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BACKGROUND LEVELS OF BENZENE IN THE POÇO DAS ANTAS BIOLOGICAL RESERVE,

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Abstract

Interpretations of benzene concentrations in the atmosphere heavily depends on background levels and although some studies on reference values for rural areas were carried out only a few evaluated the concentrations of benzene in a tropical environment. The main purpose of this paper is to establish tropical background levels of Benzene in the Poço das Antas Biological Reserve. The Poço das Antas Biological Reserve has been selected, because it is an environmental protection unit, which entrance is restricted, and there is no risk of contamination by vehicles or other fossil fuel input. Active and passive benzene sampling stations were located in the woods of the Poço das Antas Reserve, at least 200 m away from a highway. A weather station was installed in an open area, although below the canopy of surrounding trees. Charcoal Active samplers and SKC passive samplers were installed in each of the sampling stations.The analyses were carried out following the Niosh (method 1501) and measurements were performed in a GC-FID. Although the detection limits are very low all of the obtained data were bellow this limits, showing that the atmospheric concentrations of benzene in tropical rural areas can reach very low values. In the present work it was determined that in the background concentrations for the Poço das Antas Reserve, are below <0.035 ppb, that should be established as a reference value for contaminated tropical environments.

Introduction

Benzene is a colorless liquid with a sweet odor, volatile in air and very soluble in water. It is highly flammable and has shown to be a carcinogen contaminant (Kaneko et al., 1997) that is produced from any heating process of fossil fuel, including burning, distillation and other industrial processes (Tsai et al., 2007). For that reason, it has been thoroughly studied in the urban and industrial environment (Fondelli et al., 2008; Miranda and Tornaz, 2008; Wheeler et al., 2008). To protect the health of the population, guidelines for air quality were set worldwide. For example, a level of 5 $\mu g\ m^{-3}$ has been enforced as a mean calendar year limit in the European Union from 2010 (Comissão Européia, 2005)

Industrial processes are the main sources of benzene, the levels in the air can be elevated by emissions from burning coal and oil (Wu et al., 2002), benzene waste and storage operations, motor vehicle exhaust and service stations evaporation of gasoline (Periago and Prado, 2005). Tobacco smoke is another source of benzene in air (Fustinoni et al., 2005), especially in closed environments. Industrial effluents, disposal of products containing benzene, and gasoline leaks from underground storage tanks release benzene into water and soil (Silva and Alvarez, 2007).

A number of studies in temperate, but also in tropical countries has established that benzene constitute is present in ambient air of downtown cities, in tunnels and even in the closed ambient of vehicles, however the interpretations of these environmental values heavily depends on background levels that are normally established from the measurement of reference areas, that are located in rural or pristine environments (McCarthy et al., 2006; O'Donoghue and Broderick, 2007; Roberts et al., 1985). These works that were mostly done in temperate regions establish that the atmospheric concentrations of benzene may vary significantly whether from rural area (with low detectable values) to pristine areas (extremely low or undetectable values).

For the tropical environment only one work has been published on the background concentrations of benzene in a pristine area, a tropical rainy forest of Venezuela (Holzinger et al., 2001). However, it is expected a significant variability between different tropical environments. One issue that has be discussed is the environmental temperature and humidity. It is expected that under higher temperatures, an intense volatilization rate should be measured and therefore lower concentrations should be found in the atmosphere. The extremely high humidity observed in some tropical environments should retain some of the benzene in the atmosphere, therefore increasing its concentrations.

In the present work, the main purpose was to establish new tropical background levels of Benzene for the southeast Brazil, by carrying out measurements in the pristine environment of Poço das Antas Biological Reserve. The measurements considered the spatial variation and the temporal variations, and followed the variations in the meteorological parameters (temperature, humidity, wind velocity and direction.

METHODOLOGY

Study Area

The Poço das Antas Biological Reserve has been selected, because it is an environmental protection unit, which entrance is restricted, and there is no risk of contamination by vehicles or other fossil fuel inputs (through human activities). The research was authorized by the manager of the reserve, who allowed the team to stay overnight during the weekend, while there was no car traffic in the area. The Reserve is located in the Casimiro de Abreu Municipalty, RJ, between coordinates: 23K, Northing 7,500,000 – 7,510,000 and Easting 770,000 – 790,000. At the reserve, four stations were selected to carry out active and passive sampling. The stations were located in the woods, at least 200 m away from BR-101 highway. The location of Poço das Antas Reserve, as well as the location of the sampling sites are presented in Figure 1.

A weather station model WMR 968 Oregon Scientific was installed on the roof of the administrative house, in an open area, although below the canopy of surrounding trees. This position was selected deliberately, because it was necessary to measure the winds and other meteorological parameters in the level of the sampling devices. The equipment was able to measure and register wind direction and velocity, temperature, humidity and barometric pressure at intervals of 1 or 2 minutes.

Sampling

The active sampling was carried out with four SKC pumping devices that were installed in water-proof boxes at the height of about 1,60 m from the ground. To each pump, charcoal active denuders (small glass tubes filled with activated carbon and two layers of wool at each end to prevent that the contents are sucked by the pump) were installed and replaced at intervals of 2 hours, in order to survey the variation of the concentrations during the day and the night (Figure 2). After sampling period, the denuders were withdrew from the pump, their endings were capped and they were immediately stored in a -20°C freezer and prepared for transportation to the laboratory.

The sampler used for the passive sampling was the SKC MODEL 575-001. During passive sampling, it is essential to ensure accurate determination of airborne chemical levels, so the survey was validated for concentrations ranging from 0.1 to 2.0 ppm and for exposure times ranging from 7 hours to 12 hours. The passive sampler used in this study has an adsorption phase of activated carbon from coconut fiber. After being exposed to the ambient air for the established period, the passive samplers were wrapped in hermetic plastic zip-lock bags and stored in a freezer at -20°C until transportation to the laboratories.

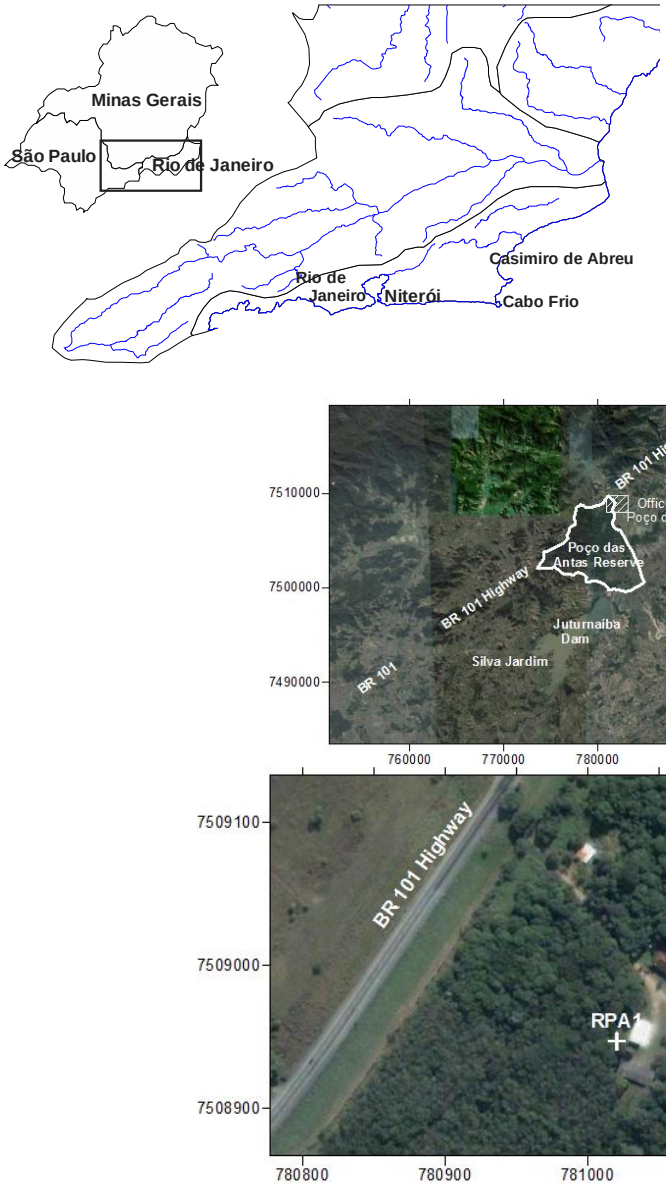

Figure 1: Location of the study area, with the position of the sampling sites.

Figure 2: Active sampler hanging in a tree. The denuder was located at about 1.60 m height.

Analytical Procedures

The benzene analyses were carried out following the Niosh (method 1501). After collection, passive and active samplers were air tightly closed, and transported to the laboratory under refrigeration. The desorption of the benzene from charcoal was carried out by a 30 minutes extraction with carbon disulfide that was followed by the injection of the extract in a GC-FID (gas chromatographer with Flame Inonization detection) equipped with a 30m x 0.32-mm ID; 1-μm film 100% PEG column. Field blanks were simultaneously analyzed and the detection limits were determined as a function of the sampled volumes. Considering that all samples were determined to be bellow the detection limits, the sampled volumes were an important parameter to establish that values were always bellow a defined concentration.

The analytical recovery for concentrations ranging between 0.1 and 2.0 ppm (or 2 and 50 g respectively) was 93.5% with a relative standard deviation of around 6.2%. There was no effect of moisture on the quality of the analytical results. The sampling rate measured was approximately 16.0 ml min^{-1}, confirmed with calculations of the precision and the accuracy from 124 experiments. The sample may wait a maximum of 14 days at room temperature or under refrigeration until analyses, without significant change in concentration.

Since no detectable values could be identified, the results were presented as tables showing the detection limits for each sample that is a function of the time (or volume) pumped, when active samplers, or just time (when passive samplers).

Results

Meteorological data

The meteorological data measured in the Poço da Antas Reserve during the days 19th and 20th April, 2008 were presented in Figures 3 – 6. The graphs in Figures 3 – 5 present the variation of the air temperature, relative humidity and barometric pressure with time. Although precipitation has been measured, no graph is presented because, although the humidity was elevated, the amount of rain during the period was insignificant (< 1 mm). Figure 6 presents the wind velocity and direction statistics during the period.

The fall in the barometric pressure (Figure 5) indicates that during the experiment there was a cold front arriving in the study area, what was confirmed a few hours after we had finished the work, when a strong rain falled in the study area. This process is very common in Rio de Janeiro, because the direction of the coast is mostly East – West and the cold fronts arrive in the state straightly from the south pole. In this case, the fall in the barometric pressure is accompanied with a consistent increase in the temperature.

The air temperature during the experiment (Figure 3) was relatively mild, reaching no more than 28°C), lower in the night and higher during the day. Following this pattern, relative humidity (Figure 4) was very high during the night, probably associated with a strong evapotranspiration process from the rich vegetation of the area. During the day, the relative humidity fall significantly by the action of the sun and heat. Both factors are important in the controlo f benzene atmospheric concentrations. Most of this compound may be originated from chemical and biological processes occurring in the soil (for instance, decomposition of organic matter) and with the increase in humidity (and evapotranspiration), an increase in the atmospheric flux of benzene is expected.

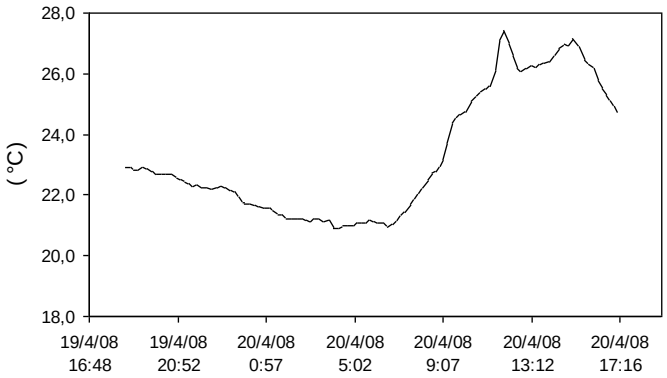

Figure 3: Variation in temperature in the Poço das Antas Reserve, starting at 16:48 of the 19th April 2008 and ending a little more than 24 hours later.

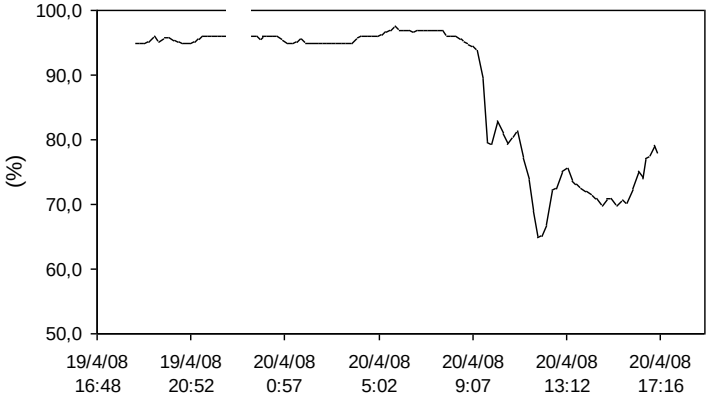

Figure 4: Variation of relative humidity in the Poço das Antas Reserve, starting in the afternoon of 9th April 2008 and finishing a little more than 24 hours later.

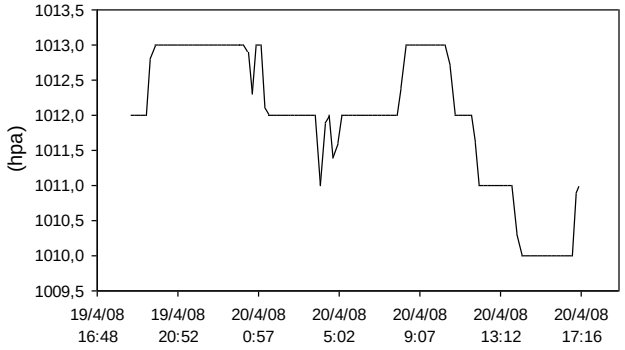

Figure 5: Variation in the barometric pressure in the Poço das Antas Reserve, starting at 16:48 of the 19th April 2008 and ending a little more than 24 hours later.

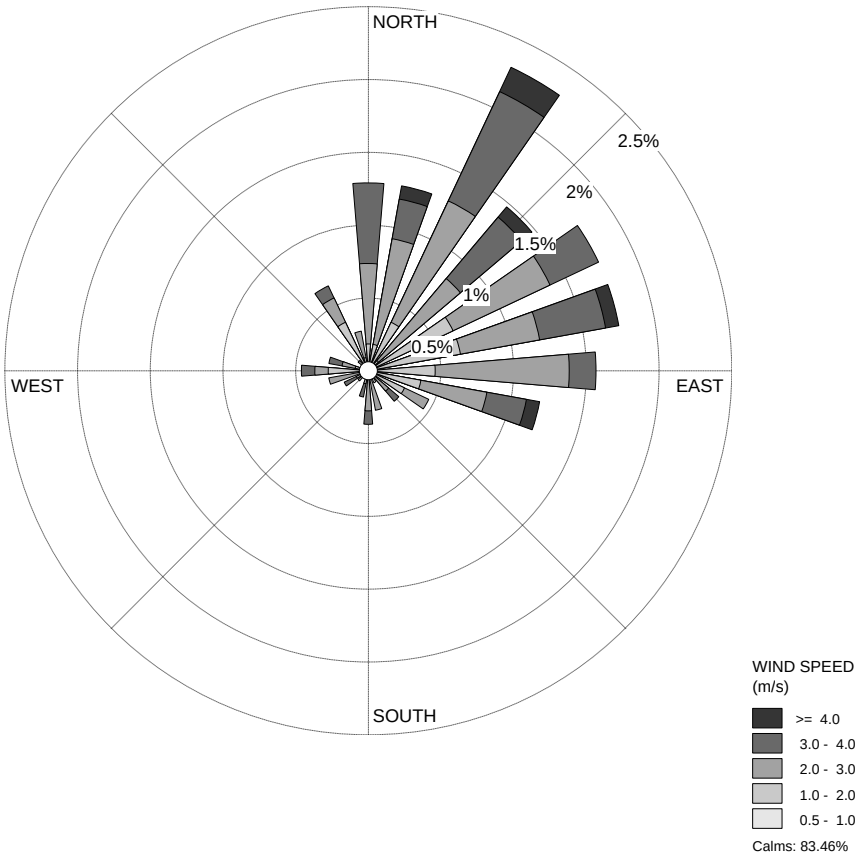

Figure 6: Wind velocity and direction statistics during the period starting at 16:48 of the 19th April 2008 and ending at 18:00 of the next day.

As shown in the Wind statistics, Wind velocities are extremely low (Figure 6), because the whole area is wind protected. The periods of calm account for 83.43% of the measured time and the most of the directions cannot be measured because of the lack f velocities. The few registrations of directions indicate a slight NE wind (2 to 3 m s^{-1}).

Benzene

The results of the limits of quantification and detection were summarized in table 1. Although the detection limits are very low (see tables 2-6), all of the obtained data were bellow these limits, showing that the atmospheric concentrations of benzene in tropical rural areas can reach extremely low values.

Even though in the present work it was not possible to identify what the background concentrations are, at least it can be said that the values are below certain limits (of quantification, or detection). The mean value of the detection limit is <0.035 ppb, while the quantification limit is <0.106 ppb, so the concentrations are certainly bellow these levels.

Table 1: Valores dos limites de detecção e de quantificação medidos na Rebio Poço das Antas.

Sampling	Limits of	Average (ppb)	Maximum (ppb)	Minimum (ppb)
Passive	Quantification	2,1	2,2	1,9
	Detection	0,6	0,7	0,6
Ative	Quantification	0,106	0,170	0,090
	Detection	0,035	0,050	0,032

A comparison with the results from the literature show that in temperate background environments the concentrations are slightly higher. McCarthy et al. (2006) evaluated the concentrations of 18 HAP toxicants in a monitoring network in the United States and observed that mean concentrations of benzene is 0.044 ppb (a little above our detection limits). On the

other hand, in Caracas (Venezuela) the concentrations can be as high as 1.1 ppb while in remote environments in Venezuela, the concentrations may be as low as 0,031 ppb.

Table 2: Benzene in station RPA1(E781020, N7508947)

setting up (day time)	lag (hours)	DL (ppb)	QL (ppb)
19/04/2008 19:18	01:36	<0.038	<0.125
19/04/2008 20:55	02:00	<0.030	<0.100
19/04/2008 22:56	02:02	<0.030	<0.098
20/04/2008 00:59	02:07	<0.028	<0.094
20/04/2008 03:09	02:17	<0.026	<0.088
20/04/2008 05:46	01:54	<0.032	<0.105
20/04/2008 07:42	02:00	<0.030	<0.100
20/04/2008 09:42	01:53	<0.032	<0.106
20/04/2008 11:40	02:00	<0.030	<0.100
20/04/2008 13:41	01:55	<0.031	<0.104
20/04/2008 15:38	01:24	<0.043	<0.143

Table 3: Benzene in station RPA 3 (E781098, N7508958).

setting up (day time)	lag (hours)	DL (ppb)	QL (ppb)
19/04/2008 19:10	01:53	<0.032	<0.105
19/04/2008 21:04	02:02	<0.030	<0.099
19/04/2008 23:08	02:00	<0.031	<0.102
20/04/2008 01:09	02:13	<0.028	<0.092
20/04/2008 03:23	02:10	<0.027	<0.090
20/04/2008 05:51	02:01	<0.030	<0.101
20/04/2008 07:54	02:00	<0.031	<0.102
20/04/2008 09:56	01:50	<0.032	<0.105
20/04/2008 11:47	02:00	<0.030	<0.099
20/04/2008 13:48	02:01	<0.030	<0.101
20/04/2008 15:50	01:12	<0.046	<0.167

Table 3: Benzene in station RPA 2 (E781098, N7508911)

setting up (day time)	lag (hours)	DL (ppb)	QL (ppb)
19/04/2008 19:00	01:54	<0.032	<0.105
19/04/2008 21:00	02:01	<0.030	<0.099
19/04/2008 23:04	01:58	<0.031	<0.102
20/04/2008 01:04	02:10	<0.028	<0.092
20/04/2008 03:16	02:14	<0.027	<0.090
20/04/2008 05:48	01:59	<0.030	<0.101
20/04/2008 07:49	01:58	<0.031	<0.102
20/04/2008 09:48	01:54	<0.032	<0.105
20/04/2008 11:43	02:01	<0.030	<0.099
20/04/2008 13:45	01:59	<0.030	<0.101
20/04/2008 15:45	01:19	<0.046	<0.152

Table 4: Benzene in station RPA 4 (E781118, N7508986)

setting up (day time)	lag (hours)	DL (ppb)	QL (ppb)
19/04/2008 19:26	01:41	<0.036	<0.119
19/04/2008 21:09	02:02	<0.030	<0.098
19/04/2008 23:13	01:58	<0.031	<0.102
20/04/2008 01:12	02:16	<0.026	<0.088
20/04/2008 03:31	02:07	<0.028	<0.094
20/04/2008 05:55	02:02	<0.030	<0.098
20/04/2008 07:59	01:59	<0.030	<0.101
20/04/2008 10:00	01:50	<0.033	<0.109
20/04/2008 11:52	01:58	<0.031	<0.102
20/04/2008 13:52	02:02	<0.030	<0.098
20/04/2008 15:55	01:10	<0.051	<0.171

Table 5: Benzene measured with passive samplers in the study area

Station	setting up (day time)	lag (hours)	DL (ppb)	QL (ppb)
RPA 1	19/04/2008 19:18	7:53	<0.61	<2.03
	20/04/2008 08:17	7:24	<0.65	<2.16
RPA 2	19/04/2008 18:53	8:25	<0.57	<1.90
	20/04/2008 08:22	7:23	<0.65	<2.17
RPA 3	19/04/2008 19:09	8:15	<0.58	<1.94
	20/04/2008 08:25	7:26	<0.65	<2.15
RPA 4	19/04/2008 19:28	8:04	<0.60	<1.98
	20/04/2008 08:28	7:30	<0.64	<2.13

Conclusions

Benzene is a dangerous air contaminant produced in petroleum refineries from distillation processes and in steel industries produced from coke ovens. Its carcinogenicity has placed this pollutant and one of the most concerned by workers unions and by environmental agencies. Considering the health hazards of benzene, the evaluation of atmospheric contamination in the urban environment requires very precise analyses and certainty of background values. In the present work although the background values could not be detected, it was determined that in the

Poço das Antas Biological Reserve, concentrations are very low (<0.035 ppb), that should be established as a reference value for contaminated tropical environments.

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References

Comissão Européia, 2005. Directrizes práticas de carácter não obrigatório sobre a protecção da saúde e da segurança dos trabalhadores contra os riscos ligados à exposição a agentes químicos no trabalho (Artigos 3.º, 4.º, 5.º, 6.º e ponto 1 do anexo II da Directiva 98/24/CE). Comissão europeia - DG Emprego, Assuntos Sociais e Igualdade de Oportunidades - Unidade F.4, Lisbon, p. 288.

Fondelli, M.C., Bauazzano, P., Grechi, D., Gorini, G., Miligi, L., Marchese, G., Cenni, I., Scala, D., Chellini, E., Costantini, A.S., 2008. Benzene exposure in a sample of population residing in a district of Florence, Italy. Sci. Total Environ. 392, 41-49.

Fustinoni, S., Consonni, D., Campo, L., Buratti, M., Colombi, A., Pesatori, A.C., Bonzini, M., Bertazzi, P.A., Foa, V., Garte, S., Farmer, P.B., Levy, L.S., Pala, M., Valerio, F., Fontana, V., Desideri, A., Merlo, D.F., 2005. Monitoring Low Benzene Exposure: Comparative Evaluation of Urinary Biomarkers, Influence of Cigarette Smoking, and Genetic Polymorphisms. Cancer Epidemiol Biomarkers 14, 2237-2244.

Holzinger, R., Kleiss, B., Donoso, L., Sanhueza, E., 2001. Aromatic hydrocarbons at urban, sub-urban, rural (8 degrees 52 ' N; 67 degrees 19 ' W) and remote sites in Venezuela. Atmos. Environ. 35, 4917-4927.

Kaneko, T., Wang, P.Y., Sato, A., 1997. Benzene-associated leukemia and its risk assessment. Journal Of Occupational Health 39, 159-178.

McCarthy, M.C., Hafner, H.R., Montzka, S.A., 2006. Background concentrations of 18 air toxics for North America. Journal Of The Air & Waste Management Association 56, 3-11.

Miranda, R., Tornaz, E., 2008. Characterization of urban aerosol in Campinas, Sao Paulo, Brazil. Atmos. Res. 87, 147-157.

O'Donoghue, R.T., Broderick, B.M., 2007. C-2-C-6 background hydrocarbon concentrations monitored at a roof top and green park site, in Dublin City centre. Eviron. Monitor. Assess. 132, 491-501.

Periago, J.F., Prado, C., 2005. Evolution of occupational exposure to environmental levels of aromatic hydrocarbons in service stations. Annals Of Occupational Hygiene 49, 233-240.

Roberts, J.M., Hutte, R.S., Fehsenfeld, F.C., Albritton, D.L., Sievers, R.E., 1985. Measurements Of Anthropogenic Hydrocarbon Concentration Ratios In The Rural Troposphere - Discrimination Between Background And Urban Sources. Atmos. Environ. 19, 1945-1950.

Silva, M.L.B.D., Alvarez, P.J.J., 2007. Assessment of anaerobic benzene degradation potential using 16S rRNA gene-targeted real-time PCR. Environmental Microbiology 9, 72-80.

Tsai, S.P., Ahmed, F.S., Wendt, J.P., Foster, D.E., Donnelly, R.P., Strawmyer, T.R., 2007. A 56-year mortality follow-up of Texas petroleum refinery and chemical employees, 1948-2003. Journal Of Occupational And Environmental Medicine 49, 557-567.

Wheeler, A.J., Smith-Doiron, M., Xu, X., Gilbert, N.L., Brook, J.R., 2008. Intra-urban variability of air pollution in Windsor, Ontario - Measurement and modeling for human exposure assessment. Environ. Res. 106, 7-16.

Wu, M.-T., Simpson, C.D., Christiani, D.C., Hecht, S.S., 2002. Relationship of Exposure to Coke-Oven Emissions and Urinary Metabolites of Benzo(a)pyrene and Pyrene in Coke-Oven Workers. Cancer Epidemiology Biomarkers Prevention 11, 311.