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PAHs and BTEX in Groundwater of Gasoline Stations from Rio de Janeiro City, Brazil

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Abstract PAHs and BTEX were studied in groundwater from monitoring wells of gasoline stations of Rio de Janeiro City, Brazil during 2003 and 2004. Total PAH concentration ranged from 0.05 to 84.9 µg/L. Total BTEX concentration varied between not-detected to 3.6×10^3 µg/L. Some samples exceeded the maximum concentration limit of Brazilian regulations for benzene in fresh or drinking water. Carcinogenic PAHs were found in few samples but only one sample in each year exceeded the regulated concentrations for benzo[a]pyrene. The concentrations of PAHs and BTEX indicate that some places may be contaminated by gasoline leakage.

Keywords Groundwater · PAHs · BTEX · Fuel stations

Polycyclic aromatic hydrocarbons (PAHs) are environmental contaminants of concern since many of them and many PAH mixtures exhibit mutagenic and/or pro-carcinogenic properties to humans (IPCS 1998; Pereira Netto et al. 2000). Among the monoaromatic hydrocarbons, benzene is the most harmful compound with well known carcinogenic properties and it is classified as carcinogenic to humans (IARC 2007). The other monoaromatic hydrocarbons (toluene, xylenes and ethylbenzene) are less toxic (IPCS 1996b, 1997) but they are of concern at least because they add odor or taste to water at ppm concentrations (Day et al. 2001). Gasoline and other petroleum derived fuels are complex mixtures that contain many hydrocarbon families such as normal, branched and cyclo-alkanes and alkenes, lower concentrations of monoaromatic hydrocarbons (benzene, toluene, ethylbenzene and xylenes – BTEX) and higher alkylated aromatic hydrocarbons, PAHs and fuel additives (IPCS 1996a; Lee et al. 1992; Odermatt 1994). Fuel composition depends also on crude oil sources, the degree of chemical modifications (cracking or re-forming) and petroleum fractionation. Many minor fuel components are of interest due to their toxicology. This is the case of PAHs and BTEX that have been studied in many media including air, water and soil (IPCS 1998; Menchini et al. 1999; Monod et al. 2001; Pereira Netto et al. 2002a, b, 2004). There is concern on gasoline leakage of underground storage tanks since hydrocarbons and other compounds can be released into the soil leading to soil and/or groundwater contamination (Iturbe et al. 2003, 2005; Odermatt 1994; Kelley et al. 1997; Rosell et al. 2003). The presence of PAHs in gasoline is well known but lighter PAHs predominate (Zoccolillo et al. 2000; Corseuil et al. 2004). Brazilian gasoline also contains up to 20% of ethanol that impacts the behavior of BTEX in soils in many ways (Powers et al. 2001). The Brazilian Regulation CONAMA 273 (2000) obligates the monitoring of PAHs, BTEX and other semi-volatile organic compounds in groundwater of monitoring wells of fuel stations but as far as we are concerned there are no published data from Brazil. This work partly addresses to fill the lack on data on

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PAH and BTEX in groundwater of gasoline stations of Rio de Janeiro City, RJ, Brazil.

Materials and Methods

A solution containing the 16 EPA target PAHs (0.200 mg/mL; AccuStandard, CT, USA), solid PAHs (Sigma, MO, USA or Aldrich Chemical Co., WI, USA) and perdeuterated PAHs (Cambridge Isotope Laboratories, MA, USA or Isotech, OH, USA) were used. Benzene, toluene, *o*-, *m*- and *p*-xylenes and ethylbenzene with purity ≥98% were from Merck (USA) and perdeuterated toluene was from Isotech (USA). Hexane, toluene, methanol and dichloromethane (Absolv, Tedia, RJ, Brazil) were used. SPE SiO_2 cartridges (3 mL; 500 mg; J.T BAKER, NJ, USA) and a SPE Vacuum Manifold (J.T BAKER) were used to clean up extracts. Ultra pure water was prepared by a Millipore Milli-Q System (MA, USA).

Water samples were collected in monitoring wells built in gasoline stations according to Brazilian Regulations (ABNT 1997, 2000). Water samples were collected after sufficient water had run off the well to eliminate stagnant water and conserved according to NBR 13895 (ABNT 1997). At least 1,000 mL of water from each well were collected in dark glass flasks without headspace. Samples were taken to the laboratory under refrigeration and stored at −4°C until analysis that always occurred within 2 days.

PAHs were extracted from 400 mL samples by liquid–liquid extraction under magnetic stirring with two portions of hexane (60 mL; 20 min each). Internal standards were added to the extract after the first extraction step. Combined extracts were concentrated up to 10 mL in rotary evaporator at temperatures ≤40°C, transferred to test tubes and dried with anhydrous sodium sulfate (Merck, USA). The organic layers were transferred and evaporated under a gentle N_2 flow after addition of 500 µL of toluene (as a keeper). Concentrated extracts were transferred onto SiO_2 SPE cartridges previously activated with dichloromethane. The PAH rich fractions were eluted with hexane, evaporated under a gentle N_2 flow and transferred to 2 mL vials that were kept in freezer until analysis. PAHs were determined by GC-MS in an AutoSystem TurboMass (Perkin Elmer, USA) with a DB5-ms column (30 m; 0.25 µm; 0.25 mm; J&W, CA, USA). Oven temperatures were 80°C for 0.5 min, heated to 120°C at 20°C/min, kept at this temperature for 2 min and increased to 290°C at 4°C/min, with a 15 min final hold. Transfer line was kept at 260°C and injector at 310°C. Injections were performed by autosampler in splitless mode (Pereira Netto et al. 2004). Electron ionization (70 eV) and source temperature of 180°C were used. Mass spectra were obtained from $m/z = 50$ to 350. Molecular ions (Tuominem et al. 1986) were used to draw reconstructed chromatograms and in selected ion monitoring (SIM). Quantitative analysis was performed in SIM with perdeuterated internal standards (naphthalene, pyrene, chrysene, benzo[a]pyrene and perylene). Calibration was performed by external standards ranging from 10.0 to 1000 µg/L.

BTEX were analyzed by purge-and-trap gas chromatography-mass spectrometry (P&T-GC-MS) with a Tekmar 3000 extractor (Tekmar-Dohrmann, OH, USA) interfaced to an AutoSystem TurboMass (Perkin Elmer, USA). Aliquots of 10.0 mL of water samples and of BTEX standards were purged by high purity helium (11 min) and retained by a Tenax® silica gel-charcoal trap at room temperature. Desorption was carried out at 200°C (2 min) with direct splitless injection in the GC-MS system. The internal standard solution was added to the samples in the P&T flask prior to extraction. BTEX were analyzed in optimized conditions with a PE-WAX column (60 m; 0.32 mm; 0.5 µm; Perkin Elmer, USA). Oven temperatures were 40°C for 20 min and heated to 90°C at 5°C/min. Helium was the carrier gas. Transfer line was kept at 250°C and source at 150°C. Electron ionization (70 eV) was used. Gravimetric 1,000 ppm standards were prepared by dilution of 28–30 µL of BTEX or perdeuterated toluene in methanol. BTEX standards (10.0–250 µg/L) containing 50.0 µg/L of perdeuterated toluene were prepared by dilution in ultra pure water. Quantitative analysis was performed in SIM with the following ions: benzene ($m/z = 77$), toluene and ethylbenzene ($m/z = 91$), xylenes ($m/z = 105$) and perdeuterated toluene ($m/z = 98$).

Results and Discussion

To put our data and Brazilian Legislation into a perspective the MCLs of PAHs and BTEX in fresh and drinking water adopted by the Brazilian legislation and the values adopted by USEPA (2003) for drinking water are compared in Table 1.

Benzo[a]pyrene was selected for the evaluation of PAH recoveries due to its toxicological importance since it is carcinogenic to humans (IARC 2007). Furthermore it was the only regulated PAH in the former Brazilian Regulation CONAMA 20 (1986) when this study started. Analysis of spiked ultra pure water at a 1.00 µg/L level led to recoveries ≥97%. Detection limits of all PAHs were better than 0.01 µg/L but this value was adopted for all PAHs since it was the former MCL of benzo[a]pyrene in fresh water (CONAMA 1986) (Table 1).

The 16 USEPA priority PAHs together and 2-methylphenanthrene, coronene and benzo[e]pyrene were evaluated in 24 samples collected in 2003 and in 22 samples collected in 2004. Maximum and minimum concentrations are shown

Table 1 Maximum concentration limits (MCL; μg/L) for fresh and drinking water, according to Brazilian legislation and to USEPA

Year:	CONAMA[a] 2005 Fresh water[d]	CONAMA[a] 1986 Fresh water[d]	MS-518[b] 2004 Drinking water	USEPA[c] 2003 Drinking water
PAHs				
Benz[a]anthracene	0.050	NR[e]	NR	NR
Chrysene	0.050	NR	NR	NR
Benzo[a]pyrene	0.050	0.010	0.7	0.2
Benzo[k]fluoranthene	0.050	NR	NR	NR
Benzo[b]fluoranthene	0.050	NR	NR	NR
Indeno[1,2,3-c,d]pyrene	0.050	NR	NR	NR
Dibenz[a,h]anthracene	0.050	NR	NR	NR
BTEX				
Benzene	5	10	5	5
Toluene	2	NR	170	1,000
Ethylbenzene	90	NR	200	700
Xylenes	300	NR	300	10,000

[a] Brazilian Environment Ministry

[b] Brazilian Health Ministry

[c] United States Environmental Protection Agency

[d] Simplified treatment and desinfection required before human consumption

[e] Indicates a non regulated MCL

in Table 2. Individual PAH concentrations ranged from <0.01 to 83.4 μg/L in 2003 and from <0.01 to 20.5 μg/L in 2004. Total PAH concentrations ranged between 0.05 and 84.9 μg/L in 2003 and 0.25 and 54.6 μg/L in 2004. Considering all PAHs, two samples in 2003 and four samples in 2004 were above the MCLs adopted by the present Brazilian Regulation (CONAMA 2005). The concentrations of benzo[a]pyrene in all samples were below its MCL in drinking water (Brazilian Health Ministry 2004) (Tables 1 and 2). The concentrations of benzo[a]pyrene were above the former MCL (0.010 μg/L) in fresh water (CONAMA 1986) in one sample of 2003 and in three samples of 2004. However considering the present Brazilian regulation (CONAMA 2005) the concentrations of benzo[a]pyrene

Table 2 Ranges of PAH concentrations (μg/L) in the 46 studied samples

PAHs	Minimum concentration (μg/L)	Maximum concentration (μg/L)	Number of samples where detected
Naphthalene	0.116	83.4	46
Acenaphthylene	<0.01	0.188	4
Acenaphthene	<0.01	0.170	17
Fluorene	<0.01	0.193	18
Phenanthrene	<0.01	1.08	40
Anthracene	<0.01	10.4	12
2-methyl-phenanthrene	<0.01	8.12	28
Fluoranthene	<0.01	0.403	35
Pyrene	<0.01	0.921	39
Benzo[b]fluorene	<0.01	0.072	1
Benz[a]anthracene	<0.01	0.688	2
Chrysene	<0.01	0.797	4
Benzo[k]fluoranthene	<0.01	1.17	4
Benzo[b]fluoranthene	<0.01	1.25	2
Benzo[e]pyrene	<0.01	0.586	16
Benzo[a]pyrene	<0.01	0.636	4
Perylene	<0.01	0.261	6
Indeno[1,2,3-c,d]pyrene	<0.01	2.46	11
Benzo[ghi]perylene	<0.01	0.031	7
Dibenz[a,h]anthracene	<0.01	21.0	2
Coronene	<0.01	8.86	14
Total PAHs	0.05	84.9	–

Table 3 Ranges of BTEX concentrations (μg/L) in the 56 studied samples

Monoaromatic	Minimum concentration (μg/L)	Maximum concentration (μg/L)	Number of samples where detected
Benzene	<0.10	8.12×10^3	30
Toluene	<0.10	3.03×10^4	37
Ethylbenzene	<0.10	9.09×10^3	31
Xylenes[a]	<0.10	3.60×10^4	35
Total BTEX	<0.10	8.35×10^4	–

[a] Sum of *o*-, *m*- and *p*-xylenes concentrations

were larger than its MCL for fresh water (0.0050 μg/L) in only one sample in each year. The samples that showed the larger concentrations of benzo[a]pyrene showed also the larger concentrations of the other PAHs indicating contaminated sites with respect to PAHs.

Naphthalene was the predominating PAH and it was found in all samples with concentrations between 0.20 and 83.4 μg/L in 2003 and between 0.116 and 20.5 μg/L in 2004. The relatively large concentrations of naphthalene are possibly due to its large concentrations in crude oils and in Brazilian gasoline (Corseuil et al. 2004) and also to its largest solubility in water when compared to other PAHs (IPCS 1998). Naphthalene was also previously found to predominate over other PAHs in contaminated sites and gasoline was considered one of its major sources (Wang et al. 2002). The presence of naphthalene in all samples is of concern since it is possibly carcinogenic to humans (IARC 2007). Other possibly carcinogenic PAHs (namely benzo[b]fluoranthene, benzo[k]fluoranthene, benz[a]anthracene and indeno[1,2,3-c,d]pyrene) and a probably carcinogenic PAH (dibenz[a,h]anthracene) (IARC 2007) were found in two samples of 2003 and five samples of 2004. In fact except for dibenz[a,h]anthracene all of them were previously found in gasoline (Zoccolillo et al. 2000).

BTEX recoveries were evaluated by analysis of ultra pure water spiked at a 10 μg/L level. Recoveries $\geq$98% and detection limits ($\leq$0.1 μg/L) were found. Maximum and minimum concentrations BTEX are shown in Table 3. Although *o*-, *m*- and *p*-xylenes were individually quantified their concentrations were summed up and expressed as xylenes since their MCL is referred to the sum of concentrations. Maximum concentrations of BTEX in 2003 were 3.60×10^3 μg/L for benzene; 3.03×10^4 μg/L for toluene; 9.09×10^3 μg/L for ethylbenzene and 3.60×10^4 μg/L for xylenes. In 2004 maximum concentrations were 8.17×10^2 μg/L for benzene; 7.49×10^2 μg/L for toluene; 9.84×10^2 μg/L for ethylbenzene and 1.43×10^3 μg/L for xylenes. Maximum total BTEX concentrations were 8.35×10^4 μg/L in 2003 and 3.68×10^3 μg/L in 2004. Six samples in 2003 and three samples in 2004 were free of BTEX. The larger concentrations of each monoaromatic were always found in the same samples indicating groundwater contamination by BTEX.

The reported concentrations of BTEX were comparable with those previously found in gasoline contaminated groundwater (Iturbe et al. 2005). Few samples showed BTEX concentrations larger than the MCLs of Brazilian legislation. Ten samples in 2003 and five samples in 2004 exceeded the individual MCLs of BTEX (CONAMA, 2005). Six samples in 2003 and only two samples in 2004 exceeded the Brazilian Health Ministry (2004) regulation for drinking water. Benzene, the most abundant monoaromatic hydrocarbon in Brazilian gasoline (Corseuil et al. 2004), was not predominant in most samples. Benzene concentrations were larger than its MCL (Table 1) in six samples of 2003 and in three samples of 2004. Six samples in 2003 and three samples in 2004 showed toluene above its MCL (CONAMA, 2005). The concentrations of toluene in seven samples were larger than its odor threshold of 160 μg/L (Day et al. 2001).

Our results show that groundwater contamination by PAHs and BTEX in gasoline stations have different magnitudes. Total concentrations of BTEX were in some cases as high as 10^2 mg/L and they were always 100–1,000 times larger than total PAH concentrations certainly due to the larger solubility of BTEX. The possible contamination of groundwater by gasoline becomes more evident because BTEX are volatile hydrocarbons that would evaporate and be dispersed in the surrounding air if they were not directly emitted into the soil. Our data show that groundwater contamination by BTEX or PAHs may occur in some of the studied locations leading to a deterioration of groundwater quality of and as a consequence a deterioration of groundwater reserves.

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