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Environmental exposure of commuters in Mexico City to volatile organic compounds as assessed by blood concentrations, 1998

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Abstract

Objective. To assess the extent of exposure for Volatile Organic Compounds (VOCs) among nonoccupationally exposed commuters in Mexico City. **Material and Methods.** Blood concentrations of benzene, toluene, ethylbenzene, m-/p-xylene, o-xylene and methyl tert-butyl ether were determined on samples collected from participants after the morning commute. **Results.** Median blood concentrations of benzene (0.11 µg/l), ethylbenzene (0.081 µg/l), m-/p-xylene (0.32 µg/l) and toluene (0.56 µg/l) in the Mexico City participants were all approximately two times higher than in a nonsmoking subset of the Third National Health and Nutrition Examination Survey population of the United States. On the other hand, median VOC blood levels were similar to medians observed in other studies involving commuters in specific U.S. cities, despite the fact that only half the Mexico City study participants commuted by personal vehicles compared with all U.S. commuters. **Conclusions.** These results reflect the extent of the air pollution problem in Mexico City. The surrounding topography exacerbates the problems caused by heavy vehicular traffic, poor emission-control devices on older vehicles, and poor maintenance practices. Elevated levels of gasoline components in the blood of non-occupationally exposed commuters emphasize the need for

Resumen

Objetivo. Evaluar la exposición a compuestos orgánicos volátiles en usuarios de transporte no expuestos ocupacionalmente en la Ciudad de México. **Material y métodos.** Se determinaron las concentraciones sanguíneas de benceno, tolueno, etilbenceno, m/p-xileno, o-xileno y metil-terbutil éter en muestras obtenidas de participantes después del traslado matutino. **Resultados.** Las concentraciones promedio de benceno en sangre (0.11µg/l), etilbenceno (0.081µg/l), m-/p-xileno (0.32µg/l) y tolueno (0.56µg/l) en los participantes de la Ciudad de México son aproximadamente dos veces más elevadas que en la submuestra de no fumadores de la Tercera Encuesta de Nutrición y Salud (Third National Health and Nutrition Examination Survey) en la población de Estados Unidos de América. Por otro lado, la mediana de los niveles de Compuestos Orgánicos Volátiles fueron similares a las medianas observadas en otros estudios de viajeros en ciudades de los Estados Unidos de América, no obstante el hecho de que sólo la mitad de los participantes de la Ciudad de México viajan en vehículos de uso personal, en comparación con los viajeros de los Estados Unidos de América. **Conclusiones.** Estos resultados reflejan el problema de la contaminación ambiental en la Ciudad de México, donde la topografía que la rodea incrementa los problemas causados

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regulatory initiatives and mass-transit options to reduce hydrocarbon emissions and thus reduce the risk for nonoccupational exposure for the residents of Mexico City. The English version of this paper is available too at: <http://www.insp.mx/salud/index.html>

Key words: benzene; blood benzene levels; volatile organic compounds; commuters; Mexico

por el tráfico vehicular intenso, el bajo control de emisiones en los vehículos viejos y las pobres prácticas de mantenimiento. Los niveles altos de componentes de gasolina en la sangre de los viajeros no expuestos ocupacionalmente enfatizan la necesidad de iniciativas regulatorias y alternativas para disminuir el tráfico que reduzcan las emisiones de hidrocarburos y, en consecuencia, el riesgo de exposición no ocupacional para los residentes de la Ciudad de México. El texto completo en inglés de este artículo también está disponible en: <http://www.insp.mx/salud/index.html>

Palabras clave: benceno; niveles sanguíneos de benceno; compuestos orgánicos volátiles; usuarios de transporte; México

Occupational exposure to benzene, a human carcinogen, results in an increased risk for developing certain types of cancers,¹⁻⁴ most notably leukemia. Additionally, nonoccupationally exposed populations may be at risk because benzene may be carcinogenic at low levels of exposure over the long term.⁵ The primary nonoccupational sources of benzene exposure are vehicle emissions (both vehicular exhaust and evaporative losses of fuel) and tobacco smoke. Studies conducted in the United States⁶ and the United Kingdom⁷ attributed 82% and 97%, respectively, of benzene emissions to vehicular emissions. Although ambient air quality is monitored in Mexico City, pollutant concentrations inside vehicles traveling in slow-moving, high-density traffic are generally higher than concentrations in ambient air.⁸⁻¹⁰ Consequently, several studies have been conducted to measure the in-vehicle exposures of commuters to vehicle emissions.⁹⁻¹⁶ In a recent study of populations in Mexico City that were occupationally exposed to gasoline fumes and/or to vehicle emissions,¹⁷ the most striking result was that the unexposed control group ($n = 10$) exhibited higher median blood concentrations for several volatile organic compounds (VOCs) in gasoline than an unexposed US population. To confirm this result, we sampled a larger ($n = 93$) nonoccupationally exposed population in Mexico City. Blood concentrations of benzene, toluene, ethylbenzene, *m*-/*p*-xylene, *o*-xylene and methyl tert-butyl ether were measured on samples collected from participants after the morning commute into Mexico City. Toluene, ethylbenzene, and the xylenes, though not human carcinogens, are often studied along with benzene because of similarities in chemical structure and sources of exposure. Toluene is present in vehicle emissions and in tobacco smoke and the others are present in vehicle emissions. Methyl tert-butyl ether, a relatively recent additive to gasoline, has

also been included because of concern about various health effects that may be associated with its use.

Material and Methods

The study population consisted of a convenience sample of adult volunteers working in a governmental office located in downtown Mexico City. Participants were informed about the risks involved in participating in the study and were asked to sign a consent form and to complete a questionnaire that provided information on their sociodemographic characteristics and their potential for exposure to VOCs. The study population was comprised of 93 volunteers (48 women) ranging in age from 19 to 59 years (median age 30 years). All participants were nonoccupationally exposed to gasoline fumes, but approximately 23 (25%) were smokers, 76 (82%) reported having a gas boiler outside the house, others used another appliance to heat the water, and 43 (45%) always kept the stove pilot flame on. During the commute, participants were asked to avoid refueling and smoking and to minimize exposure to environmental tobacco smoke. Each participant provided a 10-ml blood sample immediately after arriving at the workplace. Blood samples were obtained by venipuncture and collected into specially prepared Vacutainer tubes (Becton Dickinson, Rutherford, NJ) containing a mixture of potassium oxalate and sodium fluoride as an anticoagulant.

As in the previous study,¹⁷ blood samples were analyzed at the Centers for Disease Control and Prevention (CDC) in Atlanta, GA. Vacutainer tubes used in sample collection were previously treated to remove VOC contaminants and examined to verify that the contaminants were adequately removed.¹⁸ Blood samples were maintained at 4 °C during storage and ship-

ment. Samples can be stored in this manner for up to 7 weeks without measurably affecting the results of the analyses.¹⁹ The analysis was performed by purge-and-trap gas chromatography isotope dilution mass spectrometry as described by Ashley *et al.*²⁰ Briefly, samples, heated to 30⁻⁰ C, were purged for 15 min with helium and trapped on Tenax (Tekmar-Dohrmann, Cincinnati, OH). After dry purging for 6 min to remove absorbed water, the trap was thermally desorbed at 180⁻⁰ C for 4 min. The VOCs were cryogenically trapped at the gas chromatograph (GC) injection port, then injected onto the GC column by rapidly heating the cryogenic trap. Separation was obtained on a DB-624 (J&W Scientific, Inc., Folsom, CA) capillary GC column. High-resolution mass spectrometry was performed at full scan over a mass range of 40-200 amu at 1 scan/s on a VG 70S sector mass spectrometer (Micromass, Inc., Beverly, MA).

Before analysis, each sample was spiked with stable isotopic analogs of the native compounds of interest. The responses of specific ions from the unknown sample relative to the labeled analog were measured against a six-point calibration curve to quantitate the results.

Spiked blood samples were analyzed to determine the accuracy and precision of the method, resulting in an estimated precision of <20% relative standard deviation. Method blanks were prepared from a water source free of VOCs. The limits of detection (LODs) for the compounds reported here are: benzene 0.010 µg/l; ethylbenzene 0.031 µg/l; o-xylene 0.050 µg/l; m-/p-xylene 0.019 µg/l; toluene 0.016 µg/l; styrene 0.0083 µg/l; and methyl tert-butyl ether (MTBE) 0.021 µg/l.

The purge-and-trap method described here and a similar method based on headspace analysis are the two methods commonly used to measure VOCs in blood. Ashley *et al* have participated in inter-laboratory comparisons to ensure comparable results between the two methods.* The purge-and-trap method results in improved LODs as a consequence of more complete removal of the VOCs from the sample matrix.

Questions designed to eliminate participants who may have been exposed to the components of gasoline fumes from sources other than the morning commute did not lead to the removal of any subjects from the data set. Data were analyzed using SAS statistical software (SAS Institute, Inc., Cary, NC). The Shapiro and Wilk test indicated that the data were not normally distribut-

ed ($p=0.0001$) but were skewed to the right for most analytes. Neither the square root nor the log transform successfully produced a normal distribution for all analytes. For consistency, nonparametric methods utilizing the Wilcoxon Rank Sum Test were used for all comparisons and significance was determined at the 95% confidence level. Stratification of the data by smoking status indicated a statistically significant difference ($p < 0.05$) for most VOCs, even for VOCs not associated with smoking. However, dimethylfuran, which is considered a biomarker for smoking, was not significantly different. These results and reports by most participants of smoking less than 10 cigarettes/day suggested that the differences were not associated with smoking. Therefore, the results presented are for all commuters, regardless of smoking status. Some VOC values are missing for some of the participants because either the sample volume was insufficient for analysis or the analysis was out of control for the missing analyte(s) at the time the analysis was performed. The blood concentrations are given in terms of the maximum, minimum, median, 90th and 95th percentiles for benzene, ethylbenzene, m-/p-xylene, o-xylene, toluene and MTBE (Table I). For statistical purposes, values listed as below the detection limit were given values of half the LOD according to the method by Nehls and Akland.²¹

Results

The concentrations of the compounds related to gasoline exposure that were measured in blood samples from Mexico City commuters are presented in Table I. The primary means of commuting was by automobile for 50% (45% by personal vehicles and 5% by taxi) of the subjects and by bus for 45%; the remaining 5% designated either another (4%) or walking (1%) as their primary mode of transportation. The levels of gasoline-related compounds in the blood of automobile versus bus commuters would be expected to differ on the basis of exposure to different fuel types (gasoline versus diesel). However, in Mexico City there are two types of buses: diesel and gasoline-powered minibuses. Because the study design did not allow for a distinction between these two types of buses, an unknown number of bus commuters were also exposed to gasoline-related compounds. Consequently, a comparison of the blood VOC concentrations between participants who commuted by bus (median commute 75 min) and participants who commuted by automobile (median commute 60 min) revealed no significant differences ($p = 0.05$). Additionally, the blood concentrations for these compounds might be expected to be highest for those participants with the longest commutes; however,

* Ashley D. Quality Assurance Project/ BTX in Blood. Human Blood Samples for Interlab Comparison. Atlanta (GA): Centers for Disease Control, Public Health Services, US Department of Health and Human Services, 1997. Unpublished data.

regression analyses performed on each of the analytes showed no correlation ($R^2 < 0.01$) for either mode of travel. The one-way commute to the workplace by automobile ranged from 2 to 120 min, and by all other means, from 5 to 180 min.

Mexico City commuters had significantly lower blood levels of benzene, ethylbenzene, m-/p-xylene and o-xylene ($p < 0.05$) than the control group of beginning-shift office workers in the previous Mexico City study.¹⁷ A comparison of toluene and MTBE between commuters and office workers, however, indicated no significant differences. Because blood samples were taken after the morning commute from office workers who were not occupationally exposed, VOC blood levels would be expected to be similar to those of the commuters in the current study. However, the results indicate that, even though commuters and office workers may have been exposed to similar sources of toluene and MTBE during the commute, office workers may have been exposed to additional sources of the other four compounds. Alternatively, the differences may simply be due to analysis of a different population or to the small sample size of the office workers.

The Third National Health and Nutrition Examination Survey (NHANES III) data are used as a reference range for the general U.S. population.²² A comparison of the current data to a nonsmoking subset of the NHANES III data showed a significant difference in the distributions of the two data sets ($p < 0.01$) for all the VOCs, except for MTBE, which was not measured in NHANES III. Table II shows the median blood levels of benzene, ethylbenzene, m-/p-xylene, o-xylene, toluene and MTBE for the Mexico City commuters compared with a nonsmoking subset of the NHANES III population. For benzene, ethylbenzene, m-/p-xylene and toluene, the medians for the commuters

are approximately two to three times higher than the medians for the NHANES III population, while the o-xylene results were approximately the same. All the Mexico City participants are considered nonsmokers, because the few who did smoke, smoked fewer than 10 cigarettes/day.

Discussion

Median blood VOC levels for Mexico City commuters are consistent with medians observed in other studies involving commuters (Table II). Mexico City medians for benzene, ethylbenzene, and m-/p-xylene are approximately midway between the median blood levels for commuters in Connecticut and Alaska. For o-xylene, the medians are similar for Mexico City and Connecticut commuters; the median for Alaska commuters is 2.5 times higher. The median blood toluene level for commuters from Mexico City is 1.5 times higher than from Alaska and three times higher than from Connecticut. Mexico City commuters also had median blood MTBE levels two times higher than Connecticut commuters, even though the percentage of MTBE added to gasoline in Mexico²³ (5%) is one third that added to gasoline in the US (15%). The results for toluene and MTBE indicate the possibility of additional sources of exposure in Mexico City. Additionally, the topography surrounding Mexico City contributes to higher concentrations of air pollutants in the city and this increased concentration may be responsible for the elevated blood levels in commuters. Gasolines, formulated for maximum performance according to weather conditions and temperature extremes, differ seasonally as well as regionally. Thus, differences in the gasolines used in the Alaska (winter), Connecticut

Table 1
BLOOD LEVEL CONCENTRATIONS ($\mu\text{g/L}$) OF BENZENE, ETHYLBENZENE, M-/P-XYLENE, O-XYLENE, TOLUENE AND METHYL TERT-BUTYL ETHER (MTBE) FROM COMMUTERS IN MEXICO CITY, 1998

Analyte	n	Mexico City commuters				
		Minimum	Median	90 th Percentile	95 th Percentile maximum	
Benzene	84	0.028	0.11	0.20	0.34	0.57
Ethylbenzene	81	0.015	0.081	0.16	0.27	0.85
o-Xylene	71	0.025	0.080	0.14	0.26	1.3
m-/p-Xylene	86	0.096	0.32	0.49	0.81	2.8
Toluene	72	0.12	0.56	1.3	2.0	3.2
MTBE	82	0.037	0.24	0.69	1.2	9.2

* Some results were not included because the analysis failed to meet quality-assurance/quality-control requirements

Table II
BLOOD LEVELS ($\mu\text{g/L}$) OF VOLATILE ORGANIC COMPOUNDS DERIVED FROM GASOLINE IN COMMUTERS FROM MEXICO CITY, US CITIES, AND A NONSMOKING SUBSET FROM NHANES III

Analyte	Mexico City <i>n</i> =86 ^{&} Median	Stamford, CT [*] <i>n</i> =14 ^{&} Median [#]	Fairbanks, AK [†] <i>n</i> =26 ^{&} Median	Albany, NY [§] <i>n</i> =19 Median	NHANES III [#] <i>n</i> =546 ^{&} Median
Benzene	0.11	0.050	0.19	0.12	0.047
Ethylbenzene	0.081	0.060	0.10	0.048	0.047
m-/p-Xylene	0.32	0.24	0.44	0.14	0.16
o-Xylene	0.080	0.082	0.20	0.045	0.094
Toluene	0.56	0.18	0.38	0.16	0.21
MTBE [¶]	0.24	0.12	NM [¶]	<DL [◇]	NM [¶]

* Reference 24

† Reference 25

§ Mannino *et al.*, Unpublished data

Reference 22

& Some results were not included because the analysis failed to meet quality-assurance/quality-control requirements

¶ These values have been corrected for vacutainer background, whereas previously published data were not

¶ MTBE = methyl tert-butyl ether. Percentage of MTBE in gasoline is 5% in Mexico City²² and 15% in Stanford.²³

MTBE was not present in regular gasoline in Fairbanks²⁵ and Albany²⁴.

◇ NM = not measured

◇ <DL = less than detection limit

(winter), and Mexico City (spring) studies may partially account for the differences in the blood.

The range of blood benzene levels (BBLs) for Mexico City commuters is also consistent with ranges observed in the above studies and studies of other nonoccupationally exposed persons (Figure 1). Mexico City commuters had BBLs ranging from 0.028 to 0.57 ppb. White *et al.*²⁴ observed BBLs ranging from the LOD (=0.030 ppb) to 0.51 ppb among 14 commuters in Stamford, Connecticut. BBLs, ranging from 0.076 to 0.40 ppb, were observed among 19 commuters in Albany, New York studied by Mannino *et al.*^{*} Backer *et al.*²⁵ observed a range of 0.080 to 0.65 ppb before pumping regular gasoline for 26 participants in a Fairbanks, Alaska, study designed to measure exposure during refueling. For NHANES III, the range is from the LOD (= 0.030 ppb) to 0.55 ppb. The other analytes exhibited a similar trend. For all the above-mentioned studies, the same method was used to analyze the blood samples as for the current study. Studies by Brugnone *et al.*, using a different analytical method, showed slightly higher BBLs among 58 hospital staffers (range 0.015-1.7 ppb, median 0.23 ppb)²⁶ and among 179 nonsmoking, nonoccupationally exposed workers from an urban area (0.015 to 0.92 ppb, median 0.18 ppb).²⁷

* Mannino DM, Schreiber J, Aldous K, Ashley D, Moolenaar R, Almaguer D. Unpublished data.

Several studies^{8,11,12,28-30} have measured commuter exposure indirectly by measuring in-vehicle VOCs and comparing these values to ambient air measured at fixed monitoring stations. Chan *et al.*¹¹ and Lawryk *et al.*²⁸ reported in-vehicle medians for benzene (14, 15 $\mu\text{g}/\text{m}^3$), ethylbenzene (11, 8.7 $\mu\text{g}/\text{m}^3$), m-/p-xylene (40, 34 $\mu\text{g}/\text{m}^3$), o-xylene (15, 13 $\mu\text{g}/\text{m}^3$), and toluene (59, 54 $\mu\text{g}/\text{m}^3$) that were similar for Raleigh, North Carolina and New York City/New Jersey area commuters, respectively. Ambient concentrations were also similar except for the xylenes, which were approximately two times higher in Raleigh. In-vehicle/ambient air concentration ratios for these five VOCs indicated that in-vehicle concentrations ranged from 7 to 16 times higher than ambient air concentrations. Jo and Park³⁰ measured median in-vehicle benzene and MTBE levels of 45 and 49 $\mu\text{g}/\text{m}^3$ in Korea that produced in-vehicle/ambient air ratios of 9 and 14, respectively. By comparison, the ambient air concentration of benzene in Mexico City was 45 $\mu\text{g}/\text{m}^3$ (annual hourly mean) in 1995, similar to in-vehicle concentrations in Korea. Duffy *et al.*²⁹ provide an extensive table of in-vehicle benzene concentrations from previous studies. High blood benzene levels in Mexican commuters may increase their risk of benzene-related cancers; a study by Serrano³¹ reported that the environmental concentration of benzene as measured by personal monitoring was 17.5 $\mu\text{g}/\text{m}^3$ in Mexico City and the risk of acquired cancer was 1×10^{-4} .

In all these studies, in-vehicle concentrations greatly exceed concentrations measured at monitoring stations that are often situated several feet above and away from the roadway. The main sources of in-vehicle exposure are the exhaust of nearby vehicles and vehicle self-contamination.⁸ Several factors, including the design and condition of engines and fuel-distribution systems, ventilation conditions, traffic density and velocity, meteorological factors, and gasoline compositions, can influence local VOC emissions and/or commuter exposure levels from these sources. Lawryk *et al*²⁸ found roadway air to be the primary VOC source in vehicles with fuel injection and properly functioning carburetors. On the other hand, both Lawryk *et al*²⁸ and Jo and Park³⁰ found that most in-vehicle VOCs were higher for carbureted vehicles under low-ventilation conditions, indicating that carbureted vehicles may be more self-contaminating than fuel injected vehicles. Lawryk *et al*²⁸ found that all substituted aromatics were two times higher for carbureted vehicles; and Jo and Park³⁰ found that benzene and MTBE were 3.5 times greater. In Mexico City, the minibuses and the majority of automobiles are carbureted, thus vehicle self-contamination contributes to the high levels of VOCs found in Mexico City commuters.

Measurements of gasoline-related compounds inside vehicles have shown that models based on ambient air concentrations at monitoring stations underestimate VOC exposure to commuters. This study assesses commuter exposure by directly measuring the concentrations of these VOCs in the blood of exposed persons. Median VOC blood levels in the Mexico City commuters were two to three times higher than in the general US population represented by NHANES III but were similar to blood levels for commuters in specific US cities. These results confirm the conclusion of previous in-vehicle studies that an increase in exposure to VOCs occurs during the commute. Lofgren *et al* have predicted that commuters receive approximately 50% of their daily VOC exposure during the commute,⁹ and Wallace has stated that approximately 25% of benzene exposure results from personal activities, primarily driving or riding in automobiles, and approximately 25% from outdoor sources, primarily vehicle exhaust.¹⁵ In view of the health risks associated with exposure to gasoline-related compounds, reducing the amount of exposure to these compounds during the commute is important. As Duffy *et al*²⁹ and Chan *et al*¹¹ observed, the most effective means for an individual to reduce personal exposure to exhaust is by driving with the vents closed or with the air conditioner operating. In Mexico City, buses do not have air conditioning, and although newer-model automobiles do, few commuters use it, so

that exposure to vehicle exhaust also contributes to the increased levels of VOCs in the blood of the commuters. Providing air-conditioned buses and promoting the use of air conditioners in automobiles so equipped would reduce exposure from the exhaust of nearby vehicles. Additionally, Chan *et al*¹¹ found no significant difference in VOC levels between two well-maintained vehicles of different ages, and Lawryk *et al*²⁸ observed much higher in-vehicle VOC levels in a malfunctioning vehicle than in a correctly functioning one. These results suggest that routine maintenance and regular inspections could significantly reduce in-vehicle exposures to gasoline-related compounds. Chan *et al*¹² found in-vehicle VOC concentrations for urban routes to be about 1.5 times higher than on interstate routes. Thus, reducing urban traffic density by improving mass-transportation options or traffic flow through congested areas would also improve the quality of in-vehicle air.

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