



## Evaluation of Car Air Filters' Efficiency as Active Samplers for Polycyclic Aromatic Hydrocarbons and Heavy Metals

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### ABSTRACT

In this study, an innovative and inexpensive approach, based on car engine air filters (CAFs), was used to monitor polycyclic aromatic hydrocarbons (PAHs) and heavy metals (HMs). CAFs were collected from two taxi garages in Guangzhou and analyzed for PAHs and heavy metals. The total concentrations of eight high molecular weight PAHs ( $\Sigma$ PAHs) ranged from 923 to 11378  $\mu\text{g}/\text{CAF}$ . The average  $\Sigma$ PAHs concentration in winter was slightly higher than in summer, a seasonal signal that is observed in most studies. The most abundant individual PAH was chrysene, followed by benzo[a]anthracene, benzo[b]fluoranthene and benzo[k]fluoranthene. Concentrations of benzo[a]pyrene (BaP) varied between 8.22 and 632  $\mu\text{g}/\text{CAF}$ . Based on estimated air volumes that pass through each CAF, atmospheric PAHs and heavy metals were estimated.  $\Sigma$ PAHs ranged from  $\sim 20$  to  $\sim 200$   $\text{ng}/\text{m}^3$  for the average air volume estimate, being comparable to those reported previously using a high volume air sampler. BaP-equivalent carcinogenic potency were between 1 and 15.0  $\text{ng}/\text{m}^3$  (again, for the average scenario). The average concentrations of heavy metals in CAFs decreased in order of  $\text{Zn} > \text{Cu} > \text{Pb} > \text{Cd}$ .

**Keywords:** Car air filter; Polycyclic aromatic hydrocarbons; Heavy metals; Benzo[a]pyrene-equivalent carcinogenic potency; Particle-bound.

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### INTRODUCTION

Urban air pollution can cause acute or chronic adverse effects on human health via exposure to both gaseous (oxides of nitrogen, oxides of sulfur, oxides of carbon etc.) and particulate pollutants (organic and inorganic). Among various particulate pollutants, heavy metals (HMs) and polycyclic aromatic hydrocarbons (PAHs) are of most concern and have been intensively studied in past decades because some of these compounds are toxic even at low concentration in the air (Vassilakos *et al.*, 2007; Vijayanand *et al.*, 2008; Yang *et al.*, 2010; Delgado-Saborit *et al.*, 2011). HMs associated with particles in urban air can penetrate in the deeper parts of lungs and catalyse the oxidative stress in

the body cells, eliciting inflammatory injuries in the airway and lungs (Nel, 2005). Inhalation of airborne trace metals can therefore have long-term effects and serious impact on human health (Massey *et al.*, 2013).

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous pollutants that are mainly derived from incomplete combustion of organic materials. Some of these compounds are highly carcinogenic and/or mutagenic, several compounds have been considered as probable and possible carcinogens to humans (IARC, 1983, 1991). Because PAHs have been frequently detected in the outdoor and indoor air of different urban area (Li *et al.*, 2006; Masih *et al.*, 2010b; Yang *et al.*, 2010; Delgado-Saborit *et al.*, 2011; DEFRA, 2012; Hung *et al.*, 2012; Katsoyiannis *et al.*, 2012; Masih *et al.*, 2012; Alkurdi *et al.*, 2013), they have been identified as an important class of toxic air pollutants in the atmosphere of urban areas. PAHs are present in both gas and particle phases influencing human health through inhalation and/or ingestion (Li *et al.*, 2006; Ma *et al.*, 2010; Masih *et al.*, 2010a; Ma *et al.*, 2011). Zhang *et al.* (2009) reported that 1.6% of the lung cancer morbidity in China was due to

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inhalation exposure to ambient air PAHs. Thus, it is very important to monitor continually the levels of PAHs in ambient air and assess these exposure rates.

As described by Katsoyiannis *et al.* (2012), atmospheric pollutants in ambient air are monitored mainly by conventional sampling methods including high volume air sampling via glass fiber filters and polyurethane foam disks using active sampling (Lee *et al.*, 2007; Shi *et al.*, 2010; Yang *et al.*, 2010; Delgado-Saborit *et al.*, 2011; Birgul *et al.*, 2012; Martellini *et al.*, 2012; Cheng *et al.*, 2013) or by passive sampling techniques (e.g., semi-permeable membrane devices, Liu *et al.*, 2006; Piccardo *et al.*, 2010). Since the sampling sites selected for these methods are stationary and limited, the air concentrations are somewhat site-specific. However, Zhang *et al.* (2011) and Katsoyiannis *et al.* (2012) suggested that car air filters (CAFs) from taxis could act as “moving” high volume air samplers and provide city integrated air concentrations with low variability for particle-bound contaminants.

CAFs are used in vehicles to filter out engine-destroying dirt and maintain engine performance. Among various air filters (i.e., cotton, foam, and paper), paper air filters are widely used because they are disposable and inexpensive. City taxis/cabs normally change CAFs every 15–20 day, circulate almost exclusively within local urban area, have access to city centers and congestion zones, therefore analyses of pollutants associated with taxi CAFs could provide scientists with results that correspond broadly to a defined area and time (Katsoyiannis *et al.*, 2012).

To try the hypothesis of the afore mentioned study and to expand it to analysis of heavy metals, the concentrations of PAHs and heavy metals in taxi CAFs of Guangzhou were investigated, and their atmospheric concentrations were estimated. The seasonal variation of PAHs and heavy metals and carcinogenic potency are also discussed.

## MATERIALS AND METHODS

### Sample Collection

A CAF is located in the front part of the vehicle and filters the air that goes into the engine protecting the latter from the air particulate matter, and maintaining the engine performance at high levels.

Guangzhou, with an area of 7434 km<sup>2</sup>, is located in southern China and belongs to the Pearl River Delta region. Guangzhou is not only one of the most densely populated areas (the population being up to 14.8 million in 2010) (Guangzhou population and family planning Bureau, 2011), but is also the economic and cultural center of South China. In Guangzhou, around 2.4 million vehicles circulate (in 2012) (<http://auto.163.com/12/0711/10/864GPKNP00084TV6.html>), and there are about 18000 taxis operating daily. Among various companies of taxis, three taxi companies own around 50% of the fleet. In this study, all CAFs sampled were from taxis carrying a 1.8 or 2.0 L engine volumes and were CAFs deployed/used for 15 to 20 days.

CAFs were collected from the official service garages of two main Taxi groups in Guangzhou. Seventeen CAFs deployed in taxis during the period 10–31 of August 2012

(presented hereafter as summer samples), and eleven CAFs deployed in taxis during the period 12<sup>th</sup> of November to 2<sup>th</sup> of December 2012 (presented hereafter as winter samples) were collected and analyzed for PAHs and HMs. Three new CAFs purchased from the official service garages were taken as the field blanks and were opened to open air for 30-min time in each garage, and then transported to the lab together with the collected-used CAFs.

### Sample Treatment and Analysis of PAHs

The extraction procedure for PAHs was a modification of the method used by Katsoyiannis *et al.* (2012). Briefly, three grams of each filter (consisting of many small pieces (<0.5 cm) from various parts of the CAF surface) were spiked with phenanthrene-d<sub>10</sub> and extracted in triplicate with a 30 mL solution of hexane/acetone (1:1) in an ultrasonic bath (KH-250E, Kunshan, China) for 30 min. The extracts were centrifuged at 3000 rpm for 5 min. The organic extracts were combined and concentrated to 1.0 mL by a rotary evaporator (52-A, Yarong, China). The extracts were cleaned-up by a combined column of silica gel and alumin (Cai *et al.*, 2007). PAHs were eluted with 50 mL of dichloromethane. This fraction was collected and concentrated in a rotary evaporator again. Finally, the extracts were transferred to a 2 mL amber glass vial and evaporated at room temperature under a gentle stream of nitrogen and rediluted to 1 mL of hexane.

PAHs in extracts were determined using Agilent 7890 gas chromatography with 5975 mass selective detector (GC-MSD) equipped with a Rtx-5MS capillary column (30 m × 0.25 mm i.d., 0.25 μm film thickness) in the electron impact mode (70 eV). The column temperature was initiated at 60°C (hold 1 min), and increased to 110°C at 35 °C/min, followed by an increase to 275°C at 8.0 °C/min, then increased to 280°C at 25.0 °C/min (hold for 10 min). Injector temperature was at 250°C, and the temperatures for both the transfer line and ion source were 250°C. The carrier gas was helium at a constant flow rate of 1 mL/min. An aliquot of 1 μL was injected in splitless mode with a solvent delay of 4 min. Mass range *m/z* 50–500 was used for quantitative determinations. Target compounds were identified based on their mass spectra and retention times.

According to the reports of Li *et al.* (2006) and Ma *et al.* (2010, 2011), more than 70% (benzo[a]anthracene) even 100% (for dibenz[a,h]anthracene and benzo[ghi]perylene) of high molecular weight PAH compounds were associated with particles. Thus, the PAHs reported in this study were mainly high molecular weight PAHs, including benzo[a]anthracene (BaA, 4-ring), chrysene (4-ring), benzo[b]fluoranthene (BbF, 5-ring), benzo[k]fluoranthene (BkF, 5-ring), benzo[a]pyrene (BaP, 5-ring), indeno[1,2,3-cd]pyrene (IcdP, 6-ring), dibenz[a,h]anthracene (DahA, 5-ring) and benzo[ghi]perylene (BghiP, 6-ring).

Method blanks (solvent), field blanks, spiked blanks (standards spiked into solvent), sample duplicates were routinely analyzed with samples. All results showed very low analytes and in most cases not detectable in the blanks. The mean recoveries for the target PAHs varied between 74.2% and 98.8%.

### CAF Treatment for Heavy Metals Analysis

The samples were treated by dry ashing method. The dry ashing procedure is a modification of Laing *et al.* (2003) and Momen *et al.* (2006). Briefly, two gram sample of CAF as well as field blacks was weighed into a porcelain crucible and heated on an electric hot plate at low temperature until carbonized (no smoke). Then, the crucible was transferred into the muffle furnace and pre-ashed at a temperature of 250°C and subsequently ashed at 500°C for 2 h. After ashing was completed (white or a semi-gray ash), the crucible was left to cool. The ash was dissolved with 2 mL 1:1 (V:V) HCl and then diluted to 25 mL with double distilled water. The concentrations of heavy metals (Cu, Zn, Pb, and Cd) in the solutions were measured with atomic absorption spectroscopy (Z-2300, Hitachi, Japan). The average recoveries of Cu, Zn, Pb and Cd ranged from 85% to 96%. In the field blacks, the concentrations of Cu, Zn, Pb and Cd in solutions were below 0.04, 0.2, 0.01, 0.003 µg/mL, respectively, being far lower than those in the used-CAF solutions.

## RESULTS AND DISCUSSION

### Occurrence of PAHs in CAFs

Table 1 presents the descriptive statistics of PAH concentrations in CAFs, expressed as µg/CAF. All eight individual PAHs were detected and their total concentrations ( $\Sigma_{\text{PAHs}}$ ) ranged from 923 to 11378 µg/CAF. The most abundant individual PAH was Chr, followed by BaA, BbF and BkF. It can be seen that on average, the concentrations of PAHs are lower as the number of rings increases. It is very interesting to note the range of concentrations of individual PAHs, which spans few orders of magnitude for all PAHs, an interesting result taking into account all the uncertainty associated with this sampling method. The study of Katsoyiannis *et al.* (2012) observed ranges of one order of magnitude for 10 CAFs analyzed for a city (Manchester, UK) that is much smaller than Guangzhou. The comparison between the two studies is given in Fig. 1 (where Chr is excluded because it was not reported in the latter study). It is interesting to note that while the average  $\Sigma_{\text{PAHs}}$  and BaP are similar, the profile for the other PAHs is totally different. Manchester is an urban area with reduced

industrial activities (compared to some decades ago), while Guangzhou still have a lot of industrial activities and is also affected by regional pollution of the Pearl River Delta region. Yet, we see that the  $\Sigma_{\text{PAHs}}$  concentrations in CAFs are identical. This is likely evidence that the emissions from vehicles are those that mostly affect the PAHs fingerprint in CAFs.

Concerning the seasonal variation, the average  $\Sigma_{\text{PAHs}}$  concentrations were just slightly higher in winter (4379 µg/CAF against 4049 µg/CAF during summer) (Table 1). This difference is not considered significant and probably confirms that the PAHs occurring at street level are mainly emitted by vehicles, a process that is happening at the same extent at all periods throughout the year. The temperature difference between summer (ranging from 24 to 37°C) and winter (ranging from 7 to 26°C) (Fig. 2) is probably not affecting neither the concentration of PAHs at street level, nor the fate of PAHs on the CAF, once sampled. Additionally, the PM<sub>10</sub> concentrations (varying between 11–89 µg/m<sup>3</sup>) in both summer and winter were quite similar (Fig. 3). Seasonality of particle-bound PAHs concentrations in Guangzhou has been reported by other researchers (Li *et al.*, 2006; Tan *et al.*, 2006; Duan *et al.*, 2007; Yang *et al.*, 2010). The seasonality of PAHs is a fact seen also in most studies worldwide (e.g., Katsoyiannis *et al.*, 2011) but the aforementioned groups also pointed out that the seasonal variation can be affected by meteorological conditions such as atmospheric temperature, wind, storm, humidity.

Regarding the individual PAHs, some are significantly higher in summer (Fig. 4). The PAH that exhibits much higher concentrations during winter is Chr with average of 2633 µg/CAF, against 2218 µg/CAF in summer.

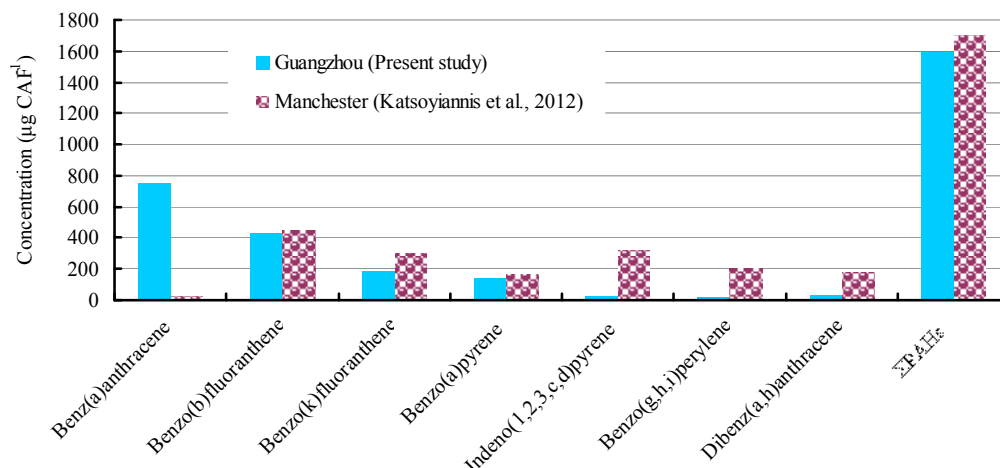
### Atmospheric PAH Levels Estimated Based on CAF Concentrations

Following the method of Katsoyiannis *et al.* (2012), PAH atmospheric concentrations can be derived through the CAF-PAH concentrations (Table 1) and the air flow. As mentioned above, CAF filters the air that goes into the engine. Thus, the air flow during the engine's operation can be calculated by Eq. (1) (Pope, 2009):

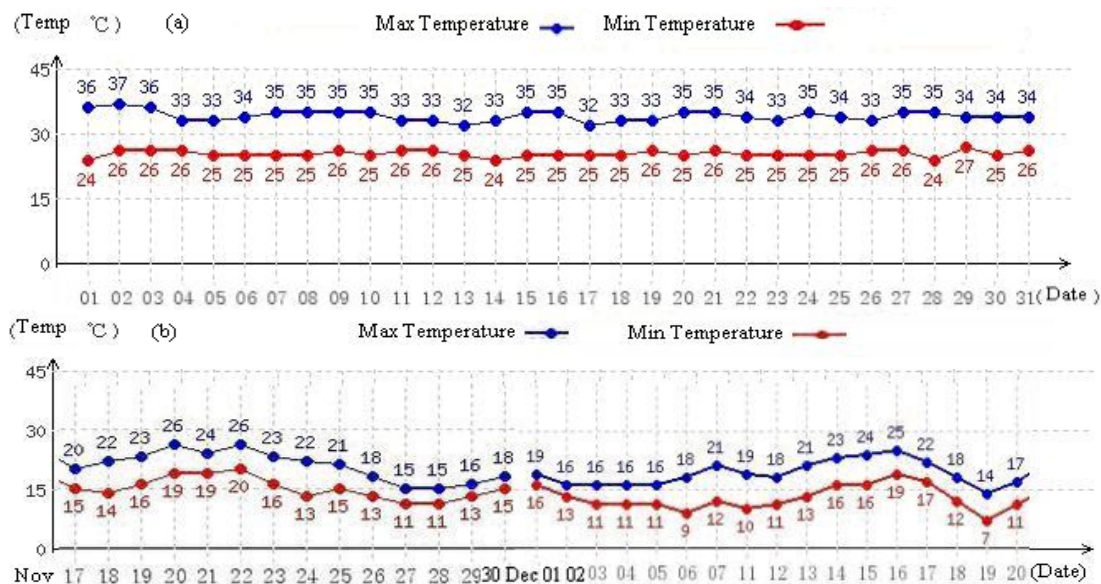
$$\text{CFM} = (\text{CID} \times \text{RPM} \times \text{VE})/3456 \quad (1)$$

**Table 1.** PAH Concentration in each CAF (µg/CAF).

	BaA	Chr	BbF	BkF	BaP	DahA	InP	BghiP	$\Sigma_{\text{PAHs}}$	$\Sigma_{\text{PAHscarce}}$
Summer (n = 15)										
Min	84.4	592	22.3	17.7	8.22	6.86	5.2	4.65	923	916
Max	2358	5463	2380	1289	632	190	33.0	43.2	9262	9239
Median	520	1491	453	184	31.1	19.1	16.5	10.5	3202	3191
Mean	735	2218	585	276	159	45.4	16.5	14.0	4379	4359
STD	727	1681	573	328	231	50.7	7.6	10.9	2963	2948
Winter (n = 11)										
Min	112	614	86.8	13.6	8.99	3.36	9.19	1.98	1319	1314
Max	3421	6363	870	296	336	99.8	114	77.1	11378	11370
Median	596	1900	230	134	78.3	33.9	42.3	9.56	2685	2656
Mean	1057	2633	323	142	116	39.0	49.4	19.7	4049	4035
STD	1118	1932	240	105	109	34.1	38.1	23.8	3057	3059



**Fig. 1.** Comparison of average PAH concentrations in taxi CAFs from Guangzhou (present study) and CAFs from Manchester (Katsoyiannis *et al.*, 2012).



**Fig. 2.** Temperature range during CAFs located in circulating engine (a) summer; (b) winter (<http://lishi.tianqi.com/guangzhou/index.html>)

where, CFM (cubic feet per minute) is the engine's air flow rate ( $\text{ft}^3/\text{min}$ ), RPM (revolutions per minute) is the engine speed ( $\text{rpm}/\text{min}$ ), VE is the volumetric efficiency (for unmodified engines is about 85%), and CID (cubic inch displacement) refers to the engine volume ( $\text{in}^3$ ). In China, the vehicle exhaust is generally expressed using liter (L) (1 liter = 61.02 cubic inches). In this study, the engine volumes of taxis were 1.8 L and 2.0 L (Table 2), respectively.

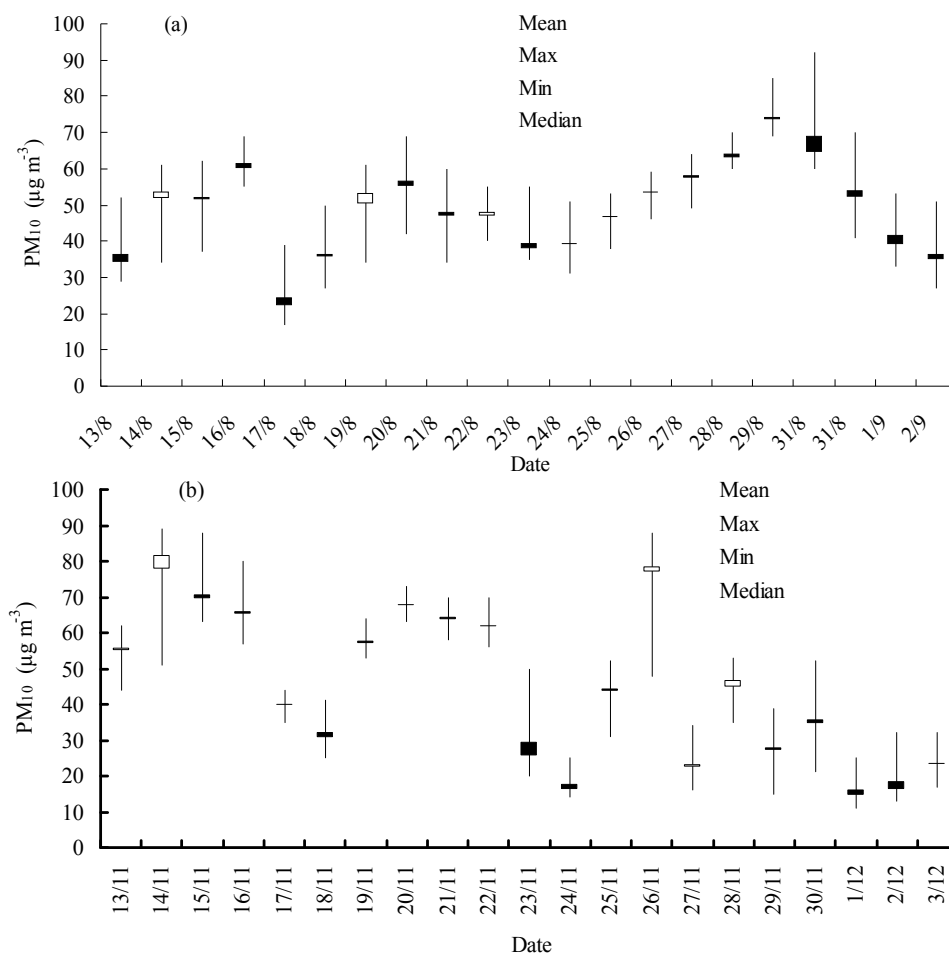
If VE and CID of Eq. (1) are constant (for a specific taxi-type), then the only parameter that results in uncertainty is the engine speed (RPM). As described by Katsoyiannis *et al.* (2012), the engine speed of taxis would generally range from 1500 to 3000 rpm when it cruises normally. In Guangzhou, according to the information from the taxis driver/garage experts, taxis circulate daily for 19 to 22 h (two shifts), and the CAF is changed normally every 15–20 days (Table 2).

In this study, we assumed four different driving scenarios

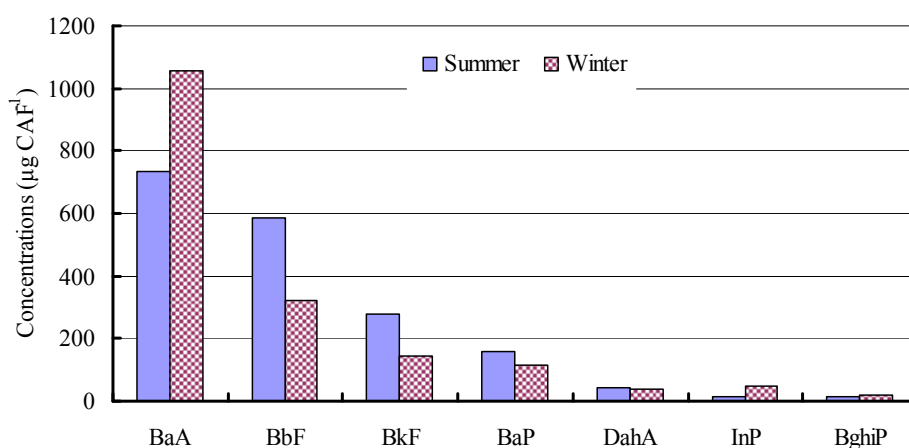
(Table 2) for the estimation of the total air volume passed through a CAF. Following these scenarios and Eq. (1), the air volume that passes through a CAF varies from 20763 to 71233  $\text{m}^3$ , with the average/conservative scenario being 44794  $\text{m}^3$  (Table 2).

Using the two extreme and the average scenarios, the atmospheric PAH concentrations were estimated and are presented in Table 3. For the most conservative scenario (71233  $\text{m}^3$  of air)  $\Sigma_{\text{PAHs}}$  varied between 18.52 and 159.72  $\text{ng}/\text{m}^3$  (in summer) with an average of 56.84  $\text{ng}/\text{m}^3$ . During winter,  $\Sigma_{\text{PAHs}}$  varied between 12.96 and 130.02  $\text{ng}/\text{m}^3$  (in summer) with an average of 61.47  $\text{ng}/\text{m}^3$ .

The  $\Sigma_{\text{PAHs}}$  concentrations estimated based on CAF analysis are comparable to those reported for Guangzhou in air particles (Li *et al.*, 2006; Tan *et al.*, 2006; Duan *et al.*, 2007; Yang *et al.*, 2010) or  $\text{PM}_{2.5}$ -bound PAHs (Gao *et al.*, 2011, 2012). In the Manchester study the PAH levels



**Fig. 3.** PM<sub>10</sub> Concentrations in Guangzhou during CAFs located in circulating engine (a) summer; (b) winter (Data from Guangzhou Environment Protection, Monitoring daily at 10 sites; <http://www.gzepb.gov.cn/comm/apidate.asp>)



**Fig. 4.** Average concentrations of individual PAHs in CAFs during summer ( $n = 15$ ) and during winter ( $n = 11$ ).

estimated through CAFs were many times higher than the concentrations measured by means of Hi-Volume air sampling (filter and polyurethane foam). The use of CAFs gives us an estimate of the PAH concentrations at road level, inside the traffic, therefore it offers insight about the exposure that people who spend big parts of their daily lives in the traffic undergo.

Regarding individual PAHs (Table 3), their estimated average concentrations for the conservative scenario were 23.63 ng/m<sup>3</sup> for Chr, 6.87 for BaA, 6.18 ng/m<sup>3</sup> for BbF, 2.57 ng/m<sup>3</sup> for BkF and 1.45 ng/m<sup>3</sup> for BaP. Especially for BaP, the range of estimated air concentrations was from 0.12 to 8.87 ng/m<sup>3</sup> and in most cases the level of BaP was well below 1.0 ng/m<sup>3</sup>. The latter value is mentioned here,

**Table 2.** Uptake air calculations.

	Vehicle exhaust (L) <sup>a</sup>	RPM (min <sup>-1</sup> )	CFM <sup>b</sup> (ft <sup>3</sup> /min)	Daily operation (h)	Time between CAF change (day)	Total air volume (m <sup>3</sup> )
Scenario 1	1.8	1500	54.02	19	15	20763
Scenario 2	1.8	3000	81.04	22	20	64110
Scenario 3	2.0	1500	60.03	19	15	23070
Scenario 4	2.0	3000	90.05	22	20	71233
Average						44794

**Table 3.** CAF-estimated concentrations (ng/m<sup>3</sup>) of PAHs in ambient air.

Summer PAHs-Air Volume (m <sup>3</sup> )										
	BaA	Chr	BbF	BkF	BaP	DahA	InP	BghiP	ΣPAH	ΣPAH <sub>score</sub>
20763										
Min	4.06	28.50	1.07	0.85	0.40	0.33	0.25	0.22	63.52	63.30
Max	113.54	263.10	114.62	62.06	30.44	9.13	1.59	2.08	547.98	547.60
Median	25.03	71.80	21.82	8.88	1.50	0.92	0.79	0.50	129.32	127.93
Mean	35.41	106.85	28.16	13.29	7.65	2.19	0.79	0.68	195.01	194.33
STD	35.03	80.97	27.60	15.81	11.11	2.44	0.37	0.52	147.24	147.35
44794										
Min	1.88	13.21	0.50	0.40	0.18	0.15	0.12	0.10	29.44	29.34
Max	52.63	121.95	53.13	28.77	14.11	4.23	0.74	0.96	254.00	253.82
Median	11.60	33.28	10.11	4.11	0.69	0.43	0.37	0.23	59.94	59.30
Mean	16.41	49.53	13.05	6.16	3.54	1.01	0.37	0.31	90.39	90.08
STD	16.24	37.53	12.79	7.33	5.15	1.13	0.17	0.24	68.25	68.30
71233										
Min	1.18	8.31	0.31	0.25	0.12	0.10	0.07	0.07	18.52	18.45
Max	33.10	76.69	33.41	18.09	8.87	2.66	0.46	0.61	159.72	159.61
Median	7.30	20.93	6.36	2.59	0.44	0.27	0.23	0.15	37.69	37.29
Mean	10.32	31.14	8.21	3.87	2.23	0.64	0.23	0.20	56.84	56.64
STD	10.21	23.60	8.04	4.61	3.24	0.71	0.11	0.15	42.92	42.95
Winter PAHs-Air Volume (m <sup>3</sup> )										
	BaA	Chr	BbF	BkF	BaP	DahA	InP	BghiP	ΣPAH	ΣPAH <sub>score</sub>
20763										
Min	5.42	29.59	4.18	0.65	0.43	0.16	0.44	0.10	44.45	44.12
Max	164.77	306.47	41.90	14.25	16.18	4.81	5.51	3.71	446.07	445.00
Median	28.71	91.54	11.07	6.45	3.77	1.63	2.04	0.46	154.20	153.68
Mean	50.92	126.83	15.55	6.84	5.57	1.88	2.38	0.95	210.90	209.95
STD	53.82	93.06	11.54	5.08	5.24	1.64	1.84	1.14	142.71	141.99
44794										
Min	2.51	13.71	1.94	0.30	0.20	0.07	0.21	0.04	20.61	20.45
Max	76.38	142.06	19.42	6.61	7.50	2.23	2.55	1.72	206.76	206.27
Median	13.31	42.43	5.13	2.99	1.75	0.76	0.94	0.21	71.48	71.23
Mean	23.60	58.79	7.21	3.17	2.58	0.87	1.10	0.44	97.75	97.32
STD	24.95	43.13	5.35	2.35	2.43	0.76	0.85	0.53	66.15	65.82
71233										
Min	1.58	8.62	1.22	0.19	0.13	0.05	0.13	0.03	12.96	12.86
Max	48.03	89.33	12.21	4.16	4.72	1.40	1.61	1.08	130.02	129.71
Median	8.37	26.68	3.23	1.88	1.10	0.48	0.59	0.13	44.95	44.79
Mean	14.84	36.97	4.53	1.99	1.62	0.55	0.69	0.28	61.47	61.20
STD	15.69	27.12	3.36	1.48	1.53	0.48	0.54	0.33	41.60	41.39

as this is the level set by the European Commission at the Directive 2004/107/EC (EC, 2004). BaP is used as a biomarker for PAHs and is also among the most carcinogenic PAHs.

#### Carcinogenic Potency of PAHs

Among 16 PAH compounds listed as priority pollutants by USEPA, seven compounds, namely BaA, BbF, BkF,

BjF, BaP, InP, and DahA, are considered to have carcinogenic effects. In order to estimate the carcinogenic potencies of PAHs, scientists have used BaP-equivalent carcinogenic power (BaP<sub>eq</sub>) as an index for better assessing aerosol carcinogenicity of PAHs (Gao *et al.*, 2011; Martellini *et al.* 2012). The BaP<sub>eq</sub> can be calculated by multiplying its concentration with the corresponding toxic equivalent

factor (TEF) (Yassaa *et al.*, 2001) as the following Eq. (2):

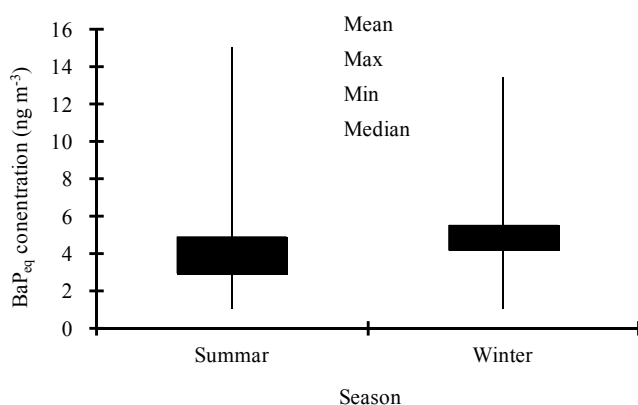
$$\text{BaP}_{\text{eq}} = (\text{BaA} \times 0.06) + (\text{BbF} \times 0.07) + (\text{BkF} \times 0.07) + \text{BaP} + (\text{DahA} \times 0.6) + (\text{InP} \times 0.08) \quad (2)$$

In this study, the  $\text{BaP}_{\text{eq}}$  was calculated and found to range from 1.06 to 15  $\text{ng}/\text{m}^3$  (average of 4.9 and 5.5  $\text{ng}/\text{m}^3$  in summer and winter, respectively, Fig. 5). The average levels are comparable to those from two urban areas of South Italy (Bari and Taranto) (Amodio *et al.*, 2009) and in three major cities of India (Kolkata, Mumbai and Chennai) (Cheng *et al.*, 2013), but higher than the mean concentrations of  $\text{BaP}_{\text{eq}}$  (1.93  $\text{ng}/\text{m}^3$ ) in  $\text{PM}_{2.5}$  of Guangzhou (Gao *et al.*, 2011). In this study, BaA, BaP and DahA made the largest contribution to  $\text{BaP}_{\text{eq}}$ .

### Concentrations of Heavy Metals

Four metal elements were analyzed in this study and their concentrations in CAFs and CAF-estimated air concentrations ( $\text{ng}/\text{m}^3$ ) are presented in Table 4. The order of average concentrations of heavy metals in both CAF and air was  $\text{Zn} > \text{Cu} > \text{Pb} > \text{Cd}$ , being consistent with that in the ambient air of the Coimbatore city, Tamilnadu, India (Vijayanand *et al.*, 2008). Zn concentrations in CAFs ranged from 4557 to 35849  $\mu\text{g}/\text{CAF}$  and the average concentration is up to 4621  $\mu\text{g}/\text{CAF}$ , while those of Cd varied between 27.8 and 117  $\mu\text{g}/\text{CAF}$  with a mean of 63.2  $\mu\text{g}/\text{CAF}$ .

The estimated atmospheric concentrations of HMs (Table 3) (again for the conservative scenario, that is volume of 71233  $\text{m}^3$ ) ranged from 24.3 to 219  $\text{ng}/\text{m}^3$  for Cu, from 64 to 503.3  $\text{ng}/\text{m}^3$  for Zn, and from 12.4 to 85.8  $\text{ng}/\text{m}^3$  for Pb, thus being comparable to those in TSP of Guangzhou and Hong Kong (Cu: 30.8–82.3  $\text{ng}/\text{m}^3$ ; Zn: 241–1190  $\text{ng}/\text{m}^3$ ; Pb: 53.5–269  $\text{ng}/\text{m}^3$ ; Cd: 1.61–7.85  $\text{ng}/\text{m}^3$ ) (Lee *et al.*, 2007), Beijing (Okuda *et al.*, 2004), and in airborne particulate matter of Ulsan, Korea (Lee and Park, 2010). The concentrations of Cd ranged from 0.4 to 1.6  $\text{ng}/\text{m}^3$  being again in line with concentrations found in Hong Kong (Lee *et al.*, 2007) and airborne particulate matter in Ulsan, Korea (Lee and Park, 2010), but lower than the values in Guangzhou (Lee *et al.*, 2007) and ambient air in Washington, DC (Melaku *et al.*, 2008).



**Fig. 5.** Seasonal variation of  $\text{BaP}_{\text{eq}}$  calculated based on CAF-derived PAH air concentrations

**Table 4.** HM concentrations in CAFs ( $\mu\text{g}/\text{CAF}$ ) and air estimates ( $\text{ng}/\text{m}^3$ ) for the conservative scenario.

		Summer	Winter	Summer	Winter
		$\mu\text{g}/\text{CAF}$		$\text{ng}/\text{m}^3$	
Cu	Min	1730	1907	24.3	26.8
	Max	15602	9893	219.0	138.9
	Median	5744	3686	80.6	51.7
	Mean	6685	4086	93.8	57.4
	STD	3670	2269	51.5	31.9
Zn	Min	4557	4685	64.0	65.8
	Max	28797	35849	404.3	503.3
	Median	16639	8709	233.6	122.3
	Mean	16668	11565	234.0	162.4
	STD	7605	8702	106.8	122.2
Pb	Min	880	960	12.4	13.5
	Max	5868	6111	82.4	85.8
	Median	3448	1761	48.4	24.7
	Mean	3246	2310	45.6	32.4
	STD	1390	1454	19.5	20.4
Cd	Min	27.8	27.8	0.4	0.4
	Max	112	117	1.6	1.6
	Median	72.8	45.0	1.0	0.6
	Mean	72.6	53.8	1.0	0.8
	STD	25.9	25.0	0.4	0.4

The average concentrations of Cd, Cu, Pb, and Zn in summer are higher by 30% or more than those in winter (Table 3). Contradictory results can be found in literature, regarding the seasonality of HMs in ambient air. Results from Washington, USA (Melaku *et al.*, 2008) reported a seasonal signal, but studies from Guangzhou and Hong Kong, China showed the opposite (Lee *et al.*, 2007). Seasonality of HMs in the ambient air needs to be further studied, nevertheless this goes beyond the scope of this short communication.

### CONCLUSIONS

This study aimed at evaluating the applicability of CAFs as sampling media for monitoring both PAHs and HMs. As shown, both PAHs and HMs were detected in CAFs collected from two Taxi garages in Guangzhou. Based on CAF analysis, the concentrations of PAHs and HMs were estimated. The concentrations measured in Guangzhou both for PAHs and HMs were in good agreement with the levels measured via high volume air sampling. The average concentrations of  $\Sigma_{\text{PAHs}}$  and some individual PAH in summer were very close to those in winter, but those of heavy metals (Cu, Zn, Pb and Cd) in summer were higher than in winter.

The results suggest that CAFs can provide city integrated air concentrations for particle-bound pollutants. This methodology is new and a lot of improvement can be achieved. With reasonably low funding, a targeted study could address issues like a) accurate air volume measurement; b) combination of navigation technology with chemical analysis results something that offer more insight, not only about the sites where the vehicle had circulated, but also at which areas the speed was higher, in order to understand where most of the air was collected; c) complete chemical analysis which

would reveal the chemicals, or classes of chemicals that can be sampled and efficiently trapped to CAFs.

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