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Sources of Polycyclic Aromatic Hydrocarbons in Urban Storm Water runoff in Tijuana, Mexico

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ABSTRACT: Eight sites were sampled during seven rain events to quantify and identify the sources of polycyclic aromatic hydrocarbons in urban runoff in the city of Tijuana, Mexico. The total Σ16 PAHs concentration rangedfrom 1113 to 4866 µg/Lin the sampled sites and thetotal suspended solid concentrations ranged from 7725 to 4413 µg/L. The high concentrations of total suspended solids were probably the result of the erosion of bare soil areas in the basin area of the sampling sites. The PAH concentration in urban runoff from industrial sites was not as high as expected in comparison to residential sites. The potential sources of PAH were identified using the diagnostic ratios between PAHs and PCA analysis. Vehicular exhaust emissions (diesel and gasoline) and used crankcase oil were the main contributors to PAHs in urban storm water runoff. Charcoal combustion, diesel oil andlubricant oil were also identified as contributors to PAHs.

Key words: PAH, Diagnostic ratios, PCA, Pollution, Suspended solids

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are organic compounds that have two or more fused aromatic rings. They are present in processed fossil fuels, tar and various edible oils. PAHs are also formed by the incomplete combustion of fossil fuels such as gasoline, diesel or coal and the pyrolysis of organic matter such as wood (Wang *et al.,* 2009, Wang *et al.,* 2007).The US EPA has designated 16 PAHs as priority pollutants, some of which have been classified as carcinogenic, mutagenic and teratogenic. Furthermore, PAHs have been identified as endocrine disruptors(Lintelmann *et al.,* 2003).

Hoffman *et al.* (1984) estimated that 36% of the environmental PAH input was due to urban runoff. Sources of PAH in urban runoff can be exhaust deposition, asphalt,tire abrasion, crankcase oil,combustion processes and lubricating oils (Latimer *et al.,* 1990; Takada *et al.,* 1991).Ellis and Chatfield (2006) found concentrations of oil and grease in urban runoff in the UK of 4.9 mg/L on residential sites and 7.1 mg/L on industrial sites. Latimer *et al.,* (1990) analyzed street dust, soil and vegetation to identify the sources of hydrocarbons in urban runoff. They found that the majority of oil came from (1) oil drips within the driving lanes on road surfacesor deposits in parking areas, and/or (2) direct dumping of waste crankcase oil into storm drains.

The city of Tijuana is located in the northwest corner of Mexico on the US-Mexico border (Fig. 1). The region has a Mediterranean climate with distinct summer and winter seasons. The average annual rainfall is approximately 220 mm, with over 90% occurring between November and April (INEGI, 1995). The limited annual rainfall results in scarce water resources for the region's rapidly growing urban population (6% annual). The increase in population has also led to a greater number of automobiles and traffic in the city. A high percentage of the automobiles that circulate in Tijuana are used vehicles imported from the US because they are cheaper than new mexican cars. However, many of them are not in optimal conditions and often leak motor oil or brake fluid. These chemicals remain on street and parking lot surfaces and are washed away by stormwater.According to governmental statistics, 95% of the automobiles in Tijuana in 1996 were more than 6 years old (SEMARNAP, 1999). The emission control system of these automobiles is usually removed resulting in higher pollutant emissions (SEMARNAP, 1999). Rogge *et al.*(1993) found that the PAH emission rates of automobiles without a catalytic converter exceed those of catalytic converter-equipped automobiles by more

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than 26-fold.Mijangos-Montiel*et al.* (2010) found high concentrations of total suspended solids (TSS) in stormwater runoff from gas stations and sites with residential land use in Tijuana. For gas stations, TSS concentration ranged from 204 to 11561 mg/L and for residential sites from 121 to 6717 mg/L. They also found high concentrations of oil and grease, ranging from non-detectable to 3436 mg/L for gas stations and 6 to 138 mg/L for residential sites. Garcia-Flores *et al.* (2010) found a concentration range between 3850 and 14200 mg kg^{-1}forn-Hexane Extractable Material (HEM) and a concentration range between1870 and 7069 mg Kg^{-1}forSilica Gel Treated n-Hexane Extractable Material (SGTHEM) in street debris. Treatment of HEM with silica gel generates a material known as Silica Gel Treated n-Hexane Extractable Material (SGTHEM). The aforementioned treatment effectively removes vegetable oils, animal fats and related matter from HEM. The compounds remaining after treatment are the total petroleum hydrocarbons.

The location of the sampling sites is shown in Fig. 1. Four sites have predominantly residential land use (SR1, SR2, SR3 and SR4). TheSR1, SR2 and SR3 sites alsocontain several auto repair shops, street food vendors and drain areas from houses owned by low-income families. Their approximate population density is 63 inhabitants/ha. Site SR4 drains an area of approximately 13 ha with a higher population density (92 inhabitants/ha) which is populated mainly by high-income families. Site SCT has commercial and transport land use and is located by a bus terminal. Site SCR,drains a mix of residential, commercial and industrial land uses. Sites SI1 and SI2 are located within a zone of industrial land use. The predominant industries in these sampling sites are called "maquiladoras" which are foreign owned facilities that produce mainly electronic, medical and plastic products. Table 1 shows the characteristics of the sampling sites.

MATERIALS & METHODS

Eight sites were sampled in seven rain events during the 2009-2010 rain season. The characteristics of the rain events sampled are shown in Table 2. In all the sites the samples were taken directly from roads and stormwater drains and inlets. Sampling was conducted by manual sampling techniques. Two samplings were conducted in each site within two hours after the rain started. In every sampling a pre-cleaned stainless steel bucketwas dippedinto the flow andthe sample wascollected withtwo clean 1 L glass bottles.The used crankcase oil sample was collected directly from the oil change (at 3000 miles)of a 1993 model automobile and the asphalt sample was taken directly from the rubble of a road repair site located in the study area. A known amount of each ofthese environmental samples was diluted in dichloromethane and cleaned using silica gel columns. The extracts were concentrated and

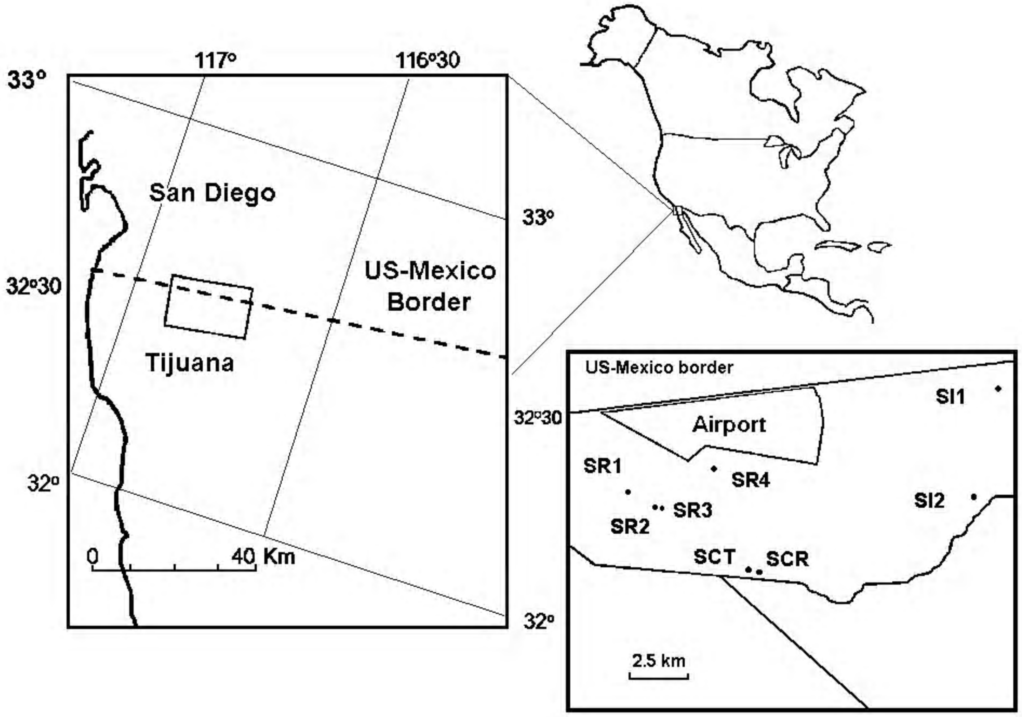

Fig. 1.The study area showing the sampling sites

Table 1. Sampling site characteristics

Site	Land use	Area (ha)	% pervious area	Average % slope
SR1	Residential and commercial	3.8	30	12.2
SR2	residential	8.0	12	4.0
SR3	residential	13.0	10	3.4
SR4	residential	13.9	17	3.2
SCT	Commercial and transport	3.9	7	1.8
SCR	Commercial, industrial and residential	163	33	7.0
SI1	Industrial	20	9	0.7
SI2	Industrial	69	8	5.1

Table 2. Characteristics of the rain events sampled

Rain event	Date (month-day-year)	Average rainfall intensity (mm/hr)	Maximum rainfall intensity (mm/hr)	Total rainfall (mm)	Dry days prior to rainfall event (days)
1	11-28-2009	1.6	4.0	10.4	39
2	12-12-2009	4.5	6.0	48.8	13
3	1-18-2010	3.8	9.0	14.5	27
4	2-05-2010	2.3	4.0	6.9	17
5	2-20-2010	2.2	3.0	8.9	14
6	2-27-2010	2.2	5.0	26.4	6
7	3-06-2010	1.0	1.0	2.5	6

analyzed for the presence of 16 PAHs using the techniques described in the following paragraph.

A standard surrogate (SUPELCO,Base-neutral surrogate spike mix 4-8925) was added to the aqueous samples to calculate recoveries in the extraction process. Then,the aqueous samples were extracted following EPAmethod 3510C. Sample pH was adjusted by adding five mL of 50% NaOH, and then subjected to three extractions with60 mL of dichloromethane; the extract was treated with anhydroussodium sulfate to eliminateremnant water. Finally, the extract was concentrated using a turbo vap500(Zymark®). After adding internal standards (Supelco 4 8902), the concentratedextracts were analyzed for PAHs by GC/MS(Agilent® 6890, with a 5973N mass selective detector)equipped with aHP-5MS 5% Phenyl Methyl Siloxane column (30m, 0.25 mm id, film 0.25 μm) in selected-ionmonitoring (SIM) mode. Helium was used as the carriergas at aflow rate of 1 mL/min. The GC oven programconsisted of an initial temperature of 55°C (1 min hold), increasing to 320°C at a rate of 25°C/min and then holding this temperature for 11.4 min (total run time:22 min).

The identity of each PAH was confirmed using a standard PAH mixture with16 PAHs. (TCL PAH Mix, Supelco, No. 48905-U). The analyzed PAHs were naphthalene (NAP), acenaphthylene (ACY), acenaphthene (ACE), fluorene (FLO), phenanthrene (Phen), anthracene (ANT), fluoranthene (FL), pyrene (PYR), benzo[a]anthracene (BaA), chrysene (CHY), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), dibenzo[a,h]anthracene (DahA), benzo[g,h,i]perylene (BghiP) and indeno[1,2,3-cd]pyrene (IcdP). Average recoveries for the16 PAHswere 82 ±8% (NAP), 83±9% (ACY), 95±13%(ACE), 77±13% (FLO), 101±11% (Phen), 90±12% (ANT), 90±11% (FL), 84±11% (PYR), 83±11% (BaA), 85±11% (CHY), 114±15.6% (BkF), 109±11% (BbF), 89±11%(BaP), 90±13% (IcdP), 85±17% (DahA) and 82±14% (BghiP).

RESULTS& DISCUSSION

The rangeand mean concentrations of PAH and total suspended solids (TSS) found in the sampling sites are shown in Table 3. The highestmean TSS concentration was observed in SR1(4412μg/L), which has a high percentage of pervious surface (30%), mostly steep unpaved streets.The second highest mean TSS concentration was found in SCT (3312μg/L), the main reason for which may be the solids transported by runoff from a stable and arodeo located in the basin area of this sampling site. The highest

Table 3. Mean PAH concentrations (µg/L), range, mean (in brackets) and standard deviation (SD) of Σ16 PAH, Range, mean (in brackets) and SD of TSS in the sampling sites, in bold the six highest PAH concentrations

	SITES							
Parameter	SR1	SR2	SR3	SR4	SCT	SCR	SI1	SI2
NAP	**316**	**190**	89	**220**	**249**	**107**	106	**217**
ACY	40	23	17	26	40	23	16	30
ACE	59	49	43	50	74	55	33	60
FLO	187	70	51	76	164	58	54	140
Phen	**769**	**321**	**196**	**220**	**491**	**193**	**171**	**379**
ANT	213	137	104	97	150	**103**	97	133
FL	**447**	**153**	**107**	91	**257**	**105**	**114**	**170**
PYR	**767**	**324**	**216**	**239**	**579**	**187**	**197**	**386**
BaA	194	56	40	47	107	53	60	76
CHY	**606**	**250**	**179**	**209**	**414**	**132**	**151**	**287**
BbF	280	119	91	110	184	67	**110**	144
BkF	126	54	53	54	107	60	57	81
BaP	**320**	129	**156**	**140**	236	55	96	161
IcdP	173	107	89	99	151	68	97	127
DahA	103	46	34	44	84	28	43	59
BghiP	311	**156**	**117**	**149**	**236**	90	**110**	**187**
Range of Σ16 PAH	1030-11600 (4866)	540-3770 (2177)	810–3290 (1577)	1020-2650 (1767)	1630-7190 (3483)	640-2070 (1137)	490-2370 (1507)	880-3160 (2594)
SD Σ16 PAH	3582	1129	831	605	1912	751	733	1973
TSS (mg/L)	484-11124 (4412)	604-3625 (1778)	740-4673 (1899)	456-1232 (725)	1023-9273 (3312)	348-3336 (3068)	411-2076 (1334)	322-1896 (1480)
SD TSS	3540	1060	1443	349	3516	2285	545	1483

SD: standard deviation. TSS: Total suspended solids

mean of theΣ16 PAH was found in SR1 (4866 µg/kg), which has commercial and residential land usesin its basin area. These concentrations are slightly lower than those found in sites with industrial land use. The second highest mean Σ16 PAH concentration was found in SCT, which is higher than the concentration observed in the industrial sites (SI1 and SI2). The high concentrations observed in SR1 and SCT in comparison with the other sites are possibly due to their small basin areas. The mean concentrations of Σ16 PAH in the industrial sites were 1507 and 2594 µg/Lfor SI1 and SI2, respectively. The concentration in site SI2 was higher than in all the residential sites except SR1. The mean concentration found in SI1 is comparable to the mean concentration found in SR3 and SR4. The main type of industryfound inthese sites are manufacturing plants, thus, the PAHs originate chiefly from the wash off from parking lots and roads, and vehicle exhaust emissions from heavy diesel trucks. The difference in mean PAH concentrations between industrial and residential land use sites were not as high as might be expected.

The three most abundant PAHs in all sites were PYR>PHEN>CHY. These three PAHs account for between 35 and 46% of the total Ó16PAH concentration. NAP, FL, BghiP and BaP are also abundant in the samples: their concentration ranges from 22 to 26% of the total Ó16PAH, although NAP is the third most abundant PAH in site SR4.

The ratios of low molecular weight (LMW) versushigh molecular weight (HMW)PAH's have been used for the identification of PAH sources (Soclo*et al.,* 2000; Brown and Peake, 2006). LMW/HMW PAHratios <1 are derived from pyrogenic sources, such as the incomplete combustion of fossil fuels or wood. On the other hand, LMW/HMW PAH ratios >1 originate from petrogenic sources such as fuel oil or light refined petroleum products. All of the ratios shown in Table 4 were lower than 1 suggesting that the sources of PAHs in the stormwater from the sampled sites are mainly of pyrogenic nature.

Table 4. Diagnostic ratios between PAHs in stormwater, combustion sources and environmental samples

Site		LMW/HMW	ANT/178	FL/ PYR+FL	BaA/228	I123P/(I123P+Bgh1P)
SR1		0.49	0.23	0.35	0.29	0.36
SR2		0.53	0.34	0.33	0.22	0.43
SR3		0.41	0.35	0.33	0.21	0.43
SR4		0.52	0.37	0.26	0.16	0.40
SCT		0.49	0.26	0.28	0.20	0.38
SCR		0.63	0.33	0.35	0.28	0.33
SI1		0.50	0.36	0.37	0.28	0.44
SI2		0.55	0.32	0.32	0.23	0.39
Gasoline combustion		-	0.11-0.22 [a,b]	0.44-0.6[a,b]	0.33-0.57[a,b]	0.09-0.22[a,b]
Diesel combustion[b]		-	0.06-0.16	0.28-0.50	0.27-0.49	0.25-0.35
Charcoal combustion[d]		0.4	0.36	0.47	0.6	0.84
Used Crankcase oil	1[c]	0.90	0.10	0.35	0.54	0.32
	2[d]	0.68	0.37	0.41	0.67	0.47
	3[e]		0.25	0.38	0.54	0.41
Asphalt	1[c]	0.24	0.09	0.13	0.37	0.00
	2[f]	-	0.10	0.30	0.26	0.00
	3[e]	-	0.14	0.43	0.28	0.31
Tire debris[e]		-	0.12	0.26	0.21	0.11

LMW: Low molecular weight PAHs; HMW: High molecular weight PAHs.
[a]Rogge et al. (1993); [b]Yunker *et al.* (2002), [c]This study, [d]Wang *et al.* (2000), [e]Boonyatumanond *et al.* (2007),
[f]Brandt and DeGroot (2001).

Table 4 also lists the diagnostic ratios between PAHs in storm water, e.g. ANT/ANT+Phen, FL/ PYR+FL, BaA/BaA+CHY and I123P/I123P+Bgh1P, which were used to investigate their origin. The diagnostic ratio values from this study were compared with those reported in the literature. A ratio ofanthracene to anthracene plus phenanthrene(Ant/ 178)<0.10 indicates the presence of petroleum while a ratio >0.10 is taken as a dominance of combustion processes (Budzinski*et al.* 1997). The ratio Ant/178 ranged from 0.23 to 0.37 in the sampling sites indicating that combustion or pyrogenic sources are the main source of PAHs. The Ant/178 ratios showed that the main source of PAH in SR1 may be gasoline exhaust, and diesel exhaust in SCT. The predominance of diesel exhaust in SCT is in accordance with its land use as two bus stations are located within the site. Used crankcase oil seems to be the main source in the rest of the sites since all of the ratios are close to the value of 0.37. The ratio value for charcoal combustion is similar to that of used crankcase oil, but is very unlikely to bethe main PAH source, especially in the industrial sites. Used crankcase oil has a pyrogenic profile because it becomes contaminated through direct contact with exhaust gases in the engine cylinders (Wang *et al.*, 2000).

Aratio value forfluoranthene to fluoranthene plus pyrene (Fl/ PYR+Fl) of 0.5 is usually defined as the petroleum/combustion transition point (Budzinsky*et al.* 1997); in this case,this point is not definitive as the ratio ant/178 value of 0.1 (Yunker*et al.*, 2002). The Fl/ PYR+Fl ratio values are below 0.5 for most petroleum samples and above 0.5 for kerosene, grass, coal and wood combustion. In the case of gasoline, diesel, fuel oil and crude oil combustion, and emissions of cars and trucks the FL/PYR+FL ratiois below 0.5 (Yunker*et al.*, 2002). The FL/PYR+FL values in this study range from 0.26 to 0.37, withratiovalues >0.30 being the most prevalent. Values of 0.26 and 0.28 were observed in SR4 and SCT. The values found in SCT suggested that the main source is diesel exhaust, and in SR4 another source is possible inwhich the main component is NAP

(Table 3). For the rest of the sites with ratio values >0.3 it is suggestedthat the main source may be used crankcase oil. However, other sources (asphalt, gasoline and diesel combustion) may also contribute to the load ofPAHs in these sites.

The ratio BaP to Bap plus CHY (BaP/228) is also used to evaluate the contribution of vehicular emissions. Several authors have found different values, for example,Gogou*et al.* (1996) reported a value of 0.33 for an urban environment where circulation of catalytic converter-equipped automobiles was predominant. Yunker*et al.* (2002) stated that BaA/228 ratios <0.20 imply petroleum, from 0.2 to 0.35 indicate either petroleum or combustion and >0.35 imply combustion. In this study, the ratio values range from 0.16 to 0.29 suggesting that combustion processes are the main PAH sources. The lowest BaA/228 value was found in SR4,with a value of 0.16, which would implicate petroleum derived compounds such as diesel oil or lubricant oil (ratio value 0.26, Yunker*et al*., 2002).

The I123P/I123P+Bgh1P ratio values <0.2 likely imply petroleum, between 0.2 and 0.50 liquid fossil fuel combustion, and ratios >0.5 imply grass, wood and coal combustion (Yunker*et al* 2002). I123P/I123P+Bgh1Pratio values found in this study range from 0.36 to 0.44 (Table 4) indicating that liquid fossil fuel combustion is the main PAH source. Comparing our results with the ratio values of I123P/I123P+Bgh1P, then, the most probable PAH sources are diesel combustion and used crankcase oil.

Principal component analysis (PCA) has been used as a tool to identify pollution sources and to statistically select independent source tracers (Guo*et al.* 2003, Nava-Martinez *et al*, 2011). Results from the application of PCA to all sites are presented in Tables 5 and 6. For SR1, SR2, SR4, SCT and SI2, two components were identified that contribute to 95, 93, 95, 97 and 96% of the variability, respectively (Tables 5 and 6). As for sites SR3, SCR and SI1, three factors were responsible for 96, 95 and 96% of the variance, respectively. The predominant component in SR1, SR2, SCT and SI2 consisted of PYR, PHEN and CHRY. These components range between 81 and 89% of the variance in these sites. PYR, PHEN and CHRY were found the predominant PAHs in diesel soot in a study conducted in Thailand (Boonyatumanond*et al.* 2007), indicating that diesel exhaust is the main source of PAHs in these sites. This is consistentwiththemain land use of these sites. In the basin areas of SR1 and SR2, old public transportbuses circulate constantly. Similarly, in the SI2 site, there is constant circulation of semi-trucks (freight trucks), which are used to transport goods manufacturedin the area. The second component in these sites (SR1, SR2, SCT and SI2) ranges from 6 to 15% of the variance. The PAHs in all of the second components allowed us to identify gasoline exhaust as the second main source in SR1, SR2, SCT and SI2.

For SR3, Phen, ANT, PYR and BaP are the main components that contribute 76% of the variance. The PAH profile for used crankcase oil from Boonyatumanond*et al.* (2007) indicates that these

Table 5. PCA analysis of PAHs in stormwater at SR1, SR2, SR3 and SCT sites

	SR1		SR2		SR3			SR4		SCT	
	P1	P2	P1	P2	P1	P2	P3	P1	P2	P1	P2
NAP	0.06	0.04	0.31	-0.59	0.14	-0.66	-0.25	0.81	-0.35	0.02	-0.60
ACY	0.02	0.01	0.04	-0.04	0.04	-0.01	0.10	0.04	0.02	0.01	-0.01
ACE	0.01	0.01	0.01	0.02	0.07	0.03	0.07	0.03	0.11	0.02	0.00
FLO	0.10	-0.16	0.10	-0.11	0.09	-0.10	0.18	0.16	0.00	0.12	-0.32
Phen	0.43	0.07	0.62	-0.36	0.42	-0.30	0.54	0.48	0.10	0.41	-0.35
ANT	0.14	0.22	0.00	0.10	0.42	-0.30	0.54	0.04	0.13	0.00	-0.05
FL	0.37	0.38	0.23	0.18	0.22	0.20	-0.30	0.11	0.30	0.34	0.08
PYR	0.53	0.17	0.55	0.29	0.50	-0.22	-0.13	0.20	0.58	0.53	-0.28
BaA	0.11	0.05	0.09	0.13	0.12	0.03	0.04	0.01	0.27	0.13	0.08
CHY	0.41	-0.84	0.34	0.36	0.28	-0.01	-0.57	0.12	0.29	0.49	0.19
BbF	0.22	-0.04	0.10	0.22	0.20	0.13	-0.09	0.08	0.23	0.17	0.14
BkF	0.08	0.10	0.03	0.14	0.10	0.14	-0.06	0.00	0.13	0.17	0.19
BaP	0.24	0.17	0.09	0.25	0.47	0.49	0.27	0.02	0.34	0.21	0.33
IcdP	0.09	0.05	0.02	0.21	0.11	0.19	-0.26	-0.01	0.12	0.13	0.20
DahA	0.08	0.06	0.02	0.13	0.04	0.08	-0.02	0.02	0.08	0.10	0.15
BghiP	0.23	0.07	0.13	0.23	0.19	0.19	-0.11	0.04	0.24	0.19	0.24
% var	0.89	0.06	0.81	0.12	0.76	0.13	0.07	0.72	0.23	0.85	0.12
Acc	0.89	0.95	0.81	0.93	0.76	0.89	0.96	0.72	0.95	0.85	0.97

% var: % variance. Acc: accumulated variance

Table 6. PCA analysis of PAHs in stormwater at SCR, SI1 and SI2 sites

	SCR			SI1			SI2	
	P1	P2	P3	P1	P2	P3	P1	P2
NAP	-0.06	0.84	-0.16	0.08	-0.52	0.46	0.15	-0.34
ACY	-0.02	0.10	-0.02	0.02	-0.08	0.05	0.02	-0.04
ACE	-0.02	0.00	0.36	0.03	-0.04	-0.02	0.02	-0.02
FLO	0.02	0.14	-0.01	0.05	-0.19	0.08	0.18	-0.52
Phen	0.02	0.44	0.33	0.27	-0.56	0.10	0.48	-0.52
ANT	0.05	0.03	0.72	0.24	0.18	0.28	0.08	-0.07
FL	0.36	-0.08	0.04	0.30	0.00	-0.04	0.23	0.01
PYR	0.45	0.09	0.21	0.55	-0.18	-0.43	0.60	0.29
BaA	0.25	-0.03	0.05	0.20	0.17	0.19	0.10	0.05
CHY	0.59	-0.09	-0.14	0.50	0.02	-0.14	0.45	0.23
BbF	0.22	0.01	-0.09	0.14	0.21	0.12	0.16	0.17
BkF	0.11	0.05	0.11	0.14	0.21	0.12	0.09	0.03
BaP	0.11	0.16	-0.29	-0.05	-0.02	-0.60	0.12	0.13
IcdP	0.33	0.11	-0.16	0.20	0.33	0.16	0.08	0.23
DahA	0.10	0.05	-0.08	0.11	0.16	0.09	0.06	0.10
BghiP	0.24	0.09	0.09	0.14	0.19	0.00	0.17	0.29
% var	0.55	0.29	0.11	0.56	0.29	0.11	0.81	0.15
Acc	0.55	0.85	0.95	0.56	0.85	0.96	0.81	0.96

% var: % variance. Acc: accumulated variance

PAHs, as well as FL, CHY and BbF, are abundant. The main source of PAHs in SR3 may be used crankcase oil. The second component accounts for 13% of the variance and is composed only of BaP, which may indicate gasoline combustion since most of the positive values are HMW PAHs. Finally, Phen and ANT are in the third component; ANT has been identified in coal combustion, coke production and wood combustion (Duval and Friendlander, 1981, Guo*et al.*, 2003, Khalili*et al.* 1995). Because none of these activities are common in SR3, the most probable source is charcoal combustion from chicken and meat grill businesses located in the basin of this site.

The first component in SR4 accounts for72% of the variance and its elements are NAP and Phen. They indicate that the main source of PAHs in this site may be diesel or crankcase oil, due to the presence of amakeshift car repair shop. The second component that contributes 23% of the variance includes FL and PYR which are indicators of vehicular emissions, specifically gasoline combustion.

The main component in SI1 is composed of FL, PYR and CHRY which contributed 56% of the variance. FL, PYR and CHRY with PHEN are predominant in diesel soot (Boonyatumanond*et al.* 2007) indicating also that diesel exhaust is the main source of PAHs. The second component which contributes with 29% is composed mainly ofIcdP with small contributions of BbF, BkF and BghiP, which are indicators of gasoline combustion and, finally, the third component contains NAP and ANT which originate probably from crankcase oil leakage. The PCA results were consistent with those obtained by diagnostic ratios.

CONCLUSION

The results show that urban storm water runoff is an important contributor of PAHs and SS to water bodies in the Tijuana area. Total Σ16 PAHs concentration ranged from 1113 to 4866 µg/Lin the sampled sites and SS concentrations ranged from 7725 to 4413 mg/L. The differencesinPAH concentrations between industrial and residential sites were not as expected.

Based on the diagnostic ratios and PCA analysis, vehicular exhaust emissions (diesel and gasoline) and used crankcase oil leakage are the predominant sources in urban storm water runoff. Charcoal combustion used in food businesses and diesel or lubricant oils are also important sources. Other sources that might be present are particles from asphalt and tire wear.

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