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Hydrocarbons Derived from Petroleum in Bottled Drinking Water from Mexico City

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Abstract This paper describes the concentrations of polycyclic aromatic hydrocarbons (PAHs) and aliphatic hydrocarbons (AHs) derived from petroleum in bottled drinking water samples that were collected over 1 year from Mexico City in two bottle sizes (1.5 and 19 L), all brought in supermarkets. The analysis was by gas chromatography with flame ionization detection. –Concentrations of AHs (9.26–1.74 μg/L) were greater than PAHs (20.15–12.78 ng/L). Individual concentrations of PAHs such as fluoranthene, benzo(b)fluoranthene, benzo(k)fluoranthene, indeno(1,2,3-cd)pyrene and benzo(ghi)perylene were comparable with data reported by the World Health Organization (WHO). Total concentrations of PAHs for all samples (BDW1: 12.78 μg/L, BDW2: 16.72 μg/L, BDW3: 14.62 μg/L, BDW4: 20.15 μg/L and BDW5: 13.23 ng/L) were below the maximum permissible European level of 100 ng/L; no regulations exist for AHs although their values were greater than PAHs (BDW1: 3.11 μg/L, BDW2: 8.45 μg/L, BDW3: 1.74 μg/L, BDW4: 4.75 μg/L and BDW5: 9.26 μg/L).

Keywords Petroleum hydrocarbons · Drinking water · Mexican population

Water pollution has become an important problem for public health. Among polluting compounds, aliphatic hydrocarbon (AHs) and polycyclic aromatic hydrocarbons (PAHs) are important classes and their widespread distribution has raised global concerns (Chen 2007). The presence of these compounds in water is across decomposition of organic matter, with dominance of low weight molecular mainly (Krauss et al. 2005). The presence of different aliphatic hydrocarbons in water varies depending upon individual compound source, solubility, degradability and availability for degradation, which partly depends on association with mineral and organic particulate material (Schulz and Emeis 2000). Once in free form in the environment they undergo a faster degradation, although some are stable enough to be used to identify original sources.

Many PAHs have deleterious effects in mammals due to their carcinogenic potential because PAH degradation intermediates (DNA-adducts) covalently bind with cellular DNA (Aas et al. 2000). The US Environmental Protection Agency (USEPA) has promulgated 16 unsubtituted PAHs in its list of 129 priority pollutants. Six PAHs including benzo(a)antracene, benzo(b)fluoranthene, benzo(a)pyrene, benzo(k)fluoranthene, chrysene, dibenzo(a)anthracene and indeno(1,2,3-cd)pyrene have been classified as potential carcinogens to humans (IARC 1987) and their occurrence in the aqueous environment therefore has been designated as a potential threat to human health. PAHs are ubiquitous pollutants found in various environments, such as the atmosphere, water bodies, and sediments (Fernandez et al. 2000). Pathways for PAHs to enter surface water bodies include atmospheric fallout, urban run-off, municipal effluents, industrial effluents, and oil spillage or leakage. Atmospheric fall-out occurs upon dry and wet deposition of particles and vapors (Badawy and Emababy 2010). PAHs, as semi-volatile organic compounds, exit in both the gaseous and particulate phase in air, and are subject to both vapor and particle washout from the atmosphere during

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precipitation. Atmospheric deposition has been regarded as the main pathway for PAHs to enter water bodies (Malik et al. 2004).

In Mexico the consumption of bottled drinking water (BDW) per head of population is one of the highest in the world, influenced by advertising campaigns by companies which affect consumer decisions over their health and well-being (Ferrier 2001). Bottled water is considered a healthy alternative to other beverages and tap water especially as the potable water system in some areas of Mexico has contamination problems and increasing urbanization has contributed to a decline in tap water quality. By contrast, BDW is perceived as pure and safe although this is not necessarily true.

The aim of this study was to evaluate the presence of AHs and PAHs in BDW in Mexico City to help understand the quality of this water and as a step towards guaranteeing its quality for the Mexican population.

Table 1 Concentrations of aliphatic and aromatic hydrocarbons in bottled drinking water from Mexico City

Compounds	Samples (μg/L)				
Aliphatics	BDW1	BDW2	BDW3	BDW4	BDW5
C11	–	0.03 ± 0.08	–	–	0.12 ± 0.26
C12	–	–	–	–	–
C13	–	0.04 ± 0.13	–	–	0.05 ± 0.10
C14	–	0.08 ± 0.15	–	–	0.05 ± 0.11
C15	–	0.06 ± 0.11	0.04 ± 0.09	–	0.14 ± 0.21
C16	0.02 ± 0.04	0.09 ± 0.09	–	–	0.26 ± 0.53
C17	0.04 ± 0.05	0.15 ± 0.23	0.03 ± 0.06	0.01 ± 0.04	0.41 ± 0.72
C18	0.28 ± 0.31	1.03 ± 1.16	0.19 ± 0.15	0.26 ± 0.40	1.20 ± 2.13
C19	0.14 ± 0.16	0.69 ± 0.94	0.15 ± 0.15	0.18 ± 0.24	1.71 ± 3.25
C20	0.38 ± 0.34	1.41 ± 1.49	0.31 ± 0.08	0.68 ± 0.71	2.27 ± 4.03
C21	0.25 ± 0.16	0.48 ± 0.43	0.19 ± 0.08	0.45 ± 0.43	0.54 ± 0.62
C22	0.41 ± 0.39	0.81 ± 0.65	0.24 ± 0.14	1.03 ± 2.04	0.58 ± 0.75
C23	0.62 ± 0.81	1.12 ± 1.15	0.26 ± 0.24	0.69 ± 1.41	0.80 ± 1.38
C24	0.47 ± 0.75	1.40 ± 1.76	0.18 ± 0.13	0.88 ± 1.11	0.82 ± 1.44
C25	0.49 ± 073	1.06 ± 1.30	0.15 ± 0.03	0.57 ± 0.97	0.32 ± 0.31
Aliphatic Total	3.11	8.45	1.74	4.75	9.26
	Samples (ng/L)				
Aromatics	BDW1	BDW2	BDW3	BDW4	BDW5
Nap (2)	0.26 ± 1.06	0.28 ± 0.81	0.25 ± 0.70	0.52 ± 0.95	0.12 ± 0.48
Acy (3)	0.10 ± 0.41	0.15 ± 0.42	0.28 ± 0.66	0.27 ± 0.58	0.38 ± 0.78
Ace (3)	–	0.26 ± 0.58	0.08 ± 0.32	0.19 ± 0.55	0.21 ± 0.63
Flu (3)	0.09 ± 0.26	0.24 ± 0.56	0.18 ± 0.41	0.11 ± 0.30	0.14 ± 0.37
Phe (3)	0.48 ± 1.02	0.81 ± 1.49	0.46 ± 1.28	0.90 ± 1.53	0.46 ± 1.16
Ant (3)	0.87 ± 2.06	1.63 ± 2.85	0.90 ± 1.90	2.43 ± 3.39	0.74 ± 1.57
Fla (4)	0.61 ± 1.30	1.68 ± 2.57	0.91 ± 1.83	1.44 ± 2.54	1.02 ± 2.39
Pyr (4)	0.35 ± 0.65	1.04 ± 1.59	0.81 ± 2.36	1.33 ± 2.02	1.29 ± 2.78
BaA (4)	3.14 ± 3.36	2.75 ± 3.56	4.09 ± 6.07	2.25 ± 2.61	3.88 ± 3.32
Cry (4)	1.93 ± 3.63	1.10 ± 2.39	1.08 ± 2.09	1.63 ± 2.87	0.61 ± 1.54
BbF (5)	0.65 ± 1.67	1.37 ± 3.33	0.96 ± 2.43	1.64 ± 2.70	0.56 ± 1.80
BkF (5)	1.38 ± 2.40	1.33 ± 2.19	1.08 ± 2.71	1.62 ± 2.81	0.89 ± 1.95
BaP (5)	0.79 ± 1.47	1.52 ± 2.06	1.29 ± 2.58	1.48 ± 2.36	1.75 ± 3.06
Ind (6)	0.64 ± 1.85	0.75 ± 1.67	0.63 ± 1.99	2.06 ± 3.47	0.10 ± 0.38
DaA (5)	0.64 ± 1.45	0.80 ± 1.56	0.65 ± 1.88	1.35 ± 3.05	0.34 ± 1.07
Bghi (6)	0.85 ± 1.90	1.01 ± 2.04	0.97 ± 2.35	0.93 ± 1.79	0.74 ± 2.04
PAHs total	12.78	16.72	14.62	20.15	13.23

– Not detected

Materials and Methods

Bottled drinking water samples (labeled DBW1-DBW6; 16 samples in total for each brand) from the south of Mexico City (the district of Coyoacan) were bought in supermarkets and stored at room temperature. The samples were in bottles of 1.5 L (DBW1–DBW3) and 19 L (DBW4–DBW6). This research took place over 1 year (November 2008–December 2009), with samples taken each month until the final 2 months when two samplings were carried out.

A 500 mL aliquot of each bottled water sample was added to a separating funnel, followed by extraction with 60 mL of hexane; a further 500 mL aliquot was extracted with 60 mL of hexane to complete 1 L of sample. The organic phase was dried over anhydrous sodium sulfate then the samples evaporated in a rotary evaporator to 5 mL. Chromatographic columns were prepared with silica gel and aluminum oxide deactivated with deionized water (5%) and topped with anhydrous sodium sulfate. The samples were passed through the columns then the AHs eluted with 20 mL of hexane while PAHs were eluted with a mixture of hexane-dichloromethane (9:1 and 1:1). The organic extract was concentrated to 1 mL using a rotary evaporator and transferred to a vial for gas chromatographic analysis according to EPA method 8100.

The concentrations and profiles of PAH compounds were analyzed using a Perkin Elmer AutoSystem gas chromatograph (Column HP-5, 30 m, 0.35 mm ID, 0.25 μm film thickness). The oven temperature was initially set at 90°C and held for 0 min before being ramped at 8°C/min to 180°C (1 min), then ramped at 5°C/min–245°C (0 min), and ramped at 2°C/min to a final temperature of 300°C (0 min). Detector and injector temperature were 320°C. The carrier gas was high purity helium (99.99%). A sample of 2 μL was injected in splitless mode.

Identification of AHs was based on matching their retention time with a Diesel range mixture No 2-GRO/DRO (Chem Service). The aliphatic compounds were in the range C11–C25. PAH compound identification was based on matching retention times with a mixture of PAH standards (Chem Service). The 16 PAHs were naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fla), pyrene (Pyr), benzo(a)fluorene (BaF), benzo(a)anthracene (BaA), chrysene (Cry), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), indeno(1,2,3-cd)pyrene (Ind), dibenzo(ah + ac)anthracene (DaA), and benzo(ghi)perylene (Bghi). Detection limits were 0.10–0.12 ng/L.

Quality control was made by analysis of fortified blanks and samples together with evaluation of the performance of the GC (CENAM 2005). Recoveries were 80%–90% except for naphthalene for which a value of 50% was obtained. Quantification of individual PAHs was made by an external standard method.

Results and Discussion

Table 1 shows that AHs in the five BDW samples ranged from 1.74 to 9.26 μg/L while PAHs ranged from 12.78 to 20.15 ng/L. In general, the distribution of AHs in the samples varied considerably but were mainly hydrocarbons with carbon numbers in the range of C18–C20 and C22–C25 while the PAHs were dominated mostly by Phe, Ant, Fla, Pyr and BaA; in some samples BbF, BkF and BaP were also present at relatively high concentrations.

Results for individual concentrations of PAHs were comparable with values in the United Kingdom for Fla (6.5 ng/L), BbF (1.6 ng/L), BkF (0.49 ng/L), Ind (0.43 ng/L) and Bghi (0.43 ng/L), as reported by WHO (2003).

Figure 1 shows that concentrations of AHs were greater than PAHs. This pattern is similar to many previously reported studies although the dominance of odd hydrocarbons indicates a possible contamination by petrogenic hydrocarbons derived from combustion of fuels (Wang et al. 2001).

There is a lot of urban and industrial development around water reservoirs in Mexico City and the presence of PAHs was probably partially associated with human activity.

The distribution of PAHs by molecular weight followed the order intermediate > high > low molecular weight (Table 2).

Figure 2 shows that using the diagnostic ratios of Ant/(Ant + Phe) versus Flu/(Flu + Pyr), all values fell in the area of pyrolytic and petroleum sources. PAHs derived from combustion tend to bind strongly to soot particles and display orders of magnitudes higher partition coefficients than those predicted by equations (Peña-Méndez et al. 2001). We also used other diagnostic ratios such as Phe/Ant (0.37–0.63, average 0.51), Cry/BaA (0.16–0.73, average 0.43) and Flu/Pyr (0.08–0.27, average 0.18) where the

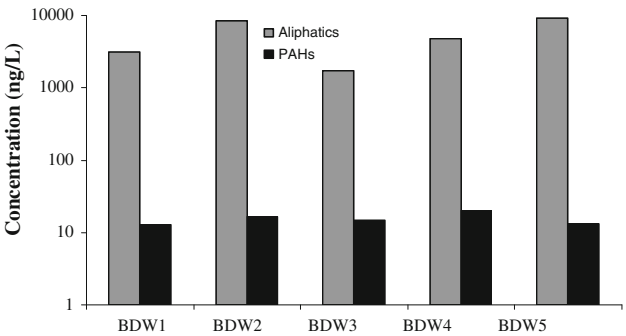

Fig. 1 Comparison of total AHs and PAHs in the samples of bottled drinking water

Table 2 Average PAH concentrations by compound type (ng/L) in BDW from Mexico City (n = 16 for each brand)

Compound type	BDW1	BDW2	BDW3	BDW4	BDW5
Low molecular weight (2 aromatic rings)	0.26 (2.0)	0.28 (1.7)	0.25 (1.7)	0.52 (2.6)	0.12 (0.9)
Intermediate molecular weight (3–4 aromatic rings)	7.57 (59.2)	9.66 (57.8)	8.79 (60.1)	10.55 (52.3)	8.73 (66.0)
High molecular weight (5–6 aromatic rings)	4.96 (38.8)	6.78 (40.5)	5.58 (38.2)	9.08 (45.1)	4.38 (33.1)
Total concentration	12.78	16,72	14,62	20,15	13,23

Numbers in parentheses represent percent of total concentration

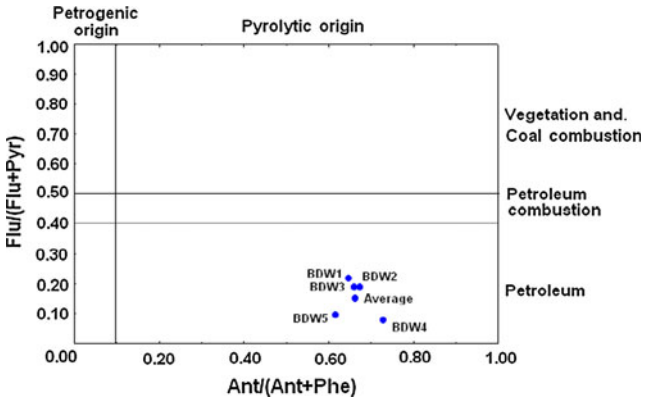

Fig. 2 PAH cross plots for the ratios of Ant/(Ant + Phe) vs Flu/(Flu + Ant) (Average represents the ratio of concentration of 5 sampling brands)

values confirm the presence of PAHs derived from combustion, typically from engines and factories(ratio values less than 10).

The presence of combustion derived PAHs has been reported in studies from China (Ma et al. 2008; Zhu et al. 2008) for surface and groundwater reservoirs and also in bottled waters (Leivadara et al. 2008). Our results showed low concentration in comparison to many studies, for example Chen (2007) found concentrations as high as 1452.9 ng/L which were due to the presence of heavy industry, although some provinces complied with the European standard (a maximum of 100 ng/L for total PAHs).

Hydrocarbons found in bottled drinking water did not represent any risk for the public in Mexico from the point of view of AHs and PAHs concentrations, according to the European standard.

The presence of PAHs is probably due to the presence of anthropogenic sources. The leaching of PAHs from soils into groundwater is negligible as the compounds tend to adsorb strongly to the soil organic matter. It is more likely that PAHs are associated with air particulate matter by adsorption and these particulates are finely dispersed into the water during wet deposition (Badawy and Emababy 2010). The results of this study did not exceed values of 40 ng/L as sum total, concentrations comparable with reports from Germany (WHO 2003).

According to Kruawal et al. (2005) some organic residues will be detected in spite of the treatment processes used for tap water and bottled drinking water production. Complete removal of micropollutants such as pesticides, disinfection by products, and surfactants cannot be guaranteed.

We recommend monitoring of the water reservoirs and bottled water over a long time period to guarantee an adequate quality for human health with regard to inorganic and organic contaminants. Further, this type of water should be considered as a strategic resource in the future. Bottled drinking water consumption rates are high in Mexico therefore a guarantee of the quality of this water would be prudent.

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References

Aas E, Baussant T, Balk L, Liewborg B, Anderson OK (2000) PAH metabolites in bile, cytochrone P4501A and DNA adducts as environmental risk parameters for chronic oil exposure: a laboratory experiment with Atlantic cod. Aquat Toxicol 51:241–258

Badawy MI, Emababy MA (2010) Distribution of polycyclic hydrocarbons in drinking water in Egypt. Desalination 251:34–40

CENAM (2005) Guía de Laboratorio para la Validación de métodos y temas relacionados. Centro Nacional de Metrología, Querétaro, México. p 67

Chen HW (2007) Distribution and risk assessment of polycyclic aromatic hydrocarbons in household drinking water. Bull Environ Contam Toxicol 78:201–205

Fernandez P, Vilanova RM, Martinez C, Appleby P, Grimalt JO (2000) The historical Record of atmospheric pyrolytic pollution over Europe registered in the sedimentary PAH from remote mountain lakes. Environ Sci Technol 34:1906–1913

Ferrier C (2001) Bottled water: understanding a social phenomenon. Discussion Paper for WWF. http://assets.panda.org/downloads/bottled_water.pdf. Accessed 10 March 2009

International Agency for Research on Cancer (IARC) (1987) Overall evaluation of carcinogenicity: an updating of IARC monographs. IARC monographs on the evaluation of carcinogenic risk to human, vol 1–42. IARC, Lyon

Krauss M, Wilcke W, Martius C, Bandeira AG, García MVB, Amelung W (2005) Atmospheric versus biological sources of

polycyclic aromatic hydrocarbons (PAHs) in a tropical rain forest environment. Environ Pollut 135:143–154

Kruawal K, Sacher F, Werner A, Müller J, Knepper TP (2005) Chemical water quality in Thailand and its impacts on the drinking water production in Thailand. Sci Total Environ 340:57–70

Leivadara SV, Nikolaou AD, Lekkas TD (2008) Determination of organic compounds in bottled waters. Food Chem 108:277–286

Ma Y, Cheng J, Jiao F, Duo K, Rong Z, Li M, Wang W (2008) Distribution, sources, and potential risk of polycyclic aromatic hydrocarbons (PAHs) in drinking water resources from Henan Province in middle of China. Environ Monit Assess 146:127–138

Malik A, Singh KP, Mohan D, Patel DK (2004) Distribution of polycyclic aromatic hydrocarbons in Gomti River System, India. Bull Environ Contam Toxicol 72:1211–1218

Peña-Méndez EM, Astorga-España MS, García-Montelongo FJ (2001) Chemical fingerprinting applied to the evaluation of marine oil pollution in the coasts of Canary Islands (Spain). Environ Pollut 111:177–187

Schulz HM, Emeis KC (2000) Sources and pathways of natural and anthropogenic hydrocarbons into the natural dump Arkona Basin (southern Baltic Sea). Environ Geol 39:839–848

Wang Z, Fingas M, Owens EH, Sigouin L, Brown CE (2001) Long term fate and persistence of the spilled Metula oil in marine salt marsh environment: degradation of petroleum biomarkers. J Chromatogr A 926:275–290

World Health Organization (WHO) (2003) Polynuclear aromatic hydrocarbons in drinking water. WHO/SDE/WSH/03.04/59. p 27

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 Hazard Mater 150:308–316