Scientific Research Publishing

Journal of Environmental Protection, 2016, 7, 1561-1570
http://www.scirp.org/journal/jep
ISSN Online: 2152-2219
ISSN Print: 2152-2197

Assessment of Organic Compounds as Vehicular Emission Tracers in the Aburrá Valley Region of Colombia

Enrique Posada[1], Miryam Gómez[2], Viviana Monsalve[1]

[1]INDISA, Group of Process, Energy and Environmental Studies, Medellín, Colombia
[2]Politécnico Colombiano Jaime Isaza Cadavid, Group GHYGAM, Medellín, Colombia
Email: enrique.posada@indisa.com

How to cite this paper: Posada, E., Gómez, M. and Monsalve, V. (2016) Assessment of Organic Compounds as Vehicular Emission Tracers in the Aburrá Valley Region of Colombia. *Journal of Environmental Protection*, **7**, 1561-1570.
http://dx.doi.org/10.4236/jep.2016.711129

Received: August 16, 2016
Accepted: October 24, 2016
Published: October 27, 2016

Abstract

The Aburrá Valley region in Colombia, with Medellín as its main city, is an urban centre with about three million people. An investigation was carried out to determine a set of baseline concentrations for VOC compounds associated with diesel fuel and gasoline, as vehicular emission tracers in the region. The VOC measurement campaigns, based on TENAX tube sampling and analysis according to TO-17 EPA method, were done in areas of low and high vehicular flow as well as on-board measurements covering major Medellín road networks during 24 hours. The results showed that there was a relation between VOCs concentrations and vehicular activity. The diesel fuel sulfur content was also found as an important factor on VOC hydrocarbon formation.

Keywords

VOCs, Vehicular Pollution Tracers, Vehicular Emissions, Urban Pollution, Rural Pollution

1. Introduction

VOCs tend to be polluting considering both their inhalation and contact effects and as a source of secondary pollutants. For the present study, they were classified into two (2) groups: poly-nuclear aromatic hydrocarbons (PAHs) and aliphatic hydrocarbons (AH). Table 1 shows the list of VOCs studied and some basic characteristics.

The studied VOCs behave differently, following the two main types (alkanes [AH], and PAH) and this has to do with their molecular weight, as shown in the behavior of their vapor pressure and boiling point, properties that have to do with their presence in the atmosphere (Figure 1 and Figure 2).

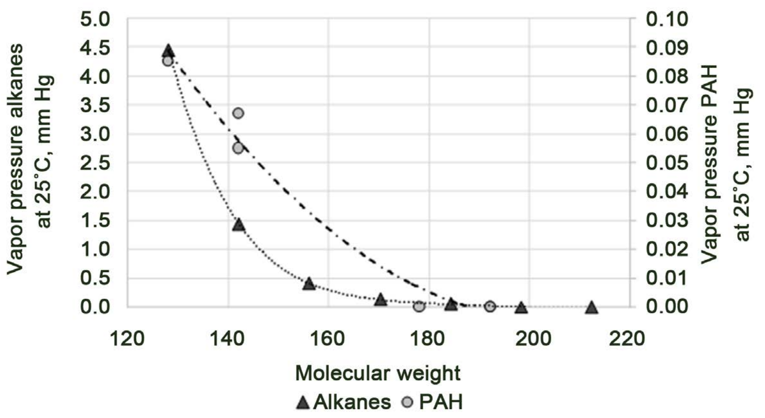

Figure 1. VOCs studied and their vapour pressures as related to molecular weight.

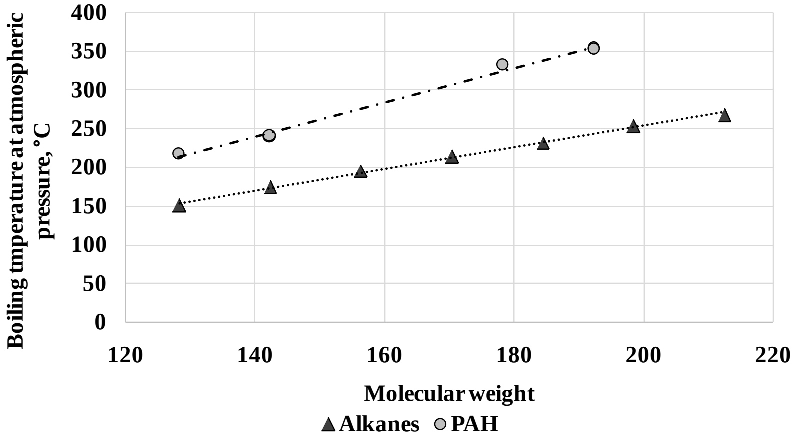

Figure 2. VOCs studied and their boiling points as related to molecular weight.

Table 1. VOCs studied

Compound	Molecular weight	Vapor pressure at 25˚C, mm Hg	Boiling temperature at atm. pressure, ˚C	Nature	Formula
n-Nonane	128.3	4.45	150.6	AH	C_9H_{20}
n-Decane	142.3	1.43	174.2	AH	$C_{10}H_{22}$
n-Undecane	156.3	0.412	196.0	AH	$C_{11}H_{24}$
n-Dodecane	170.4	0.135	214.0	AH	$C_{12}H_{26}$
n-Tridecane	184.4	0.0560	232.0	AH	$C_{13}H_{28}$
n-Tetradecane	198.4	0.0116	253.0	AH	$C_{14}H_{30}$
n-Pentadecane	212.4	0.00310	268.0	AH	$C_{15}H_{32}$
Naphthalene	128.2	0.0850	218.0	PAH	$C_{10}H_8$
1-Methylnaphthalene	142.2	0.0670	240.0	PAH	$C_{11}H_{10}$
2-Methylnaphthalene	142.2	0.0550	241.0	PAH	$C_{11}H_{10}$
Phenanthrene	178.2	0.000121	332.0	PAH	$C_{14}H_{10}$
1-Methylphenanthrene	192.3	0.0000501	354.0	PAH	$C_{15}H_{12}$
2-Methylanthracene	192.3	0.0000727	353.5	PAH	$C_{15}H_{12}$

A review [1] [2] of the health impact and occupational limits of the studied VOCs is shown in Table 2.

In general, VOCs play an important role in environmental problems by their accumulation and persistence in the environment [3]. Some VOCs, especially those of high molecular weight, resist oxidation processes and become persistent, being adsorbed on particles and transported over long distances [4], powering the global greenhouse effect.

So far no studies of these compounds have been done locally, so it is deemed important to carry out an exploratory work, in parallel with the fact that sulphur content of diesel fuel is undergoing changes at the time, from 2000 to 50 ppm and it is desired to correlate those changes with the said VOCs concentrations.

Alkanes tend to be emitted by vehicles, as they are components of fuels. Table 3 shows typical contents of studied VOCs in low sulfur diesel and gasoline [5]. The other studied PAHs come from oil and coal tars and incomplete combustion, including wood combustion; Phenanthrene is also associated with cigarette and marihuana smoke and charcoal broil.

Table 2. Occupational data for some of the VOCs studied. studied

Compound	Residence half time in air, hr	Health impact	Occupational limits
n-Nonane	40.8	Irritation eyes, skin, nose, throat; headache, drowsiness, dizziness, confusion, nausea, tremor, discordination	TLV: 200 ppm (1050 mg/m^3)
n-Decane	33.2	Irritation eyes, skin. Little impact	TLV Not established
n-Undecane	29	No clear indication of risks	TLV Not established
n-Dodecane	27	Irritation eyes, skin. Little impact	TEEL-0: Concentration below which people will experience no adverse health effects is 0.015 ppm (105 μg/m^3)
n-Tridecane	24	Irritating to eyes and skin. Inhalation causes irritation of the lungs and respiratory system.	TLV Not established
n-Tetradecane	19.2	Irritation eyes, skin. Inhalation causes irritation of the lungs and respiratory system	TLV Not established
n-Pentadecane	17	No clear indication of risks	TLV Not established
Naphthalene	18	Irritating to skin and eyes	TWA 10 ppm (50 mg/m^3)
1-Methylnaphthalene	7.3	Irritation. Toxic by all routes (*i.e.*, ingestion, inhalation, and skin contact)	TLV = 0.5 ppm (2.9 mg/m^3)
2-Methylnaphthalene	7.4	Irritating to skin	TLV = 0.5 ppm (2.9 mg/m^3)
Phenanthrene	36 - 1570	A known irritant, photosensitizing skin to light. Potential occupational carcinogen	TWA = 0.028 ppm (0.2 mg/m^3)

Table 3. Typical contents of studied VOC in low sulfur diesel and gasoline

Compound	Type	% in typical diesel low S fuel	% in gasoline
n-Nonane	AH	0.84	0.24
n-Decane	AH	0.92	0.19
n-Undecane	AH	0.93	0.15
n-Dodecane	AH	1.01	0.11
n-Tridecane	AH	1.61	0.09
n-Tetradecane	AH	1.21	0.03
n-Pentadecane	AH	1.09	0.01
Total studied AH	AH	7.61	0.82
Naphthalene	PAH	0.36	0.30

2. Materials and Methods

The apparatus set up for the sampling is described in Figure 3.

The sampling method applied was EPA TO-17 using 90 mm length, 5 mm diameter stainless steel TENAX adsorption tubes filled with appropriate sorbent materials, prepared and supplied by the DRI (Desert Research Institute at Reno, Nevada, USA). The chemical analysis of the studied VOCs was also done at the DRI, using the Agilent Thermal Desorption-Gas Chromatograph/Mass Spectrometer (TD-GC/MS) system.

The environmental samples were taken in a measurement campaign conducted in three sites, two of them with heavy traffic, the other one with low or inexistent traffic, from July to August 2011, with sampling periods of 24 hours. Each zone was evaluated during a week.

Additional samples were taken in the discharge of a diesel motor working under standardized laboratory conditions with diesel fuel of variable sulfur content. Run cycles followed standard ECE-M2 at 2420 rpm. Figure 4 shows a scheme for the run cycle.

3. Methodology and Results

3.1. Urban and Rural Sites

The VOC measurement campaign was conducted in three sites, two of them with heavy traffic (Poblado zone and Botanical Garden Park), the other one with low or inexistent traffic (Arví Park), from July to August 2010, with sampling periods of 24 hours. Each zone was evaluated during a week. Another sample was taken sampling during 24 hours continuously within a vehicle moving through designed zones in the city (On Board test). In the Figure 5, the sampling sites are located in the Aburrá Valley map. Table 4 shows the concentrations in the urban and rural zones, and in the on-board 24 hour samples. It is clear that rural areas have lower VOCs concentrations than urban ones.

Figure 6 compares the VOC concentrations found for the zones. It was found that the higher concentrations of the studied tracers correspond to pentadecane and naph-

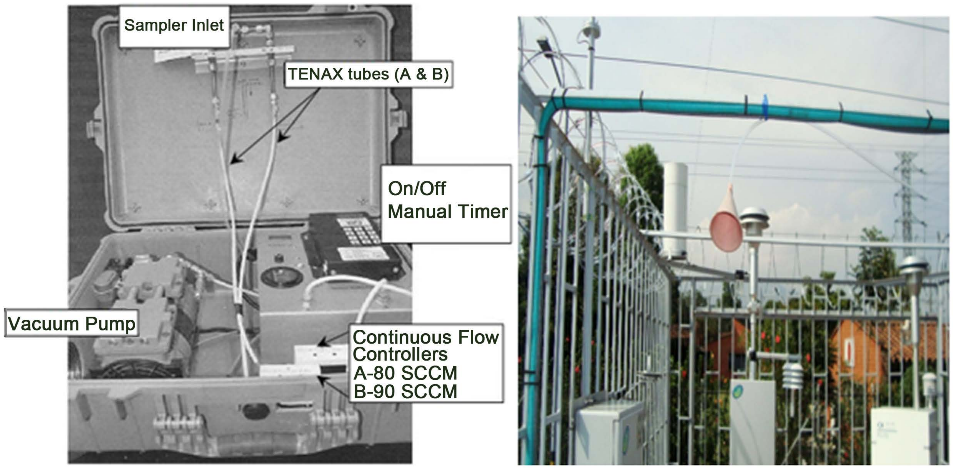

Figure 3. Description apparatus for VOC measurement (left) and apparatus located in the sampling zone (right).

Table 4. Concentrations in urban and rural zones, and in the on-board 24-hour samples studied.

Compound	Poblado 05/08/10	Poblado 07/08/10	Poblado 10/08/10	Botanic Garden 20/08/10	Arvi Park 31/08/10	On-Board 02/09/10
Type of zone	urban	urban	urban	urban	rural	urban
n-Nonane	0.870	0.736	0.769	1.896	0.060	1.919
n-Decane	0.980	0.696	0.693	2.273	0.046	1.986
n-Undecane	0.668	0.473	0.467	1.417	0.038	1.728
n-Dodecane	0.389	0.301	0.324	0.685	0.025	0.564
n-Tridecane	0.274	0.237	0.237	0.516	0.031	0.730
n-Tetradecane	0.244	0.218	0.225	0.583	0.027	1.588
n-Pentadecane	0.241	0.190	0.207	0.986	0.057	6.379
Naphthalene	0.989	0.839	0.836	2.269	0.139	0.637
1-Methylnaphthalene	0.212	0.179	0.200	0.741	0.010	0.322
2-Methylnaphthalene	0.428	0.357	0.407	1.520	0.016	0.576
Phenanthrene	0.038	0.023	0.022	0.141	0.005	1.279
1-Metylphenanthrene	0.000	0.000	0.000	0.158	0.000	0.426
2-Methylanthracene	0.000	0.000	0.000	0.182	0.000	0.523
Total studied VOC	5.334	4.248	4.388	13.369	0.456	18.657
Total studied AH	3.666	2.851	2.922	8.357	0.286	14.894
Total estudied PAH	1.667	1.398	1.466	5.012	0.170	3.763

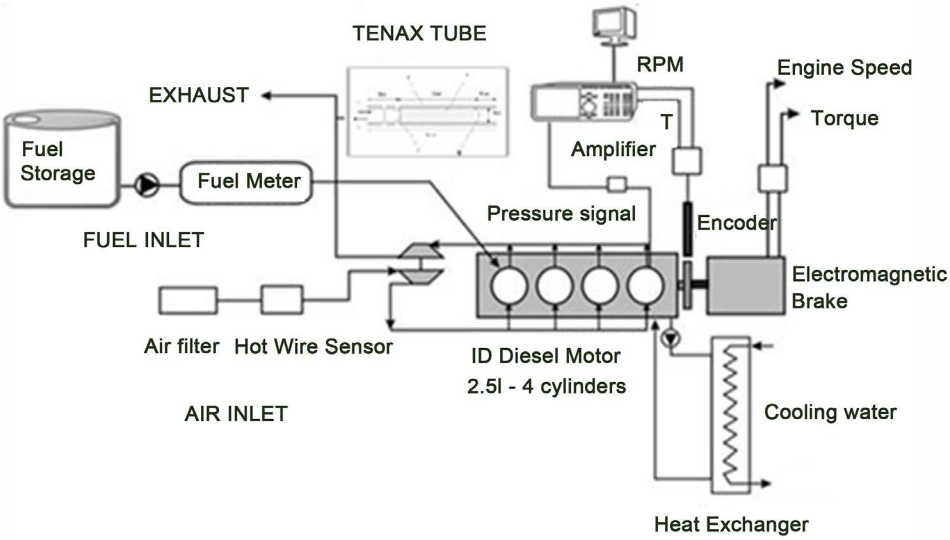

Figure 4. Run cycle scheme.

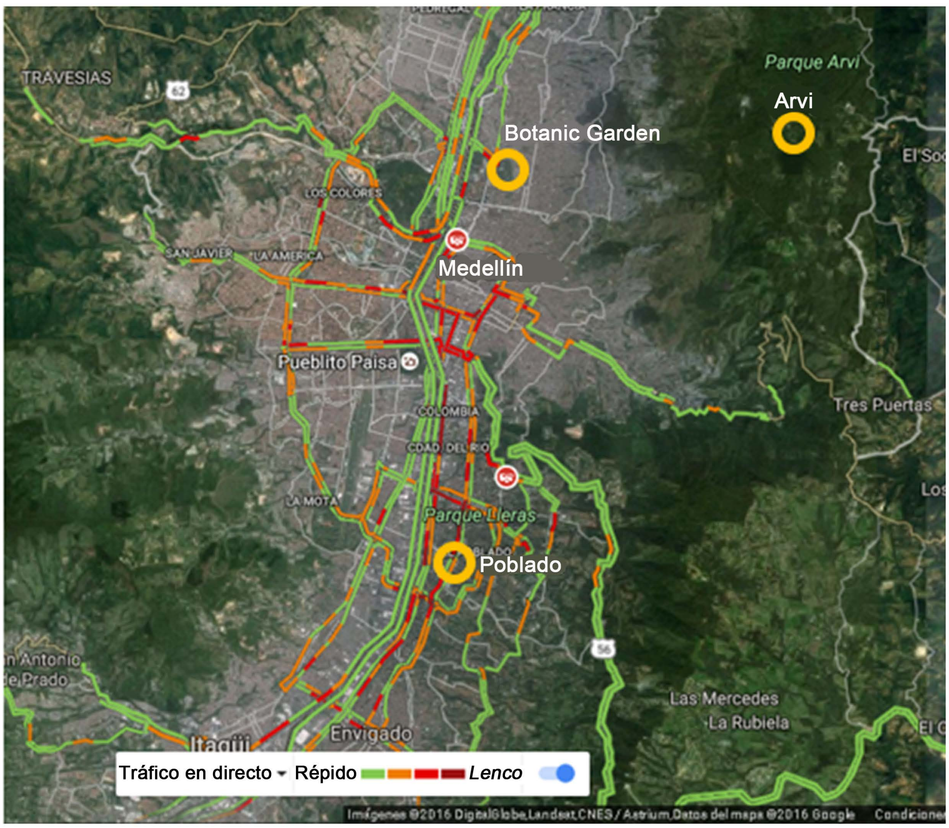

Figure 5. Sampling sites (Google map image 2016).

thalene. The on-board sample shows higher VOC's concentrations than the other sampling sites. Probably because the on board test environment was in continuous contact with mobile sources. Figure 7 shows comparative result for all the zones in terms of total VOCs.

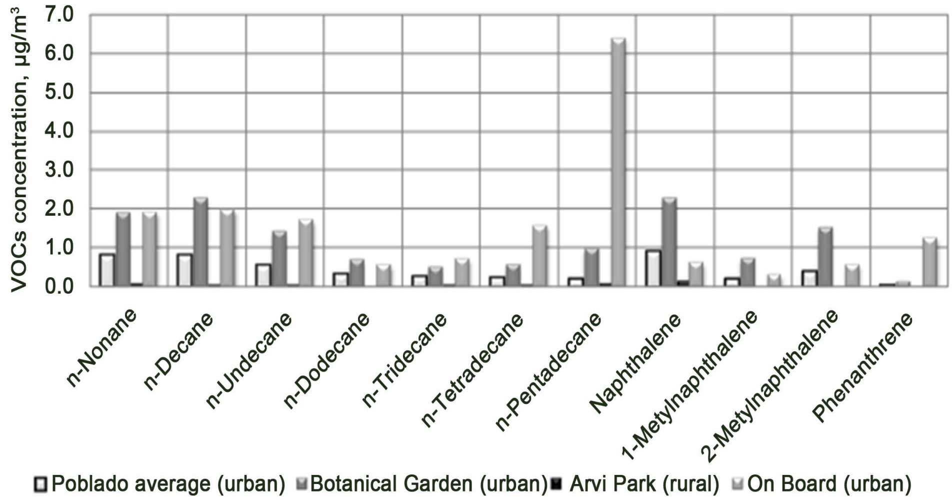

Figure 6. Comparative results for VOC concentrations in all studied zones.

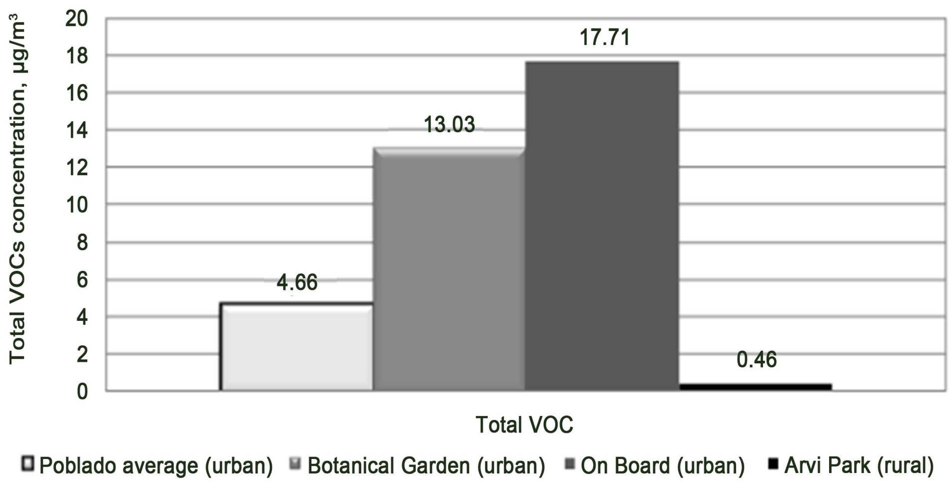

Figure 7. Total VOC concentrations for the studied zones.

It is clear in **Figure 7** that the concentrations of VOCs in urban areas are clearly greater than the ones in rural areas. Urban total VOCs were about 25 times greater than the rural area. All concentrations, as expected, are clearly much lower than the reported occupational limits for the substances shown in **Table 2**.

3.2. A Review of VOC Concentrations in Urban and Rural Areas around the World

Following results reported elsewhere [2] [6]-[9], **Table 5** was prepared to compare values reported around the world with the ones found in the present study, in order to have a comparative measure of the magnitude of the problem in the Medellín region.

This analysis shows, in general, local values lower than the typical ones reported around the world. The typical values shown were chosen by the authors after elimination, at their own criteria, of extreme high values in the reported data.

Table 5. VOC concentrations (range and typical) around the world and in this study.

	Concentrations in urban areas (μg/m^3)			Concentrations in rural areas (μg/m^3)		
Compound	Range around the world	Typical around the world	Average of this study	Range around the world	Typical around the world	Average of this study
n-Nonane	0.07 - 467	5.06	1.24	0.0 - 58.2	4.067	0.060
n-Decane	0.16 - 1100	18.68	1.33	0.0 - 161.2	5.919	0.046
n-Undecane	0.15- 59	7.66	0.95	0.018 - 0.54	0.279	0.038
n-Dodecane	0.0 -160	0.97	0.45	0.0 - 0.25	0.044	0.025
n-Tridecane	0.18-2.7	0.93	0.40	0.01-0.12	0.066	0.031
n-Tetradecane	0.0 - 36	8.46	0.57	0.0 - 0.116	0.058	0.027
n-Pentadecane	0.19 - 158	15.47	1.60	0.01 -0.149	0.080	0.057
Naphthalene	0.0 - 77	2.27	1.11	-	-	0.139
1-Methylnaphthalene	0.00 - 5.1	0.59	0.33	-	-	0.010
2-Methylnaphthalene	0.00 - 1.1	0.39	0.66	-	-	0.016
Phenanthrene	0.01 - 129	1.08	0.30	0.0 -0.032	0.006	0.005
Total		61.58	8.94		10.52	0.456

3.3. Diesel Engine Exhaust Concentrations

At the time of the study, S content of diesel fuel used in the region was undergoing changes, from 2000 ppm to 50 ppm and it was desired to correlate those changes with VOCs concentrations in the exhaust gases coming from a diesel motor working under standardized laboratory conditions.

Table 6 shows the results, which show a clear effect of the sulfur content of the fuel on the emissions of the studied VOCs.

4. Conclusions

- The region atmosphere shows presence of VOCs.
- The concentrations in urban areas are clearly greater than the ones in rural area. In the average urban total VOCs are 27 times larger.
- The values found in rural and urban areas tend to be smaller than the typical values reported, around the world, in the literature. Total VOCs show values around 15% of the reported typical values for urban areas and about 5% for rural areas.
- The VOC concentrations are related to vehicle emissions, especially to diesel fuel vehicle emissions.
- An initial baseline has been established which should be useful for future work and public policy in relationship to vehicle related pollution control.
- Reducing S content on diesel fuel has been a beneficial step in this direction.

Table 6. VOC concentrations in diesel fuel motor exhaust and sulfur content in diesel fuel.

Compound	Fuel with sulfur at 50 ppm, μg/m^3	Fuel with sulfur at 500 ppm, μg/m^3	Fuel with sulfur at 2100 ppm, μg/m^3
n-Nonane	177	62	160
n-Decane	407	153	528
n-Undecane	254	203	501
n-Dodecane	199	250	649
n-Tridecane	186	311	586
n-Tetradecane	111	311	450
n-Pentadecane	61	361	356
Naphthalene	179	140	141
1-Metylnaphthalene	87	134	176
2-Metylnaphthalene	170	218	317
Phenanthrene	1.43	12.83	5.60
Total studied VOC	**1832**	**2155**	**3869**
Total studied AH	**1395**	**1650**	**3230**
Total estudied PAH	**437**	**505**	**639**

Acknowledgements

This work was supported by POLITÉCNICO COLOMBIANO JAIME ISAZA CADAVID and ECOPETROL. We acknowledge the DRI Institute for the analytical and sampling assistance and the University of Antioquia, GIMEL group, for the work done in the laboratory motor testing.

References

[1] (1995) Toxicological Profile for Polycyclic Aromatic Hydrocarbons. U.S. Department of Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry.

[2] Data Base for the VOCs. http://www.ncbi.nlm.nih.gov/

[3] Wiederkehr, P., *et al*. (1998) Urban Air Pollution. European Aspects. Kluwer Academic Publishers, Dordrecht, 403-418.

[4] Guo, H., So, K.L., Simpson, I.J., Barletta, B., Meinardi, S. and Blake, D.R. (2007) C1-C8 Volatile Organic Compounds in the Atmosphere of Hong Kong: Overview of Atmospheric Processing and Source Apportionment. *Atmospheric Environment*, **41**, 1456-1472. http://dx.doi.org/10.1016/j.atmosenv.2006.10.011

[5] Chin, J.-Y. and Batterman, S.A. (2012) VOC Composition of Current Motor Vehicle Fuels and Vapors, and Collinearity Analyses for Receptor Modeling. *Chemosphere*, **86**, 951-958. http://dx.doi.org/10.1016/j.chemosphere.2011.11.017

[6] Sánchez, J.M. and Alcántara IX, A. Compuestos orgánicos volátiles en el medio ambiente, en Anales de la Real Academia Nacional de Farmacia.

[7] Barletta, B., Meinardi S., Sherwood, F., Chan, C.-Y., Wang, X.M., Zou, S.C., Chan, L.Y. and

Blake, D.R. (2005) Volatile Organic Compounds in 43 Chinese Cities. *Atmospheric Environment*, **39**, 5979-5990. http://dx.doi.org/10.1016/j.atmosenv.2005.06.029

[8] Derwent, R.G., Davies, T.J., Delaney, M., Dollard, G.J., Field, R.A., Dumitrean, P., Nason, P.D., Jones, B.M.R. and Pepler, S.A. (2000) Analysis and Interpretation of the Continuous Hourly Monitoring Data for 26 C2-C8 Hydrocarbons at 12 United Kingdom Sites during 1996. *Atmospheric Environment*, **34**, 297-312. http://dx.doi.org/10.1016/S1352-2310(99)00203-4

[9] Pacheco, J., Franco, J., Behrentz, E., Belalcazar, L. and Clappier, A. (2009) VOCs Concentrations in the Ambient Air of Bogota City: Source Identification and Apportionment. Grupo de Estudios en Sostenibilidad Urbana y Regional, Universidad de los Andes, Colombia. Escuela Politécnica Federal de Lausanne (EPFL). Jeune Chercheur Boursier, KFPE, Suiza.