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Concentrations of benzene and toluene in the atmosphere of the southwestern area at the Mexico City Metropolitan Zone

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Abstract

The Mexico City Metropolitan Zone (MCMZ) presents important emissions of hazardous air pollutants. It is well documented that the MCMZ suffers a critical air pollution problem due to high ozone and particulate matter concentrations. However, toxic air pollutants such as benzene and toluene have not been considered. Benzene has accumulated sufficient evidence as a human carcinogen, and the ratio benzene/toluene is an excellent indicator to evaluate control strategies efficiency.

In order to evaluate the levels of these two air toxic pollutants in the MCMZ, ambient air samples were collected in canisters and analyzed with a gas chromatograph with a flame ionization detector, according to procedures described in the United States Environmental Protection Agency (USEPA) method TO-15. Quality assurance was performed collecting duplicate samples which were analyzed in replicate to quantify the precision of air-quality measurements.

Three different sites located in the Southwestern area in the MCMZ were selected for the sampling: the University campus, a gas station, and a vertical condominium area, in the same neighborhood, which presents different activities. At these sites, grab air samples were collected during the morning hours (7–8 a.m.), while for the University area, 24 h integrated air samples were collected simultaneously, with grab samples.

Benzene concentrations (24 h sampling) in the atmosphere around the University campus have similar present levels as in other cities of North America. Mean values in this site were about 1.7 ppb.

A significant variation exists between the benzene and toluene concentrations in the studied sites, being the more critical values than those registered at the gas station (an average of 25.8 ppb and a maximum of 141 ppb of benzene). There is a fuel regulation for gasoline in Mexico, which allows a maximum of 1 percent of benzene. However, since more than 60 percent of vehicles do not have catalytic converters (models before 1991) it is expected that most of this benzene be emitted through exhaust pipe. Another strategy being implemented is the use of vapor recovery systems at the gas stations. Vehicles emission control technology must be matched with adequate fuel characteristics in the problem area where it will be implemented, to achieve maximum emission reductions.

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1. Introduction

The Mexico City Metropolitan Zone (MCMZ) is located in the southwestern corner of the Mexico Basin at an altitude of 2240 m above sea level. The basin's

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topographical situation does not allow, the major part of the time, the free circulation of winds and good ventilation, presenting a diurnal pattern of wind blowing from the northwest and the northeast. The industrial area comprises more than the 30 percent of the whole national industry and is located in the northern sector of the MCMZ.

The present population of the MCMZ is more than 20 million inhabitants (about a fifth of Mexico's total population) and is still growing. Located in the basin there are more than 30,000 industries and 12,000 service facilities. Furthermore, around 3-million motor vehicles (buses, minibuses, taxis, trucks and private cars), burn above 20 million of liters gasoline daily. Diesel fuel and LPG usage have been increasing also in the MCMZ.

The MCMZ represents an example of a mega city where the air pollution problem has reached an important evolution in a very short time causing risks in the health of the population.

The air pollution problem in the MCMZ began several decades ago, and it has increased drastically since the middle of the 1980s. It is important to recognize that in the 1960s, 1970s and the first half of the 1980s, the main pollutants were sulfur dioxide, total suspended particles and lead (Aldana et al., 1999a, b). However, since the second half of the 1980s, ozone has been the most important air pollutant. A dramatic increase in the ozone concentrations in 1986 was detected at the University of Mexico air-quality monitoring station (Bravo et al., 1988, 1997). Air-quality strategies and their negative effect resulting in an increase in the ozone levels at MCMZ had been discussed (Bravo et al., 1993, 2000; Bravo and Torres, 2000). Other important air pollutants at present are suspended particles (PM_{10}) and toxic pollutants such as benzene and toluene.

2. Importance of benzene

Benzene is present in petroleum products such as fuels, diesel fuels, crude oil, and is a significant component of gasoline. Gasoline is produced from crude petroleum by a variety of refining and manufacturing processess (catalytic cracking, coking, alkylation, and catalytic reforming) which yield and modify its character. Gasoline constitutes one of the most complex mixtures of chemicals (it contains over 1000 possible substances) to which humans can be exposed. The composition of gasoline varies, depending on the geographic region, the season, performance requirements (octane rating), blending of stock, and the source of the crude oil. It contains a large number of chemicals and additives, some of which are carcinogenic, among them benzene and toluene must be considered.

Benzene has been shown to cause cancer in both animals and humans, therefore is currently classified by the Environmental Protection Agency (EPA), the American Conference of Governmental Industrial Hygienist (ACGIH), and the International Agency for Research on Cancer (IARC) as a human carcinogen (Mehlman, 1994; Fromme, 1995).

Motor vehicles are a significant source of air pollution emissions, including benzene. There is evidence that humans (specifically children) who live near heavily traveled streets or highways may be at an elevated risk of developing cancer, including leukemia (Pearson et al., 2000).

It is accepted that benzene is a genotoxic carcinogen and that therefore no absolutely safe exposure level can be defined. Nevertheless, for practical purposes some countries (i.e. United Kingdom and Japan) use and recommend an air-quality standard for Benzene of 1 ppb annual average (EPAQS, 1991; EA, 1999).

VOCs profiles of the emissions from gasoline and diesel vehicles were determinated in tunnels in México City through the 1990s, the most abundant being the two carbon compounds, as a result of the combustion, and compounds related to fuel composition, like isopentane, xylenes, toluene among others. The ratio toluene/benzene was about 2.8 and 5.6 for gasoline and diesel vehicles, respectively (ppbC toluene/ppbC benzene) or 2.4 and 4.8, respectively (ppb toluene/ppb benzene) (Mugica et al., 1998, 2001).

3. Experimental section

Ambient air concentrations of benzene and toluene were collected in 6 l stainless steel SUMMA® polished canisters and measured according to DKK Corporation System designed by Maeda et al. (1995, 1998), which is equivalent to the EPA's Method TO-15 (US-EPA, 1999). This method specifies steps for collecting samples of ambient air in passivated stainless steel canisters, and analyzing them using a gas chromatograph with flame ionization detection. The canisters were cleaned and evacuated before being placed at the sampling sites. After cleaning the canisters, they were analyzed for the presence of VOCs to verify that the canisters were clean before the final evacuation and the initiation of the next sampling event. The ambient air samples were preconcentrated by a multiadsorbent technique and then analyzed with a gas chromatograph with a flame ionization detector. The detection limits were about 0.1 ppb, for benzene and toluene.

The analytical system is located at the National Center for Environmental Research and Training (CENICA). The system consisted of a dynamic dilution system, a humidity controller, a sample concentrator, and a gas chromatograph with a flame ionization detector. The humidity controller was operated at 25°C. After that, the sample was preconcentrated in a

trap which was cooled to 10°C by liquid carbon dioxide. The trap was packed with tenax, activated aluminum and activated carbon. The compounds were thermally desorbed at 250°C with helium as the purge gas (flow: 5.98 ml/min) for 4 min. The analytical conditions consisted of two columns connected in series aluminum plot (i.d. 0.53 mm, 30 m) and methylsilicone (i.d. 0.5 mm, 30 m) columns. The oven temperature program was 40°C, 4 min, 8°C/min up to 100°C, 6°C/min up to 240°C, 10 min. The sample flow employed was 84 ml/min; and total analytical run time was 60 min. Benzene and toluene were identified with HC calibration standard (1 ppm each component, SAAN Co.) using a ten-time dilution mixture, and performed by using retention times and areas obtained during calibration.

Duplicate samples and replicate analysis were carried on. The comparison of concentrations from replicate analysis characterizes analytical precision (how precisely the laboratory analysis were carry out), and comparison of concentrations from duplicate samples characterizes sampling and analytical precision (how precisely field sampling techniques and laboratory analytical techniques were performed).

The experimental program included three sampling sites in which grab samples were collected (University campus, condominium and gas station) each six days, from August to October 1999, and from July 2000 to February 2001 (Sosa, 2001; Bravo et al., 2001). In these sites grab air samples were collected during the hours with higher values of VOCs experienced at the MCMZ (7–8 a.m.). For the University area, 24 h integrated air samples were collected simultaneously with grab samples. During these periods, 33 sampling days (series) were evaluated including 158 air-collected samples and 268 analysis. The summary of the number of samples, replicates, and duplicates is presented in Table 1.

4. Results

Benzene and toluene concentrations (grab samples) in the atmosphere during the different sampling days (series) are presented in Fig. 1. Table 2 presents benzene and toluene average concentrations obtained in the atmosphere of the sampling sites.

Air-quality monitoring studies recommend to evaluate the precision of both the analytical and the sampling technique. The Urban Air Toxic Monitoring Program (UATMP) in the United States uses the relative percent difference (RPD) in order to evaluate precision (USEPA, 1997). As a relative indicator of precision, the RPD expresses average concentration differences relative to the magnitude of the concentration observed. Table 3 shows RPD for the case of benzene concentrations, both for duplicate samples as well as for replicate analysis.

In order to evaluate the air-quality variation with the time, Fig. 2 shows the distribution of benzene and toluene average concentrations during the days of the week.

The relation between benzene concentrations determinated both as grab sampling and integrated 24 h sampling at the University of Mexico is presented in Fig. 3. Grab samples at this site presented higher values (about 40 percent), compared to integrated (24 h) sampling.

The ratio toluene/benzene was determinated for all the samples. Table 4 shows the average of the ratio at the sampling sites.

5. Discussion

The distribution pattern of the average concentrations of benzene and toluene shows a significant variation among the days of the week for the gas station and the condominium area. In these sites, the day with the highest levels of benzene and toluene was the Saturday due to the increase in the activity of the mobile sources.

The University campus site presented similar concentrations along all the days of the week for the sampling periods (grab and integrated). This situation could occur since this site is located on the roof of a two-floor building relatively at a distance from high-traffic avenues.

A significant variation for benzene and toluene concentrations exists for the urban sites (condominium and University campus) with the gas station. The gas station presented the most critical values (an average of 25.8 ppb and a maximum of 141 ppb of benzene).

Table 1
Number of samples, replicates, and duplicates

Sampling site	Samples	Replicates	Duplicates	Total
University (integrated sampling)	26	17	0	43
University (grab sampling)	33	31	11	75
Condominium (grab sampling)	33	31	11	75
Gas station (grab sampling)	33	31	11	75
Total	125	110	33	268

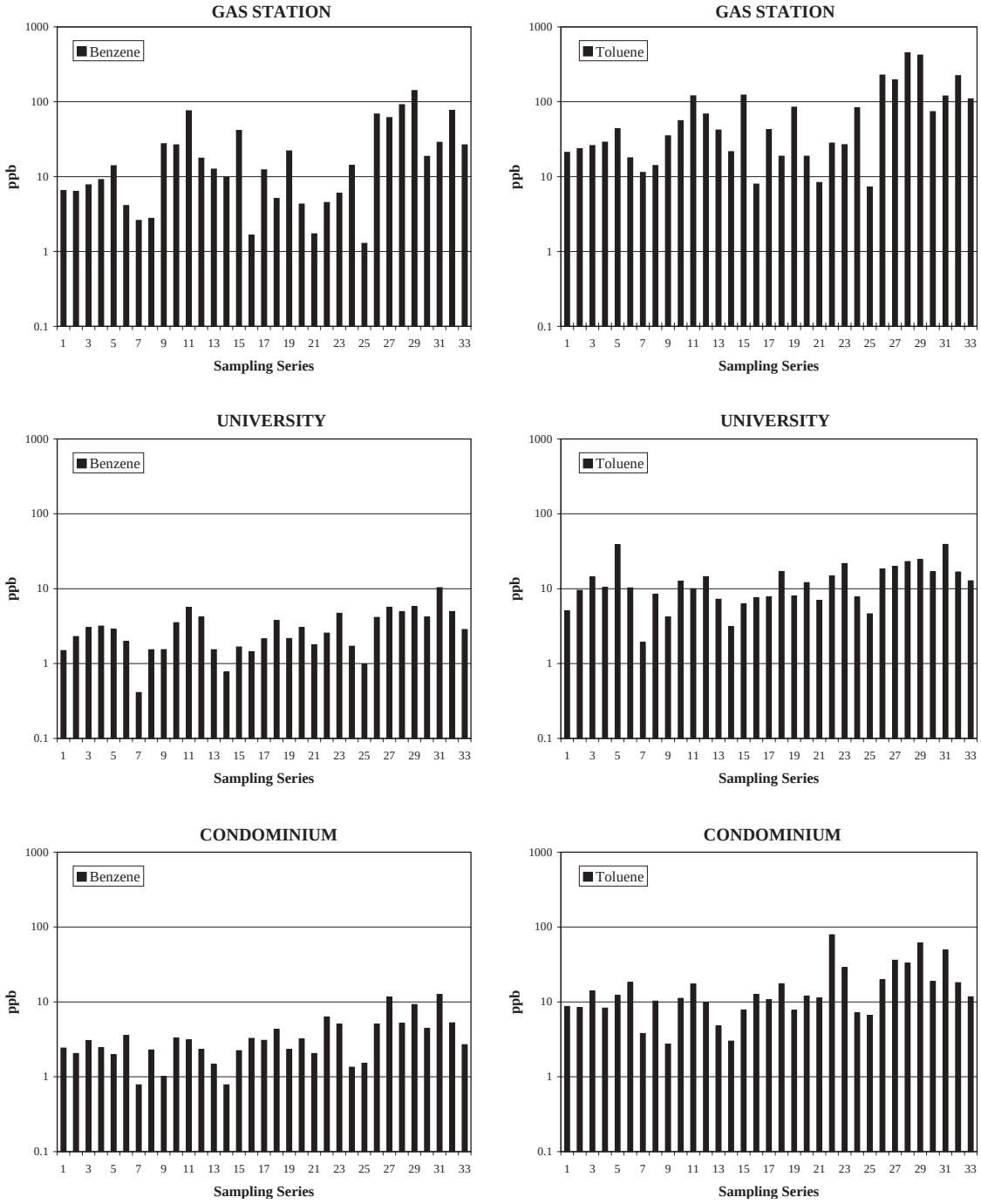

Fig. 1. Benzene and toluene concentrations during the sampling series.

The comparison between benzene concentrations determinated in both grab sampling and integrated 24 h sampling at the University campus, resulted in a good correlation coefficient (0.79). The grab sampling values were higher than 24 h integrated values (about 40 percent), since that grab samples were collected at the hours of maximum levels of VOCs.

The toluene/benzene ratios show an influence from mobile source emissions at the three monitoring sites. For the University campus and the condominium site

Table 2
Average concentrations of benzene and toluene

Sampling sites	Benzene (ppb)	Toluene (ppb)
University (integrated sampling)	1.66±0.24	7.50±0.94
University (grab sampling)	3.11±0.35	13.19±1.53
Condominium (grab sampling)	3.67±0.49	17.63±2.96
Gas station (grab sampling)	25.83±5.64	84.87±18.93

the ratio toluene/benzene presented levels observed in influenced areas, both for diesel vehicles as well as for gasoline vehicles (4.30 for the University campus and 4.81 for the condominium site). In the gas station the contribution due to evaporative emissions and gasoline vehicle emissions resulted in a lower ratio of toluene/benzene (3.89).

The average concentration of benzene obtained at the University campus by the integrated sampling was 1.7 ppb. This level is higher than the air-quality standard (AQS) in other countries (1 ppb). It is important to mention that this is relatively a clean site.

Table 3
Relative percent differences for benzene concentrations

Sampling sites	Replicates	Duplicates
University (integrated sampling)	17.8	—
University (grab sampling)	10.3	14.5
Condominium (grab sampling)	6.6	12.5
Gas station (grab sampling)	7.6	24.1

6. Conclusions and recommendations

The feasibility of an AQS for benzene should be evaluated in Mexico, accepting that absolute safety cannot be guaranteed and therefore we recommend that continuously controlling steps need to be taken to reduce concentrations below this standard.

For practical purposes, we consider that a concentration level of benzene (AQS) must be established at which the risks are exceedingly small and can be detected by any existing method.

Although there is a fuel regulation for gasoline in Mexico, it permits a maximum of 1 percent of benzene, hence more than 60 percent of vehicles do not have catalytic converter, it is expected that most of this benzene is emitted through exhaust.

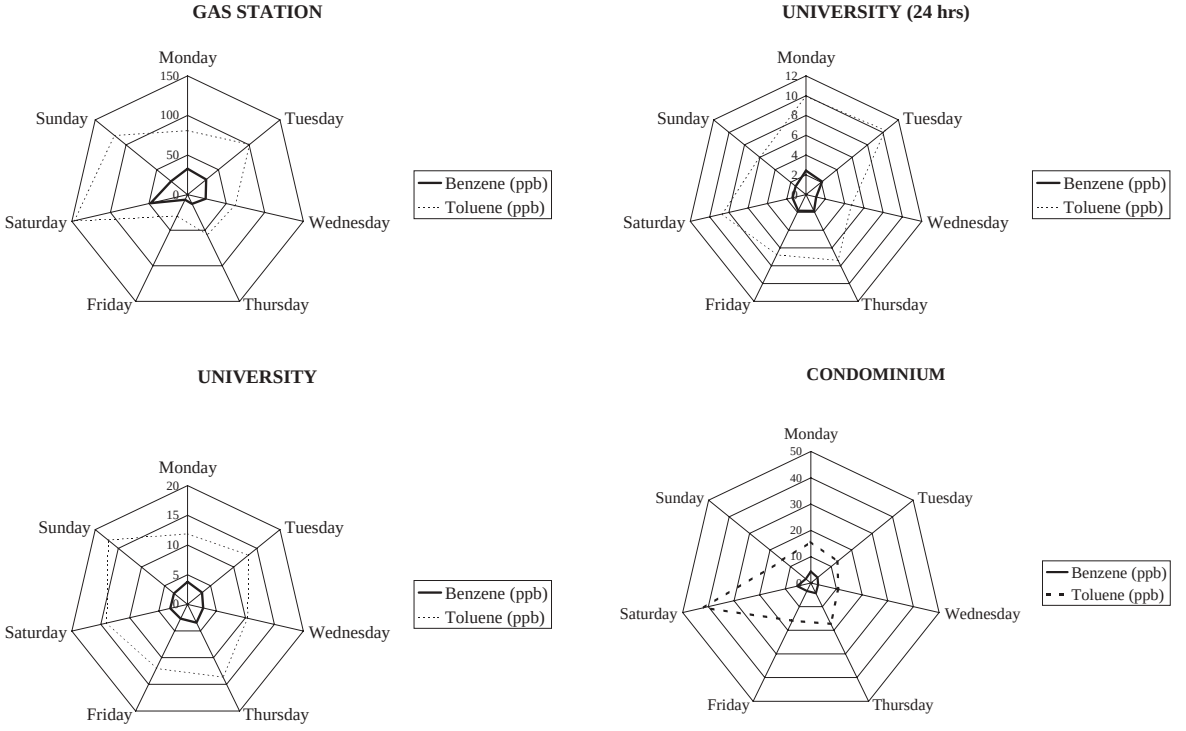

Fig. 2. Distribution of benzene and toluene concentrations during the days of the week.

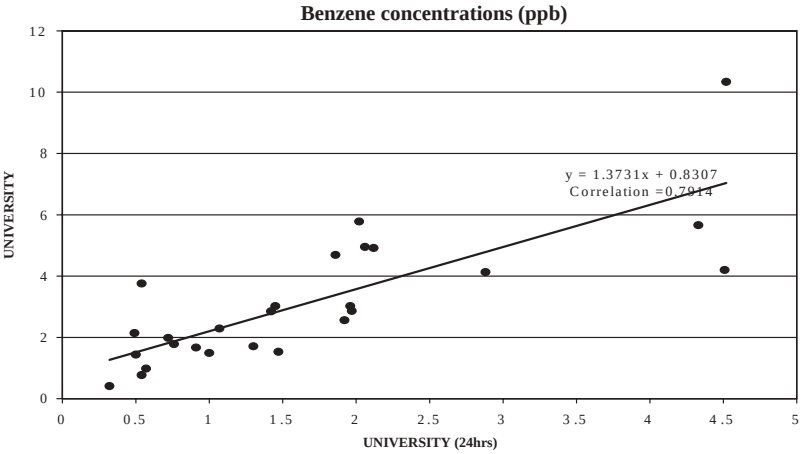

Fig. 3. Correlation between grab and integrated (24 h) sampling at the University.

Table 4
Ratio of toluene/benzene at the sampling sites

Sampling sites	Toluene/benzene
University (integrated sampling)	4.75
University (grab sampling)	4.30
Condominium (grab sampling)	4.81
Gas station (grab sampling)	3.89

Besides, integrated 24 h air sampling followed at the University campus, extends this kind of sampling to the other sites (condominium and gas station).

Adequate operation of vapor recovery systems at the gas stations must be evaluated.

The hazardous air pollutants (HAPs)(toxics), such as benzene and toluene are very important and need to be considered in the environmental control regulations and programs in Mexico and through the world.

In the MCMZ, control strategies for COVs should be directed considering not only their importance as ozone precursors, but taking into account that some specific compounds are HAPs.

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