 2.

Results and Discussion

Until the publication of a study by the World Health Organization (WHO, 1998) the dangers of PAHs in the environment received little attention. In that study it was determined that the natural concentration of individual PAHs in surface and coastal waters is ~0.05µg·l^{-1}, and concentrations above this point indicate some contamination. Eight of the 16 PAHs evaluated were found in measurable concentrations in the water from Tecocomulco Lake (Table II); concentrations of 6 out of the 8 were found to be at concentrations above 0.05µg·l^{-1} in at least one area of the lake.

TABLE II
CONCENTRATIONS OF THE 16 PRIORITY POLYCYCLIC AROMATIC HYDROCARBONS IN WATER FROM SIX LOCALITIES IN TECOCOMULCO LAKE

Compound	Concentration in water (ml·g^{-1})					
	Area 1	Area 2	Area 3	Area 4	Area 5	Area 6
Naphthalene	0.087	<0.030	0.033	<0.030	0.033	<0.030
Acenaphthylene	<0.020	<0.020	<0.020	<0.020	<0.020	2.400
Acenaphthene	0.025	<0.020	<0.020	<0.020	<0.020	0.300
Fluorene	0.024	<0.020	<0.020	<0.020	<0.020	0.200
Phenanthrene	<0.030	<0.030	<0.030	<0.030	<0.030	1.500
Anthracene	0.070	<0.020	<0.020	<0.020	<0.020	1.700
Pyrene	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040
Fluoranthene	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040
Benzo[*a*]anthracene	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050
Chrysene	<0.060	<0.060	<0.060	<0.060	0.086	<0.060
Benzo[*b*]fluoranthene	<0.100	<0.100	<0.100	<0.100	<0.100	<0.100
Benzo[*a*]pyrene	<0.150	<0.150	<0.150	<0.150	<0.150	0.200
Benzo[*k*]fluoranthene	<0.150	<0.150	<0.150	<0.150	<0.150	<0.150
Benzo[*g,h,i*]perylene	<0.750	<0.750	<0.750	<0.750	<0.750	<0.750
Dibenz[*a,h*]anthracene	<0.900	<0.900	<0.900	<0.900	<0.900	<0.900
Indeno[1,2,3-*c,d*]pyrene	<1.700	<1.700	<1.700	<1.700	<1.700	<1.700

The high-molecular-mass PAHs, such as benzo[*k*]fluoranthene, benzo[*g,h,i*]perylene fluoranthene, dibenz[*a,h*] anthracene and indeno[1,2,3-*cd*]pyrene, were not detected in the water samples, although this can be attributed to their lower water solubility. Benzo[*a*]pyrene is one of the most potent PAH carcinogens (WHO, 1998) and is often used as a maximum-limit indicator (ATSDR, 1995; Anyakora and Coker, 2006). A lifetime exposure of 0.7mg·l^{-1} of these compounds corresponds to an excess lifetime cancer risk of 10^{-5} (WHO, 1998). This corresponds generally to a concentration of about 0.01µg·l^{-1} in drinking water. The U.S. EPA has suggested that ingesting each day the following amounts (in mg·kg^{-1} body weight) of individual PAHs is not likely to cause any harmful health effects: 0.06 acenaphthene, 0.04 fluorene, 0.30 anthracene, 0.04 fluoranthene and 0.03 pyrene (Zhou *et al*., 1998).

In the Lake of Tecocomulco, benzo[*a*]pyrene was found in an average concentration of 0.2mg·l^{-1} only in Area 6. However, since the water from the lake is not used directly as drinking water, it is not clear what effects this level might have on local residents. There have been few studies on the human health effects of this compound, because

TABLE III
CONCENTRATIONS OF THE 16 PRIORITY POLYCYCLIC AROMATIC HYDROCARBONS IN SEDIMENT FROM SIX LOCALITIES IN TECOCOMULCO LAKE

Compound	Concentration in sediment (mg·kg^{-1})					
	Area 1	Area 2	Area 3	Area 4	Area 5	Area 6
Naphthalene	<0.030	<0.030	<0.030	0.030	<0.030	2.125
Acenaphthylene	<0.020	<0.020	<0.020	0.030	<0.020	<0.020
Acenaphthene	<0.020	0.030	<0.020	0.070	<0.020	<0.020
Fluorene	<0.020	0.070	<0.020	0.050	<0.020	<0.020
Phenanthrene	<0.030	<0.030	<0.030	0.070	<0.030	<0.030
Anthracene	<0.020	0.230	<0.020	0.070	<0.020	<0.020
Pyrene	<0.040	0.100	<0.040	0.050	<0.040	<0.040
Fluoranthene	<0.040	0.130	<0.040	0.050	<0.040	2.060
Benzo[*a*]anthracene	<0.050	0.070	<0.050	<0.050	<0.050	<0.050
Chrysene	<0.060	0.070	<0.060	<0.060	<0.060	<0.060
Benzo[*b*]fluoranthene	<0.100	<0.100	<0.100	<0.100	<0.100	<0.100
Benzo[*a*]pyrene	<0.150	0.620	<0.150	0.062	<0.150	<0.150
Benzo[*k*]fluoranthene	<0.150	<0.150	<0.150	<0.150	<0.150	<0.150
Benzo[*g,h,i*]perylene	<0.750	2.070	<0.750	2.870	<0.750	<0.750
Dibenz[*a,h*]anthracene	<0.900	<0.900	<0.900	<0.900	<0.900	<0.900
Indeno[1,2,3-*c,d*]pyrene	<1.700	<1.700	<1.700	<1.700	<1.700	<1.700

of inappropriateness of studies on humans. Nevertheless, in early studies, human subjects that were skin-painted with benzo[*a*]pyrene developed skin lesions (Cottini and Mazzone, 1939; Rhoades *et al.*, 1954), so the potential dangers of contact with this and other PAHs (Habs *et al.*, 1984; Warshawsky and Barkley, 1987) are obvious, though the degree of actual contact by local residents is not known. Benzo[*a*]pyrene, not produced commercially, is a byproduct of the combustion of petroleum products, particularly exhaust fumes from engines of all types (ATSDR, 1995), burning of organic material (Okuda *et al.*, 2002; de Gouw *et al.*, 2006), and cooking processes (Le Marchand *et al.*, 2002).

Acenaphthylene, anthracene and phenanthrene were the PAHs found at the highest concentrations in water from Area 6 (Table II). Finding acenaphthylene, benzo[*a*]pyrene and phenanthrene at levels higher than other PAHs usually indicates road traffic as a major source of PAH pollution (Shukla and Upreti, 2009), but the lake is in a rural setting with little automobile traffic. However, as part of ecotourism, local residents take visitors on tours of the lake and some local fishermen use the same boats when they are available. The motors of these boats release exhaust gases below the surface of the water and thus are a probable source of these contaminants. Local residents regularly burn the centrally located dense stands of aquatic plants when they are dry, which also may cause contamination with combustion-related PAHs. Area 1 also is frequented by fisherman's boats, lending support to boat motors as a source of these contaminants, but it is also near fields that are sometimes burned to clear unwanted plants.

Anyakora *et al.* (2005) reported levels of these same contaminants from 0.34mg·l^{-1} to 1.72mg·l^{-1} in waters heavily contaminated with petroleum products, but Anyakora and Coker (2006) reported concentrations of 0.00195mg·l^{-1} for relatively clean stream water to 0.0109mg·l^{-1} for the most polluted water. According to studies done in the U.S., in four major cities the total PAHs in drinking water ranged between 0.0047 and 0.600mg·l^{-1} (ATSDR, 1995). The concentrations of PAHs found in water from Tecocomulco Lake (0.024 to 2.400mg·l^{-1}) were generally similar to the lowest concentrations reported by the studies cited herein. However, the highest concentrations reported by the above-mentioned authors were for heavily contaminated water. The lake is not near any industrialized area or direct source of petroleum contamination, so it is difficult to explain the high concentrations of some PAHs (acenaphthylene 2.400mg·l^{-1}, anthracene 1.700mg·l^{-1}, and phenanthrene 1.500mg·l^{-1}). Nevertheless, the higher concentrations are all located in Area 6, a pathway heavily traveled by boats and surrounded by cattails that are burned frequently to restrict growth.

The remaining PAHs were found to be present in more moderate amounts, but there is no hypothesized local source. For example, chrysene has no known use but fluorene is used as a chemical intermediate in many chemical processes, in the formation of resins, and in the manufacture of dyes, and no industries that potentially could use these compounds exist in the area around the lake.

Soil and sediment are the major sinks for PAHs, primarily because of the low solubility of these compounds and their strong affinity for organic carbon in particulate matter. PAH concentrations in sediments are generally much higher than those detected in surface waters, i.e., in the range of μg (ppb) rather than ng (ppt) per kg (i.e., at least 1000 times that of concentrations found in water). Twelve of the 16 PAHs evaluated were found in measurable concentrations in sediments from Tecocomulco Lake (Table III), and 11 of the 12 had concentrations >0.05μg·l^{-1} in at least one area of the lake. Interestingly, more types of PAHs were found in Areas 1 and 6 in water but more were found in Areas 2 and 4 in sediments; no PAHs were registered in Areas 2 and 4 in water and none were registered in Areas 1, 3, and 5 in sediments. At this time there is no explanation for this pattern. Benzo[*g,h,i*]perylene, a heavy compound, was found in sediments at a concentration of (2.870mg·kg^{-1}) that was higher than any other PAH registered. Naphthalene, a simpler molecule, also was found at a high concentration (2.125mg·kg^{-1}). Fluoranthene had the third highest concentration (2.06mg·kg^{-1}). Fluoranthene was found in Areas 2, 4, and 6, but the highest concentration was in Area 6. Naphthalene was found only in Areas 4 and 6, again with the highest concentration in the latter one. However, benzo[*g,h,i*]perylene was found at high concentrations only in two localities, Areas 2 and 4. The pattern of distribution of these compounds also suggests that there is some underlying pattern, although it might be more complicated than that previously mentioned. At present there is no explanation for this pattern.

Anyakora *et al.* (2005) reported average concentrations of the same 16 PAHs examined herein that were similar to those found in Tecocomulco Lake. However, these authors also reported the presence of 3.880, 2.880, 18.320, and 11.450 mg/kg, respectively, of benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, dibenz[*a,h*]anthracene and indeno[1,2,3-*cd*]pyrene, all large molecules that were not found in sediments at Tecocomulco. Olajire-Abbas and Brack (2005) reported levels of PAHs between 0.005-0.44mg·kg^{-1} (calculated from their Table II) in soil contaminated with petroleum products. The highest concentration reported was naphthalene (0.044mg·kg^{-1}), followed by anthracene (0.038mg·kg^{-1}), and fluoranthene (0.037mg·kg^{-1}), all small molecules; benzo[*g,h,i*]perylene was found at a much lower average concentration (0.016mg·kg^{-1}) than in Tecocomulco, but concentrations of the other PAHs found in the lake were similar to those reported by Olajire-Abbas and Brack (2005). As noted, there have been no reports of direct contamination with petroleum products in the lake, so the frequent burning of aquatic vegetation seems to be the likely source. These fires are clandestine and it is possible that local residents douse the cattails with diesel oil, kerosene, or other flammables to support combustion of the humid vegetation. However, there is no direct concrete data for the evaluation of these hypotheses.

TABLE IV
CONCENTRATIONS OF THE 16 PRIORITY POLYCYCLIC AROMATIC HYDROCARBONS IN WATER, SEDIMENT AND TOTAL PAH$_S$ FROM SIX LOCALITIES IN TECOCOMULCO LAKE

Compound	ΣPAHs (mg·l^{-1}; mg·kg^{-1})		
	Water	Sediment	Total
Naphthalene	0.153	2.155	2.308
Acenaphthylene	2.400	0.030	2.430
Acenaphthene	0.325	0.100	0.425
Fluorene	0.224	0.120	0.344
Phenanthrene	1.500	0.070	1.570
Anthracene	1.770	0.300	2.070
Pyrene	<0.040	0.150	0.150
Fluoranthene	<0.040	2.240	2.240
Benzo[*a*]anthracene	<0.050	0.070	0.070
Chrysene	0.086	0.070	0.156
Benzo[*b*]fluoranthene	<0.100	<0.100	<0.100
Benzo[*a*]pyrene	0.200	0.682	0.882
Benzo[*k*]fluoranthene	<0.150	<0.150	<0.150
Benzo[*g,h,i*]perylene	<0.750	4.940	4.940
Dibenz[*a,h*]Anthracene	<0.900	<0.900	<0.900
Indeno[1,2,3-*c,d*]pyrene	<1.700	<1.700	<1.700
ΣPAHs (2-3 ring)	6.372	2.775	9.147
ΣPAHs (4-6 ring)	0.286	8.152	8.438
Ratio 2-3 ring:4-6 ring	22.3:1	0.3:1	1.1:1
ΣPAHs (total)	6.658	10.927	17.585

In general, 4, 5, and 6 rings PAHs were dominant in sediment samples from Areas 2, 4 and 6 in Tecocomulco Lake (Figure 2, Table IV). In contrast, in water samples 2 and 3 rings PAHs were dominant. One likely reason for this is that PAHs are less soluble in water and solubility decreases as the molecular weight rises. Larger molecules quickly move into sediment, thus they dominate in soil samples. The ration of 2-3 ring PAHs to 4-6 ring PAHs (Olajire-Abbas and Brack, 2005) was 22.3:1 in water and 0.3:1 in sediment, while for total PAHs (water + sediment) the ratio was 1.1:1, supporting the hypothesis that the absence of large-molecule PAHs in water is due to a low solubility of these compounds in water and a higher one in sediments.

The global movement of PAHs in Tecocomulco Lake can be summarized as follows: PAHs released to the atmosphere by combustion (probably of aquatic vegetation and local crop residues) or other sources (small boat engines) are subject to short-range transport (run-off from local fields) or direct deposit (exhaust from boat engines released into water and carbon and ashes from burning vegetation) and are deposited into the lake water. Lack of solubility of PAHs moves heavier compounds into the sediment where they bind with soil particles, while lighter molecules remain dissolved in the water (about 44% by weight of total PAHs; Table IV). In shallow waters of the Tecocomulco Lake (0.2-2.0m; Bautista-Hernández *et al.*, 2008) wind-driven water currents and movement of small boats could stir up bottom sediments, re-exposing water to PAHs that could re-dissolve into the water and then back into sediment. PAHs in sediments can enter groundwater and be transported in an aquifer such as those that run under the lake (Huízar-Álvarez *et al.*, 2005).

Finally, it should be recognized that some sources of contamination, such as the exhausts of small boats of fishermen and tour guides, will continue to enter this ecosystem. Each source must be reduced as much as possible, and the effect of any contaminant that does enter the ecosystem should be dealt with appropriately in order to reduce or counteract its effect. There is a clear need for the removal of excess aquatic vegetation of the lake (Bautista-Hernández *et al.*, 2008) but, although plants do not bioaccumulate hydrocarbons (Greenberg, 2003), burning the vegetation increases the amount of PAHs in the environment (Hock-Seng *et al.*, 2007). One possibility is to cut or remove vegetation and compost it (Barker and Bryson, 2002) for application to the surrounding fields as organic fertilizer. Similar ecologically-friendly solutions would be applied to other sinks of PAHs. It is essential to seek these solutions given the importance of the Tecocomulco Lake as a national preserve (Ramsar, 2003).

Conclusions

PAHs were found at concentrations above that recommended (0.05µg·l^{-1}; 0.05µg·kg^{-1}) indicating contamination. In general, smaller-sized molecules were found dissolved in water and heavier molecules were recovered from sediments. However, the distribution of PAHs among the six sampling areas was inconsistent, and presence and concentrations were not correlated between water and sediment.

The current study provides identification of contaminants in the Lake of Tecocomulco, which could be a possible health risk for local inhabitants. The process of bioaccumulation moves toxic compounds higher up the trophic food chain and thus represents a latent risk for environmental and human health. Future studies should include surveys of organisms from the lake, particularly those used as food by local residents, in order to quantify and, then, reduce possible health risks.

REFERENCES

Allamandola LJ, Bernstein MP, Sandford SA, Walker RL (1999) Evolution of interstellar ices. *Space Sci. Rev. 90*: 219-232.

Anyakora C, Coker H (2006) Determination of polynuclear aromatic hydrocarbons (PAHs) in selected water bodies in the Niger Delta. *Afr. J. Biotechnol. 5*: 2024-2031.

Anyakora C, Ogbeche A, Palmer P, Coker H (2005) Determination of polynuclear aromatic hydrocarbons in marine samples of Siokolo Fishing Settlement. *J. Chromatogr. A 1073*: 323-330.

ATSDR (1995) *Toxicological Profile for Polycyclic Aromatic Hydrocarbons*. Agency for Toxic Substances and Disease Registry. U.S. Department of Health and Human Services. Atlanta, GA, USA. 469 pp.

Barker AV, Bryson GM (2002) Bioremediation of heavy metals and organic toxicants by composting. *Sci. World J. 2*: 407-420.

Barron MG, Carls MG, Heintz R, Rice SD (2004) Evaluation of fish early life-stage toxicity models of chronic embryonic exposures to complex polycyclic aromatic hydrocarbon mixtures. *Toxicol. Sci. 78*: 60-67.

Bautista-Hernández CE, Hernández-Hernández DL, Monks S, Pulido-Flores G (2008) Lago de Tecocomulco. In Pulido-Flores G, Monks S, Miranda R, Galicia D (Eds) *Estudios Científicos de Lago de Tecocomulco, Hidalgo, y Zonas Aledañas*. Universidad Autónoma del Estado de Hidalgo and Universidad de Navarra. Pachuca, Hidalgo, Mexico. pp. 15-22.

Chen Y, Zhu L, Zhou R (2007) Characterization and distribution of polycyclic aromatic hydrocarbon in surface water and sediment from Qiantang River, China. *J Haz. Mat. 141*: 148-155.

Cottini GB, Mazzone GB (1939) The effects of 3,4-benzpyrene on human skin. *Am. J. Cancer 37*: 186-195.

de Gouw JA, Warneke C, Stohl A, Wollny AG, Brock CA, Cooper OR, Holloway JS, Trainer M, Fehsenfeld FC, Atlas EL, Donnelly SG, Stroud V, Lueb A (2006) Volatile organic compounds composition of merged and aged forest fire plumes from Alaska and western Canada. *J. Geophys. Res. Atm. 111*: D10303.

Delistraty D (1997) Toxic equivalency factor approach for risk assessment of polycyclic aromatic hydrocarbons. *Toxicol. Env. Chem. 64*: 81-108.

Di Toro DM, McGrath JA, Hansen DJ (2000) Technical basis for narcotic chemicals and polycyclic aromatic hydrocarbon criteria. I. Water and tissue. *Env. Toxicol. Chem.* 19: 1951-1970.

EPA (1996) SW-846 EPA Method 3550C: Ultrasonic extraction. In *Test Methods for Evaluating Solid Waste: Physical/Chemical Methods*. United States Environmental Protection Agency. Washington, DC, USA.

Greenberg BM (2003) PAH interactions with plants: uptake, toxicity and phytoremediation. In Douben PET (Ed.) *PAHs: an Ecotoxicological Perspective*. Wiley. West Sussex, UK. pp. 263-273.

Habs M, Jahn SA, Schmahi D (1984) Carcinogenic activity of condensate from coloquint seeds (*Citrullus colocynthis*) after chronic epicutaneous administration to mice. *J. Cancer Res. Clin. Oncol. 108*: 154-156.

Hock-Seng T, Mohd-Tahir N, Radzi-Abas M (2007) Aliphatic and PAHs emissions from open burning of selected tropical woods. *Malay. J. Anal. Sci. 11*: 36-41.

Huízar-Álvarez R, Jiménez-Fernández E, Juárez-López C (2005) La laguna de Tecocomulco. Geo-ecología de un desastre. Universidad Nacional Autónoma de México. 232 pp.

Law RJ, Kelly C, Baker K, Jones J, McIntosh AD, Moffat CF (2002) Toxic equivalency factors for PAH and their applicability in shellfish pollution monitoring studies. *J. Env. Monit. 4*: 383-388.

Le Marchand L, Hankin JH, Pierce LM, Sinha R, Nerurkar PV, Franke AA, Wilkens LR, Kolonel LN, Donlon T, Seifried A, Custer LJ, Lum-Jones A, Chang W (2002) Well-done red meat, metabolic phenotypes and colorectal cancer in Hawaii. *Mutat. Res. 506-507*: 205-214.

Mastandrea C, Chichizola C, Ludueña B, Sánchez H, Álvarez H, Gutiérrez A (2005) Hidrocarburos aromáticos policíclicos. Riesgos para la salud y marcadores biológicos. *Acta Bioquím. Clín. Latinoam. 39*: 27-36.

Miranda R, Galicia D, Pulido-Flores G, Monks S (2008) First record of *Girardinichthys viviparus* in Lake Tecocomulco, Mexico. *J. Fish Biol.* 73: 317-322.

Monks S, Pulido-Flores G, Gaytán-Oyarzún JC (2008) Introducción: una visión moderna de la investigación científica. In Pulido-Flores G, Monks S, Miranda R, Galicia D (Eds) *Estudios Científicos de Lago de Tecocomulco, Hidalgo, y Zonas Aledañas*. Universidad Autónoma del Estado de Hidalgo and Universidad de Navarra. Pachuca, Hidalgo, Mexico. pp. 7-13.

NOM (2005) *NOM-050-PESC-2004. Pesca Responsable en el Embalse del Lago de Tecocomulco en el Estado de Hidalgo. Especificaciones para el Aprovechamiento de los Recursos Pesqueros*. Norma Oficial Mexicana. Secretaría de Agricultura, Ganadería, Desarrollo Rural, Pesca y Alimentación. Diario Oficial, 4 de agosto de 2006. Mexico.

Okuda T, Kumata H, Zakaria MP, Naraoka H, Ishiwatari R, Takada H (2002) Source identification of Malaysian atmospheric polycyclic aromatic hydrocarbons nearby forest fires using molecular and isotopic compositions. *Atm. Env. 36*: 611-618.

Olajire-Abbas A, Brack W (2005) Polycyclic aromatic hydrocarbons in Niger Delta soil: contamination sources and profiles. *Int. J. Env. Sci. Technol. 2*: 343-352.

Ramsar (2003) Ramsar Convention (Peck D, Ed.). Ramsar International. Gland, Switzerland, www.ramsar.org/wn/w.n.mexico_10new.htm (Cons. 09/15/2008).

Reynaud S, Deschaux P (2006) The effects of polycyclic aromatic hydrocarbons on the immune system of fish: a review. *Aquat. Toxicol. 77*: 229-238.

Rhoades CP, Smith WE, Cooper NS, Sullivan RD (1954) Early changes in the skin of several species including man, after painting with carcinogenic materials. *Proc. Am. Assoc. Cancer Res. 1*: 40.

Sánchez-Brunete C, Miguel E, Tadeo JL (2007) Analysis of 27 polycyclic aromatic hydrocarbons by matrix solid-phase dispersion and isotope dilution gas chromatography-mass spectrometry in sewage sludge from the Spanish area of Madrid. *J. Chromat. 1148*: 219-227.

Shukla V, Upreti DK (2009) Polycyclic aromatic hydrocarbon (PAH) accumulation in lichen, *Phaeophyscia hispidula* of DehraDun City, Garhwal Himalayas. *Env. Monit. Assess. 149*: 1-7.

Walker CH (2001) *Organic Pollutants: an Ecotoxicological Perspective*. Taylor & Francis. London, U.K. 282 pp.

Warshawsky D, Barkley W (1987) Comparative carcinogenic potencies of 7H-dibenz[*c,g*]carbazole, dibenz[*a,j*]acridine and benzo[*a*]pyrene in mouse skin. *Cancer Lett. 37*: 337-344.

WHO (1998) Polynuclear aromatic hydrocarbons. In *Guidelines for Drinking-Water Quality: Health Criteria and other Supporting Information*. Vol. 2. World Health Organization. Geneva, Swizterland. pp. 123-152.

Zhou JL, Fileman TW, Evans S, Donkin P, Llewellyn C, Readman JW, Mantoura RFC, Rowland SJ (1998) Fluoranthene and pyrene in the suspended particulate matter and surface sediments of the Humber Estuary, UK. *Mar. Pollut. Bull. 36*: 587-597.

Zhu L, Chen Y, Zhou R (2008) Distribution of polycyclic aromatic hydrocarbons in water, sediment and soil in drinking water resource of Zhejiang Province, China. *J. Haz. Mat. 150*: 308-316.