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Car Engines Air Filters. A Useful Ambient Air Sampler and/or a Possible Hazardous Waste?

Athanasios Katsoyiannis[*]

Norwegian Institute for Air Research (NILU). FRAM – High North Research Centre for Climate and the Environment, Hjalmar Johanssens gt 14, NO-9296 Tromsø, Norway

ABSTRACT

Car-engine air filters (CAFs) have been recently used as inexpensive alternative air sampling media for hydrophobic organic compounds such as polycyclic aromatic hydrocarbons, polychlorinated dibenzo-*p*-dioxins and furans and also for heavy metals. This "active-passive" sampling methodology is a promising way for urban air monitoring, being able to offer invaluable advantages. Two approaches have been proposed for the estimation of the air volume that passes through the CAFs and are herein reviewed and compared.

Chemical analysis of CAFs shows that after their use in vehicles, they have accumulated a considerable amount of toxic chemicals which render CAFs as potentially hazardous materials. The CAF chemical loads are presented and evaluated and the need to characterize CAFs as special waste is discussed.

Keywords: CAFs; Hazardous waste; PAHs; PCDD/Fs; HMs.

INTRODUCTION – BACKGROUND

To date, one of the most acknowledged environmental problems is caused by the emissions from vehicles, industrial establishments, domestic heating facilities etc. The particulate matter that is emitted from the above sources, stays dispersed in the environment can have negative effects in humans and the environment. To remove particles, air filters have been introduced in a variety of applications, like in ventilation systems or in motor engines. For the latter, pleated paper filters (Fig. 1) are used to prevent airborne particles from entering the engine, a process that is essential for maintaining the engine's performance at high levels. Recently, two studies, in Beijing, China (Zhang *et al.*, 2011) and in Manchester, UK, (Katsoyiannis *et al.*, 2012) independently from each other, collected car air filters (CAFs) and exploited them as urban air pollution samplers. More recently, Cai *et al.* (2014) repeated the analytical procedure of the work by Katsoyiannis *et al.* (2012) in CAFs from Guangzhou, China. In these three studies, concentrations of polycyclic aromatic hydrocarbons (PAHs), polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs) and some heavy metals are reported. According to the authors of the afore-mentioned papers, this methodology has a great potential and can offer various solutions to environmental scientists. The present short communication summarizes the published studies and presents further considerations and possibilities. It aims at promoting further the idea of using CAFs as atmospheric air monitors, and at seeking further validation of CAFs, mainly by research groups who are routinely active on urban air monitoring campaigns and can therefore offer detailed comparisons between CAFs and stationary sampling media. Furthermore, and taking into account that air filtering is a way of removing particles from air, it can be reasonably expected that all kinds of organic and inorganic particle-bound chemicals will also stay trapped on CAFs. This suggests that CAFs are a carrier of considerable amounts of

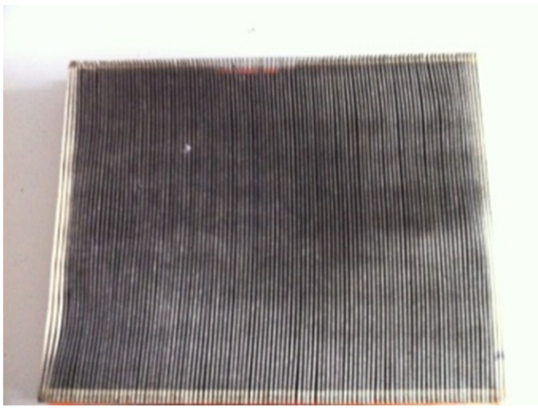

Fig. 1. A used car air filter (photo taken by Athanasios Katsoyiannis).

[*] Corresponding author.
Tel.: +47 77750386; Fax: +47 77750376
E-mail address: aak@nilu.no

toxic pollutants and to this direction, the present viewpoint would also aim at raising concern about how CAFs should be treated after their use in vehicles.

CURRENT KNOWLEDGE

Zhang *et al.* (2011), Katsoyiannis *et al.* (2012) and Cai *et al.* (2014) used CAFs to analyze polychlorinated dibenzo-*p*-dioxins/furans (PCDD/Fs), polycyclic aromatic hydrocarbons (PAHs) and Cu, Zn, Pb and Cd, respectively and then compared with air concentrations from conventional static air sampling and concluded that the analysis of CAFs can be a very useful "active air sampler" for airborne chemicals that tend to bind on particles. Three main problems/challenges were associated with the exploitation of CAFs as air samplers.

1) How can the "sampled" air volume be measured?
2) Which geographical area could be linked to the pollutants analyzed on CAFs?
3) Will the captured/sampled particles and chemicals bound on particles stay trapped on the CAF until the analysis time? Will there be any desorption, volatilization, degradation, especially if the high temperatures occurring in the engine's area are borne in mind?

Zhang *et al.* (2011) and Katsoyiannis *et al.* (2012) used two different approaches for the air volume estimation. Zhang *et al.* (2011) proposed a method which estimates the air volume based on the carburant consumption (Eq. (1)), while Katsoyiannis *et al.* (2012) used a standard engineering equation (Eq. (2)), which is directly proportional to the vehicle's speed.

$$V_{\mathrm{air}} = (14.7 \times \rho_{\mathrm{petro}} \times V_{\mathrm{petro}} \times s)/\rho_{\mathrm{air}} \quad (1)$$

where, V_{air} is the air volume passing through the CAF (L), ρ_{petro} is the density of fuel (g/L), V_{petro} is the petroleum consumption per kilometer (L), s is the driving distance (km) and ρ_{air} is the air density (g/L).

$$\mathrm{CFM} = (\mathrm{CID} \times \mathrm{RPM} \times \mathrm{VE})/3456 \quad (2)$$

where, CFM is the engine's air flow rate (cubic feet per minute, cf/m), CID is the cubic inch displacement, RPM is the engine speed (revolutions per minute, min^{-1}) and VE is the volumetric efficiency (for unmodified engines is about 90%) and 3456 is a conversion factor from cubic inches to cubic feet.

To evaluate the two methods, the air volume passing through the CAFs at the Zhang *et al.* (2011) study, was recalculated using the method of Katsoyiannis *et al.* (2012). It was found that the air volume estimation comparisons produced relatively similar results; 445 m^3 (1) vs. 405/607/809 m^3 (if the vehicles' speed of 60 km/h corresponds to a speed of 1000/1500/2000 rpm, respectively), therefore a quite satisfactory agreement, taking into account all the associated uncertainty. It should also be noted that Zhang *et al.* (2011) used for their calculations the air density value at 0°C (1.293 g/L), though probably the correct value should be somewhat smaller (e.g., 1.184 g/L at 25°C).

To address the second challenge, Katsoyiannis *et al.* (2012) suggested that if the CAFs are collected from taxis/cabs, the results will be a time weighted, average sample for an entire city, while Zhang *et al.* (2011) used defined itineraries, thus directly linked to a specific area. Potentially, the existing satellite navigation technology can also offer the necessary assistance in registering the itineraries of the vehicles, whose CAFs are used for chemical analysis.

Finally, to assess the third question, or the retaining of pollutants on CAFs, Katsoyiannis *et al.* (2012) plotted the subcooled liquid pressure of the chemicals of interest with temperature and suggested that hydrophobic compounds will probably be trapped effectively. They also mentioned that temperature at the CAF deployment area is likely not increasing to very high levels, because this would result in melting of the plastic lid, or of the plastic/rubber surfaces of the CAF. Zhang *et al.* (2011) went one step further and spiked CAFs prior to their deployment with labeled standards. Labeled compounds acted as performance reference compounds and it was found that for short-term usages of CAFs, the recovery rates varied between 63–90%, thus in unexpectedly high levels.

FURTHER CONSIDERATIONS

Authors of the three published studies mention that perceiving vehicles as a "moving hi-vol sampler" and CAFs as the sampling medium for airborne particles can be a good alternative, particularly for monitoring of street-level air, thus, air that road-related populations are exposed to (drivers – through open windows/roofs, or at cars without pollen filters –, pedestrians, cyclists and riders, workers, traffic policemen etc.). Due to the proximity to various sources (e.g., automotive exhausts), it is expected that measured concentrations will be higher than those measured by means of static samplers placed on building roofs; however the CAF results might be more representative, especially for exposure assessment purposes.

Using CAFs as air samplers is a low-cost option (actually the sampling cost is inexistent) offering also unlimited availability, as hundreds of vehicles (taxis) circulate at all cities. Analysis of a reasonable number of CAFs used at the same period will be a safe way to report average urban air levels for a variety of chemicals. By looking at the samples of Katsoyiannis *et al.* (2012) (n = 10) and after removing the high and low outliers, one can see that ΣPAHs ranged between 21.2 and 50.3 $\mathrm{ng/m}^3$ (median of 30.2 $\mathrm{ng/m}^3$), thus a very low variation. Surely, this constitutes also a disadvantage of CAFs. That only "area-specific average concentrations" can be measured. Never the less, CAFs can be the ideal medium for a big number of pollutants, due to the variety of chemicals that bind on particulate matter (PM). Almost all important hydrophobic organic compounds have been detected on atmospheric PM; polycyclic aromatic hydrocarbons (PAHs, Cincinelli *et al.*, 2007; Castro-Jimenez *et al.*, 2012; Martellini *et al.*, 2012), persistent organic pollutants (POPs), including polychlorinated biphenyls (PCBs) and polychlorinated dibenzo-*p*-dioxins/furans (PCDD/Fs, Kouimtzis *et al.*, 2002; Katsoyiannis *et al.*, 2010), polybrominated diphenylethers (Wang *et al.*, 2010; Ni *et al.*, 2011; Birgul *et al.*, 2012; Lin *et al.*, 2012; Besis *et al.*, 2014; Cincinelli *et al.*, 2014), organochlorine pesticides (Wang *et al.*, 2008), aliphatic hydrocarbons (Cincinelli *et al.*, 2004, Schnelle-Kreis, 2005; Wang *et al.*, 2013), levoglucosan (Giannoni *et al.*, 2012) as well as almost all important inorganic contaminants (like heavy metals, Pb, Cd, Ni, Cr, V, Mn, Cu and Fe, Samara and Voutsa, 2005; Berg *et al.*, 2008). Many of these chemicals are associated with carcinogenicity, and some of them (Benzo[a]pyrene (BaP), As, Cd, Hg, Ni) are regulated within the European Union by the Council Directive 2004/107/EC.

Katsoyiannis *et al.* (2012) mentioned that CAFs can also be used for retrospective monitoring; for example, after an environmental episode has taken place at a site where active monitoring is not taking place. Numerous times has happened that after a big industrial fire (for example) scientists are trying to quantify the environmental impact for chemicals like dioxins, PCBs or PAHs, but in absence of previous monitoring efforts, such attempts are not feasible. CAFs can be an invaluable tool for such cases, at least for "reconnaissance" type sampling. The short periods over which CAFs are used in utility vehicles (like taxis, or buses, tracks etc.) make them a better tool than "natural passive samplers", like for example pine needles or grass (Hassanin *et al.*, 2005; Ratola *et al.*, 2006). In addition, due to the facts that: 1) taxis/cabs circulate almost exclusively to city centres and even to congestion zones, and: 2) exist to every small town or big city, this approach can be considered as almost globally applicable. If one looks at a nocturne satellite picture of Europe (for example, Fig. 2), one can see that all dense lightings correspond to smaller or bigger cities and at any moment, alternative air sampling through CAFs is taking place.

Another consideration generated after seeing the first results of CAF analyses, is that used CAFs may contain a considerable amount of toxic substances. Zhang *et al.* (2011) measured hundreds of pg of dioxins and furans at each exposed CAF and Katsoyiannis *et al.* (2012) reported an average of 1700 µg/CAF for the heavier PAHs. Cai *et al.* (2014) reported an average of 4170 µg/CAF of PAHs (again, only the heavier PAHs were reported) and also 63.2, 2778, 5385 and 14116 µg/CAF, of Cd, Pb, Cu and Zn, respectively. It is reasonably anticipated that CAFs are capturing also all other classes of the afore-mentioned chemicals, that tend to bind on PM. This trapping and accumulation of organic chemicals is something that should be taken into consideration by environmental agencies and/or local authorities, because CAFs, at the end of their deployment lifetime constitute a type of a "special waste" which should not be disposed of carelessly, as it is happening so far. Treatment of CAFs as normal waste, suggests that in the end of their use, the persistent chemicals that have been accumulated on their surfaces are returning to the environment. A fast estimation of the amount of chemicals that are returning to the environment, as a result of the improper disposal of CAFs, results in hundreds of kilos of toxic chemicals. Just in the UK alone, according to an English website (Waymarking.com, 2009), there are 52000 taxis. If we assume that every taxi changes the CAF at least every month and every CAF collects on average 1700 µg of heavier PAHs, (the amount of PAHs detected by Katsoyiannis *et al.*, 2012), this suggests that 1.5 kilos of heavier PAHs are accumulated in the taxi/cabs CAFs alone. Taking into account all other vehicles, trucks, busses etc., and applying this calculation globally, it is easy to understand the significance of disposing of and treating CAFs responsibly.

Fig. 2. A nocturne satellite photograph of Europe. Dense lights correspond to populated areas, thus areas where CAFs are readily available. (Taken from the website: http://www.savethenight.eu/Lights%20in%20Europe.html, who in turn copied it from Light Pollution Science and Tecnology Institute (ISTIL) with the following credit/copyright statement: Credit: P. Cinzano (University of Padova and ISTIL), F. Falchi (University of Padova), C. D. Elvidge (NOAA National Geophysical Data Center, Boulder). Copyright 2001 ISTIL, Thiene)

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