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Commuters' exposure to $PM_{2.5}$, CO, and benzene in public transport in the metropolitan area of Mexico City

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Abstract

A survey was carried out to measure commuters' exposure to $PM_{2.5}$, CO, benzene, and the chemical composition of $PM_{2.5}$ on different routes and modes of transport in Mexico City. $PM_{2.5}$ ($n = 62$), CO ($n = 54$) and benzene ($n = 22$) are presented from morning (6:30–9:30 a.m.) and evening (17:30–20:30) rush hours on minibuses, buses and Metro (underground or subway system). Three routes were selected from a previous commuters' exposure study covering some of the most important thoroughfares of the valley. For $PM_{2.5}$, mass concentration was determined for all the samples. Nitrates, sulphates, inorganic elements and carbon fraction were analysed. CO was sampled using electrochemical sensors and 6-l canisters with flow controller devices were used to collect integrated samples for benzene. Minibuses had a slightly higher geometric mean $PM_{2.5}$ concentration in the morning than other modes of transport, but the ranking of geometric mean $PM_{2.5}$ by mode of transport is opposite in the evening and the variability within modes is approximately double the difference between modes. The highest single measurement was a concentration of $137\,\mu g\,m^{-3}$ on a bus during an evening rush hour. The main component identified in $PM_{2.5}$ was carbon. Carbon monoxide levels in this study were approximately 3 times lower than those found in a commuter exposure study conducted in 1991. A strong association was shown between wind speed and $PM_{2.5}$ exposure in minibuses ($r^2 = 0.50$) and buses ($r^2 = 0.54$). The relationship between wind speed and CO exposure was strong only in minibuses ($r^2 = 0.52$).
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Keywords: Mexico city; Public transport; Commuters' exposure; $PM_{2.5}$; CO; Benzene

1. Introduction

The Metropolitan area of Mexico City is one of the biggest and most important developing urban areas with serious air pollution problems. Mexico City has a vehicle fleet of approximately 3.2 million vehicles and an

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atmosphere containing a complex cocktail of pollutants covering an area where more than 20 million people work, live, and commute every day. The transport sector (Colvile et al., 2001), has been identified as a major source of air pollution. In 1994, the trips per person registered were 20.6 million in the metropolitan area of Mexico City (SETRAVI, 2002). The modal distribution of the transport sector in the city has shifted from medium (buses) and high capacity (Metro, light rail and trolleybus) to low-capacity motor vehicles (minibus, combis, taxis and private cars) in the past 15 years. For low-capacity vehicles, minibus shows the highest shift from carrying 6% of commuters in 1986 to 55% in 2000 (SETRAVI, 2002). In order to decrease this trend, the local authority is implementing a scheme to replace old minibuses with new buses.

Concentrations of the pollutants $PM_{2.5}$, CO and benzene are indicators of health effects of pollution originating from inefficient combustion. In Mexico City, $PM_{2.5}$ has been measured and chemically characterised using different state of the art techniques at the urban scale (Aldape et al., 1996; Miranda et al., 1998; Edgerton et al., 1999; Chow et al., 2002). The potential health effects caused by $PM_{2.5}$ have also been investigated, including mortality (Borja-Aburto et al., 1998; Castillejos et al., 2000) and cardiovascular dysfunctions in different cohorts (Holguin et al., 2001). For CO (Riveros et al., 1998) and benzene (Bravo et al., 2002; Meneses et al., 1999; Ortiz et al., 2002), some studies have been conducted to evaluate levels in different microenvironments as well as at the urban scale level to understand the complexity in the formation of air pollutants in the city. However, the exposure during morning and evening rush hours have not been evaluated for $PM_{2.5}$, CO and benzene simultaneously. In Mexico City, only one study has been conducted to evaluate CO levels of commuters in different transport modes (Fernandez-Bremauntz and Ashmore, 1995). In Europe, studies evaluating commuters' exposure for one or more pollutants (Kingham et al., 1998) have been carried out within different means of transportation, measuring levels of $PM_{2.5}$ (Adams et al., 2001a) and elemental carbon (see Adams et al 2002), CO (Clifford et al., 1997), and VOCs (Van Wijnen et al., 1995). In the United States, several studies have conducted measurements in transport microenvironments, mainly in private cars. They evaluated one or more of the pollutants selected for this study (Brice and Roesler, 1966; Chan et al., 1991a, b; Ott et al., 1994; Rodes et al., 1999). In Asia, exposure in public transport was evaluated in Hong Kong (Chan and Liu, 2001; Chan et al., 2002a) and China (Chan et al., 2002b) but these studies did not measure the same pollutants and modes of transport as this study. Chemical speciation of particles has been conducted only in a few studies (Adams et al., 2002; Zielinski et al., 1997), to identify potential sources and determinants of commuters' exposure (Adams et. al., 2001b). The overall aim of this study was to quantify the levels of commuter exposure to $PM_{2.5}$ and its chemical composition, CO and benzene during morning and evening rush hours, focusing on three public transport modes on three different routes in Mexico City.

2. Methods

2.1. Selected public transport and corridors

The campaign methods were based on a combination of two studies conducted to assess the personal exposure of transport users in Mexico City (Fernandez-Bremauntz and Ashmore, 1995) and London (Adams et al., 2001a). The public transport modes chosen for the study were minibuses, buses and the Metro. According to local authorities, these means of transportation represent 78% of the modal distribution in Mexico City (SETRAVI, 2002). Measurements focused more on minibuses than buses and Metro because minibuses represent 55% of the transport modal distribution.

Three routes were selected out of the five sampled by Fernandez-Bremauntz and Ashmore (1995). The criterion for selecting the routes was to cover the four cardinal points of the city from North to South (Indios Verdes–San Angel) and East to West (Pantitlan–Tacuba). A third route Northeast-Centre (La Villa–Auditorio) was evaluated to assess the exposure inside the area where the highest concentrations of PM_{10} have been registered in previous years in the Ambient Air Monitoring Network of Mexico City (GDF, 2001a). Fig. 1 shows the map of these routes.

2.2. Sampling design

The study was conducted from 6 May to 1 June 2002. Measurements of $PM_{2.5}$, CO, and benzene were made during 4 weeks from Monday to Saturday. 6 days were sampled during each week for the selected modes of transport (minibus, bus and the Metro). Rush hour and off-peak times of day were sampled on alternate days. On the 3 days per week when rush hours were sampled, journeys were made in one direction in the morning (06.30–09.30) and in the opposite direction in the evening (17.30–20.30). On the other 3 days of the week, the same journeys were made at 11.00–14.00 and 14.00–17.00, but these data will be reported elsewhere.

On the 12 days when sampling was conducted during rush hour, six measurements per day were made—three outbound and three return. During 1 week, one mode of transport per day was sampled simultaneously on the three routes. During the other 3 weeks, one route per day was sampled with three modes of transport

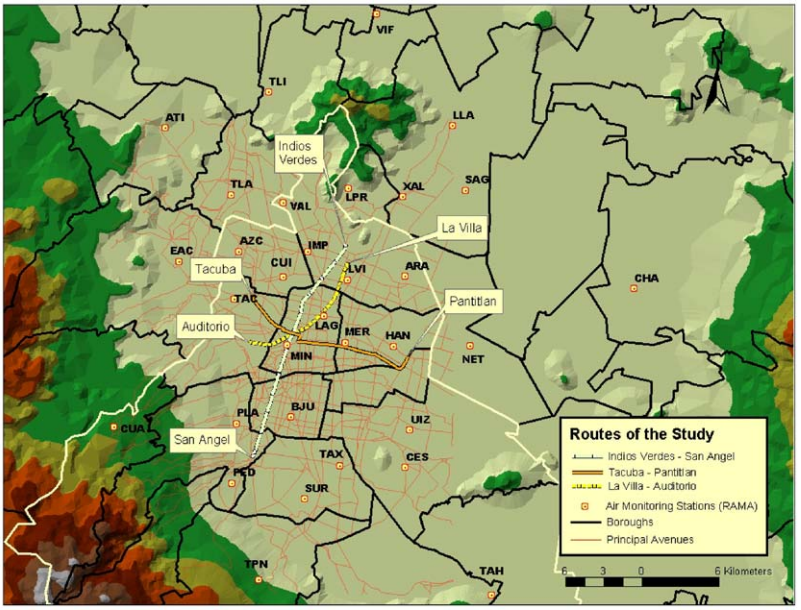

Fig. 1. Map of the study area.

simultaneously, except for 3 days when two route-mode combinations per day of $PM_{2.5}$ were left unsampled to allow a duplicate of one of the other measurements to be made instead.

$PM_{2.5}$ and CO were measured during every sampling period. Benzene samples were taken randomly. After quality control (see Section 2.5), for $PM_{2.5}$, 105 valid samples were collected. Of these, 69 were sampled in morning and evening journeys including 6 duplicates, 23 were for the midday journeys, and 13 were field blanks. The number of valid CO measurements was 89, of which 63 were made on morning and evening journeys including 9 duplicates, and 26 were for midday journeys including 2 duplicates. From 26 valid benzene samples, 22 were taken on morning and evening journeys and only four were taken on midday journeys. Data from midday journeys are not reported here.

2.3. Sampling and measurement equipment

$PM_{2.5}$ was sampled from the breathing zone of trained technicians travelling on the selected modes of transport. Air was drawn through filters using high flow portable sampling (HFPS) pumps (Casella Vortex Ultraflow mass flow controlled at 16 l/min) with particle size selection using a foam inset within a conical inlet (Adams et al., 2001c). The measurement of CO was carried out using electrochemical sensors (Langan Model T15 equipped with a DataBear® data logger). 6-l stainless-steel canisters (SUMMA) with flow controller devices (Parker Instruments model SC235XFTHT) were used to sample benzene (USEPA, 1999a).

At the beginning of every journey, participants turned on the sampling pump for $PM_{2.5}$. Immediately after this, the valve of a 6-l vacuum canister, controlled by a flow controller device, was opened to start collecting a sample of benzene. CO monitors were programmed to measure 1-min averages during the whole journey. The participants turned off the pump of the $PM_{2.5}$ sampler and closed the valve of the canister when they arrived at the end of the journey. They filled in a time-activity diary during the trip to identify potential problems with the equipment, malfunction of vehicles, as well as to identify particular high exposure events produced mainly by smokers or other sources. They were asked not to smoke during the commuting periods.

2.4. Laboratory analysis

For $PM_{2.5}$ samples, the two types of filters used during the study were 37 mm diameter quartz-fibre filters (Whatman®) and 37 mm diameter polymethylpentane ringed teflon-membrane filters (Gelman Science). Teflon-membrane filters were used for gravimetric and elemental analysis. Quartz fibre filters were used to analyse carbon, nitrates and sulphates. Forty four of the samples (71%) were collected on teflon filters and 18 (29%) were collected on quartz filters. A disproportionate number of the quartz filters (10, or 56%) were exposed in minibuses, where elemental carbon (EC) concentrations were expected to be highest, distributed

at random throughout the sampling programme. Because of the need to strike a compromise between number of samples per journey and number of journeys sampled, with a limited amount of equipment available and total weight of equipment carried by each commuter, samples of $PM_{2.5}$ were not taken on teflon and quartz filters for the same mode of transport simultaneously.

Gravimetric analysis was conducted with a microbalance Cahn® model C-35 before and after sampling. The preparation of filters for sampling was in a laboratory with controlled temperature ($22^{\circ}C \pm 3^{\circ}C$) and relative humidity ($40\% \pm -5\%$). Filters were left for conditioning for 48 h before and after sampling periods (CENICA, 2002). For elemental analysis, a non-destructive X-ray fluorescence (XRF) instrument (Jordan Valley AR, model 6600) was used to detect 15 elements (Si, S, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Se, Br, Pb) (USEPA, 1999b). Total carbon (TC), organic carbon (OC) and EC were determined by a thermal optical reflectance TOR system (DRI, model 2001, Atmoslytic, Inc.) using the protocol IMPROVE (Chow et al., 1993). For the analysis of carbon, every sampled quartz filter was punched with a stainless steel punching tool. Two circles with a diameter of $0.526\,cm^2$ each were removed. The rest of the filter was used for nitrate and sulphate analysis. Water extraction for anion analysis was conducted to detect nitrates and sulphates (CARB, 1992). The equipment used for this analysis was an ion chromatograph (Dionex, model DX500). Benzene was characterised using a gas chromatograph with flame ionisation detector (GC/FID) and a preconcentration system (DKK Corporation) (Maeda et al., 1995, 1998).

2.5. Quality assurance and quality control

Flow audits were conducted for the pump of the HFPS and the flow controller devices for 6-l canister before and after every sample journey. A weekly calibration was performed to verify the readings of CO monitors (USEPA, 1977). For benzene, the GC/FID system was verified every week with a standard of 100 ppbV of VOCs. Data capture for $PM_{2.5}$ and benzene was 96% and 93%, respectively. For CO, data capture was 88%. For $PM_{2.5}$, four samples were invalidated. On one occasion (midday journey time), a filter was damaged during handling. Another sample (morning journey) was invalidated because the participant took the wrong mode of transport in the wrong direction. The other two samples not only for $PM_{2.5}$ but also CO and benzene were not taken because the participant designated to take the morning and evening journeys on a Saturday did not attend in the first week of the study. The main loss of data, 10 measurements, was for CO monitors due to disconnected cables internally (2%) or uncharged batteries (8%).

2.6. Data analysis

Descriptive statistics were calculated for the data obtained for every pollutant. The distributions of the measurements were tested for normality using Kolmogorov–Smirnov test. A material balance method was used to estimate the chemical composition of $PM_{2.5}$, grouping geological material, non-crustal elements, organics, EC, ammonium nitrate and ammonium sulphate, and the unidentified part of particles (Chow et al. 2002). For this study, salt, ammonium, and the element aluminium (Al) were not measured. Regression analysis, to assess the effect of wind speed on exposure to $PM_{2.5}$ and CO, was carried out using wind speed data from the closest fixed air-monitoring stations of Mexico City on the evaluated routes as independent variable and the natural logarithm of the minibus and bus commuters' concentrations as dependent variable. Wind speed data were averaged for each of the morning and evening commuting journeys evaluated in this study. Only wind speed information was used for regression analysis because it represents one of the main determinants of temporal variation in commuters' exposure (Adams et al., 2001b). Regression diagnostics were carried out, including residual analysis. The statistical analysis was conducted with SPSS version 10.

3. Results

3.1. Descriptive statistics

Descriptive statistics are shown in Table 1 for selected pollutants divided by mode of transport and time of day. The levels of the selected pollutants divided by mode of transport presented minimal differences. Buses and minibuses had the highest concentrations for all the pollutants. Morning rush commuting periods showed the highest values for all the pollutants mainly in minibuses. On the Metro, the exposure of commuters was similar for morning and evening journeys for CO and benzene. $PM_{2.5}$ was only slightly higher in the evening period.

3.1.1. $PM_{2.5}$

The levels for $PM_{2.5}$ in the selected modes of transport ranged between 12 and $137\,\mu g\,m^{-3}$. The maximum single-journey exposure of $137\,\mu g\,m^{-3}$ was measured in a bus on an evening journey. The lowest single-journey $PM_{2.5}$ exposure was measured in a minibus ($12\,\mu g\,m^{-3}$) in the evening. In the morning period, the highest geometric mean $PM_{2.5}$ concentrations were measured for minibuses ($83\,\mu g\,m^{-3}$). In the evening period, the geometric mean exposure on the Metro ($58\,\mu g\,m^{-3}$) was slightly higher than on other modes.

Table 1
Descriptive statistics for $PM_{2.5}$, CO, and benzene

		$PM_{2.5}$ ($\mu g\,m^{-3}$)						CO (ppm)						Benzene (ppb)					
Mode	Journey	*N*	AM	GM	GSD	Max	Min	*N*	AM	GM	GSD	Max	Min	*N*	AM	GM	GSD	Max	Min
Minibus	a.m.	13	84	83	1.2	106	50	11	18	18	1.3	24	10	6	8	8	1.5	14	5
	p.m.	15	53	48	1.7	96	12	12	12	11	1.4	24	8	6	6	4	2.7	11	1
	a.m. & p.m. combined	28	68	62	1.6	106	12	23	15	14	1.4	24	8	12	7	6	2.2	14	1
Bus	a.m.	8	78	75	1.4	117	46	8	13	13	1.5	20	7	2	7	6	2.0	10	4
	p.m.	8	63	56	1.7	137	23	7	10	10	1.3	14	7	2	5	4	2.6	9	2
	a.m. & p.m. combined	16	71	65	1.6	137	23	15	12	11	1.4	20	7	4	6	5	2.0	10	2
Metro	a.m.	9	61	56	1.5	96	32	8	8	8	1.3	11	5	3	4	4	1.2	4	3
	p.m.	9	61	58	1.5	99	31	8	6	6	1.3	10	4	3	4	4	1.5	5	2
	a.m. & p.m. combined	18	61	57	1.5	99	31	16	7	7	1.3	11	4	6	4	4	1.3	5	2

N: sample size, AM: arithmetic mean, GM: geometric mean, GSD: geometric standard deviation; Max: maximum, Min: minimum.

3.1.2. Chemical composition of $PM_{2.5}$

Fig. 2 shows the averaged composition of $PM_{2.5}$ for minibuses calculated using the method of Chow et al. (2002). Carbon (TC) was the most abundant species found in this particular set of samples with almost 50% of $PM_{2.5}$. The main component of TC was organic carbon (OC), which accounted for 37% of the total composition of $PM_{2.5}$. Ammonium sulphate (21%) was the second highest constituent identified. The third largest component was the geological material (13%) followed by elemental carbon EC (11%). The components, ammonium nitrate (4%) and non-crustal elements (3%) had similarly low levels of abundance. An average of 11% of the total $PM_{2.5}$ mass from the gravimetric analysis remained unidentified. The elements with the highest arithmetic mean values (from all samples analysed, not only minibus samples) were S, Si, and Fe. The data for the three modes are similar, except for higher organic carbon on the Metro, but the small number of samples analysed for OC from the Metro makes it difficult to determine if this is an artefact of the way the samples were selected for this analysis.

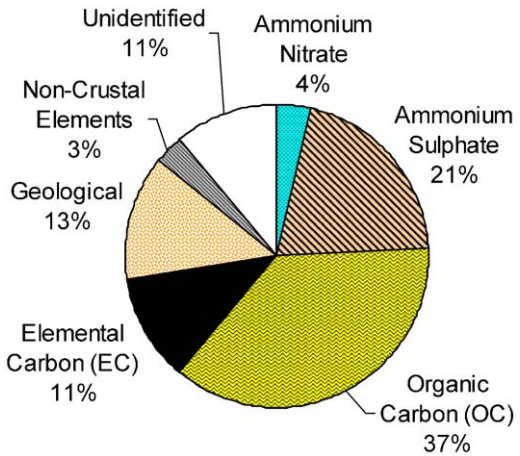

Fig. 2. Chemical composition of $PM_{2.5}$ on minibus. May 2002. Mexico City. The chemical composition was estimated using the method described in Chow et al. (2002).

3.1.3. CO

The levels of CO by mode of transport ranged between 7 and 14 ppm (Table 1). The highest exposure was measured in minibuses at all times of day (morning GM = 18 ppm, evening 11 ppm, combined 14 ppm). The maximum single-journey CO exposure was measured inside a minibus (24 ppm) and the lowest in the Metro (4 ppm).

3.1.4. Benzene

The concentrations for benzene in all modes of transport were between 1 and 14 ppb. The highest levels were measured in minibuses during the morning (GM = 8 ppb). The maximum single value measured during the campaign was in a minibus (14 ppb) during a morning rush hour journey. The lowest concentration was measured in the Metro (GM = 4 ppb).

3.2. Association between wind speed and mode of transport

Wind speed showed a strong association with $PM_{2.5}$ in buses ($r^2 = 0.54$) and minibuses ($r^2 = 0.50$) (Table 2). CO had a strong relationship with wind speed only for minibuses ($r^2 = 0.52$). In minibuses, the regression coefficient β indicates that when wind speed increases by $1\,m\,s^{-1}$, the $PM_{2.5}$ and CO concentrations decrease by 22% and 18%, respectively. For buses, β indicates that for an increase of $1\,m\,s^{-1}$ in wind speed, $PM_{2.5}$ decreases by 24% but CO only by 12%. For benzene, no

Table 2
Regression coefficients and variability for the study using wind speed as a predictor (natural logarithm transport commuters' levels) for minibuses and buses

	$PM_{2.5}$				CO			
Mode	n	β	Intercept	r^2	n	β	Intercept	r^2
Minibus	28	−0.20	4.64	0.50	23	−0.16	3.03	0.52
Bus	16	−0.21	4.61	0.54	15	−0.11	2.63	0.25

n: Number of samples; β: regression coefficient; r^2: variability.

regression analysis was conducted due to the small number of samples taken.

4. Discussion

4.1. Comparison with other studies

4.1.1. $PM_{2.5}$

The $PM_{2.5}$ levels measured in buses in this study (AM = 71 μg m^{-3}) were double than those measured in central London (AM = 33 μg m^{-3}) (Adams et al., 2001a). Exposure levels to $PM_{2.5}$ in buses in Guangzhou, China (AM = 145 μg m^{-3}) (Chan et al., 2002b) were 50% higher than the level found in this study. For minibuses, no studies have evaluated commuters' exposure to $PM_{2.5}$. The $PM_{2.5}$ concentration of commuters in China in the subway (AM = 44 μg m^{-3}) was lower than in Mexico City, and in London higher (AM = 247.2 μg m^{-3}). The difference among commuters' exposure inside the Metro in these three cities might be mainly due to the type of brake system and tyre composition, as well as the ventilation system and depth of tunnel, since all are alike in their use of electric motive power.

4.1.2. Chemical speciation of $PM_{2.5}$

The characterisation of particles found inside public transport has been considered in few studies. Several studies only analysed carbon composition (Adams et al., 2002; Zielinski et al., 1997). For this study, from the total $PM_{2.5}$ mass collected, the TC fraction measured was around 50%. In other studies, the concentration of the TC has not been reported for $PM_{2.5}$. EC is normally the part of carbon that is reported because it is considered an indicator of diesel emitted from vehicle exhausts (DETR, 1999). In Adams et al. (2002), the percentage of EC in $PM_{2.5}$ ranged between 50% and 77% of the total samples collected in the winter and summer seasons for commuters using bicycles, buses and cars in central London. In Mexico City, EC in minibuses comprised 11% of the total concentration of $PM_{2.5}$. This is lower than the levels detected in central London. The main reason might be the different amount of diesel consumption in the two cities. In London, a higher percentage of vehicles in the city are powered by diesel compared with Mexico City. In Mexico City only heavy-duty goods and passenger vehicles, 5% of the total vehicle fleet of the Metropolitan area, consume diesel (GDF et al., 2001b), whereas in London it is used for nearly all taxis and light goods vehicles, and a significant number of private cars. The role of diesel engine heavy vehicles in Mexico City, bringing goods and people daily to the capital from all over the country as well as locally within the city, is an important one in the nation's economy which suffers from the resulting congestion alongside other road users. Furthermore, the vehicles in this particular fleet are old. The local authority is therefore currently trying to identify schemes to substitute these vehicles (SETRAVI, 2002).

The large contribution of sulphate (21%) can be attributed to the 22,466 tons of sulphur dioxide released into the atmosphere of Mexico City per year (3.7 times that of London), of which 55% is from industry. Twenty one percent of sulphur emissions are from mobile sources (GDF et al., 2002) due to relatively high levels of sulphur in petrol in Mexico (400 ppm) and diesel (322 ppm).

For the material balance method used to estimate $PM_{2.5}$ chemical composition in this study, a similar behaviour was found in the project IMADA (Edgerton et al., 1999; Chow et al., 2002) where measurement and characterization of particles were evaluated in different areas of Mexico City. In this study, the level of organic and elemental carbon in $PM_{2.5}$ were in the range between 22–37% and 11–20% respectively.

For the Metro, the levels of $PM_{2.5}$ measured may be caused by two factors. First, $PM_{2.5}$ released from motor vehicle exhausts on the streets may penetrate into the ventilation grids of the Metro system. Secondly, the friction produced by the braking system or the abrasion of tyres made the rubber produce particles. Both might represent sources of fine particles with variable levels of the chemical composition.

For this study, the number of samples was not representative for the chemical composition on public transport. Therefore, further comprehensive studies are needed to identify the content of $PM_{2.5}$, the mechanisms that might generate high levels of exposure for commuters using not only the Metro system but also the other two modes of transport evaluated in this study (minibus and bus).

4.1.3. CO

Measures have been taken by the government to reduce the levels of CO. These strategies, focused on transport and industry, included improvement of fuel quality, the introduction of new technologies such as catalytic converters in vehicles, and a program of

Table 3
Commuters' exposure and ambient levels to CO (ppm) after 10 yr

Route	Mode	Shift	Average (ppm)		Ratio	SD (ppm)		Commuting time (min)		No. of trips	
			1991[a]	2002	91/02	1991[a]	2002	1991[a]	2002	1991[a]	2002
1. Indios Verdes–Sam Angel	Minibus	a.m.	55	16	3.5	4.6	6.3	56.2	63.8	10	4
		p.m.	37	11	3.5	3.4	2.2	83.1	87.7	9	4
	Bus	a.m.	38	12	3.1	2.4	5.9	59.9	58.5	9	4
		p.m.	31	10	3.0	2.1	3.5	98.9	84.3	10	3
	Metro	a.m.	25	7	3.8	1.8	2.1	37.8	39.0	16	2
		p.m.	18	7	2.6	3.4	4.2	38.7	38.5	10	2
2. Tacuba–Pantitlan	Minibus	a.m.	63	18	3.4	3.3	2.3	47.5	59.3	29	3
		p.m.	43	14	3.1	2.2	6.0	56.5	75.3	24	5
	Metro	a.m.	22	9	2.5	1.3	2.6	45.6	38.5	28	4
		p.m.	17	6	2.7	0.9	1.0	39.2	37.8	22	4
3. La Villa–Auditorio	Minibus	a.m.	43	20	2.2	2.9	1.7	39.0	46.5	22	4
		p.m.	32	9	3.4	2.9	1.5	45.3	43.3	22	3
	Bus	a.m.	34	15	2.3	2.7	3.1	39.8	57.5	18	4
		p.m.	26	10	2.7	3.5	2.4	44.5	50.5	20	4
	Metro	a.m.	N/D	8	N/D	N/D	2.1	N/D	52.3	N/D	2
		p.m.	N/D	6	N/D	N/D	0.7	N/D	47.3	N/D	2

Ambient		Average (ppm)		Ratio
Five fixed air monitoring stations	Rush hour	1991[a]	2002	91/02
	a.m.	11	3	3.9
	p.m.	7	2	4.6

N/D: No data available.
[a] Fernandez-Bremauntz and Ashmore (1995).

inspection and maintenance. Therefore, the levels of commuters' exposure for CO measured in 2002 were lower than in a previous study conducted in 1991 (Fernandez-Bremauntz and Ashmore, 1995). Table 3 shows the comparison of transport users' exposure to CO after 10 yr divided by route, transport mode and journey. The same tendency is observed for morning and evening commuting periods after more than 10 yr. Table 3 also shows that morning shifts still present the highest CO average concentrations in all transport modes for 1991 and 2002. Similar to 1991, the highest concentration was detected in route 3 (Tacuba–Pantitlan) for minibuses. CO levels decreased in ratios that ranged from 2.5 to 3.4 over the 10-yr period. It is important to mention that the number of samples was lower for the campaign of 2002 compared with the study conducted in 1991. Seasonal variation might represent another important determinant that explains the difference in CO levels found in 2002 compared with those detected in 1991. The study of 1991 was conducted during the winter whereas this campaign took place in spring.

Table 3 also shows that the ratio of ambient levels from 1991–2002 decreased by a factor of 5 (averaged over all morning and evening rush hours). Meanwhile, for commuters' exposure the average ratio from 1991–2002 (Table 3) was 3, ranging from 2.2 to 3.8. Despite the reduction of commuters' exposure levels to CO, the problem still exists. The CO levels measured in this study were still high compared with studies conducted in other urban areas (Chan and Liu, 2001; Ott et al., 1994). For minibuses, concentrations in Mexico City (AM = 15 ppm) were 5 times higher than in Hong Kong (AM = 3 ppm) (Chan and Liu, 2001). In previous studies in the US, exposure in private cars (mean = 9.5 ppm) (Ott et al., 1994) were lower than those found in the public transport of Mexico City in this research.

4.1.4. Benzene

In Mexico City, benzene comes from exhaust emissions and volatilisation of unburnt fuel of vehicles powered by petrol. For those vehicles consuming diesel, benzene is emitted only from the exhaust as a product of incomplete combustion (Vega et al., 2000). The percentage of benzene in petrol in Mexico is lower than in previous years (Ortiz et al., 2002). However, high levels of exposure are still measured due to the fact the 60% of the total vehicle fleet of the city do not have catalytic converters. Other commuters' studies demonstrate that the passengers of older and poorly maintained vehicles

and those without catalytic converters, are exposed to double concentrations of benzene compared to new vehicles during rush hours (Duffy and Nelson, 1997; Jo and Park, 1998). For the evaluation of benzene, the main objective in this campaign was to measure commuters' exposure using an integrated sampling technique. More measurements are recommended to identify the levels of exposure of commuters in public transport to provide scientific evidence for authorities at local and national level with the aim of establishing an air quality standard for this pollutant as exists in Japan and the European Union.

4.1.5. Wind speed and in-vehicle exposure

A strong relationship between wind speed and exposure concentrations in two modes of transport was detected. A strong association between wind speed and temporal variability in $PM_{2.5}$ and CO was shown for minibuses. Adams et al. (2001b) identified wind speed as one of the most important determinants, not only for temporal variability in commuters' exposure to $PM_{2.5}$, but also for fixed air monitoring stations. In the same study, the mode of transport with the strongest association with wind speed was private cars during winter ($r^2 = 0.40$). Other important factors, such as vehicle speed (Fernandez-Bremauntz and Ashmore, 1995) and ventilation (Chan et al., 2002a), also play an important role in exposure to different pollutants for transport users.

4.2. Limitations of this study and recommendations for future work

4.2.1. Comparison between modes of transport

This study provides information on levels of $PM_{2.5}$ and its chemical characterisation, and levels of CO and benzene for selected public transport modes (minibuses, buses and Metro) in Mexico City. The *variability* of exposure among the selected modes of public transport during morning and evening rush hours was evaluated. However, the study did not aim to measure *differences* between modes of transport, and was not designed to obtain statistically significant data quantifying these differences. Nevertheless, some patterns do emerge.

During morning rush hours, the geometric mean concentrations for minibuses ($PM_{2.5}$ 83 $\mu g\,m^{-3}$; CO 18 ppm; benzene 8 ppb) were slightly higher than in other modes of transport. For CO, the difference between surface modes and the Metro was greater than the variability within a mode of transport, but not for $PM_{2.5}$ or benzene. A future study designed with sufficient statistical power will be able to verify if these consistent trends with $PM_{2.5}$ and benzene are real, and if CO behaves differently, or if these apparent findings have emerged at random from the noise in the data in this study.

Several findings were consistent across more than one mode of transport. Organic carbon levels were higher than elemental carbon in all modes of transport, and the second largest component was ammonium sulphate in all modes of transport. A strong association was found between wind speed and in-vehicle exposure for $PM_{2.5}$ and CO in both surface modes of transport.

4.2.2. Deployment of analytical methods

For this study, the chemical characterisation of particles was conducted to identify the general composition of the particles and levels of the main components, and not to conduct an accurate quantitative analysis of exposure to specific components. The distribution of quartz filters throughout the sampling data set was randomly carried out before exposure, but the selection of which teflon filters to analyse for elements (71% of those exposed were selected) was carried out after the gravimetric analysis with preferential selection of the most highly polluted samples in which the largest number of elements were likely to be present at quantifiable levels. Now that the general levels of components of $PM_{2.5}$ in Mexico City are known, it will be useful in future to consider the selection of filters randomly, or to sample all journeys on one mode of transport, using the results of this first campaign to design the second to measure specific parameters within a degree of precision that can be predicted.

For benzene, an integrated sampling technique was applied successfully for exposure analysis, having previously been deployed in Mexico City only for the evaluation of fixed microenvironment concentrations in petrol stations and ambient levels (Bravo et al., 2002). Nevertheless, the small number of samples means no clear trends in benzene concentrations can be seen in the selected modes of transport. It is important to take a large number of samples in future campaigns to identify the levels of this carcinogenic compound. This information will provide scientific evidence to support future air quality legislation to protect the health of commuters as well as the population close to main roads and avenues in Mexico city.

4.2.3. Comparison with earlier studies

Carbon monoxide was measured in three of the five routes evaluated in 1991. CO levels were lower in 2002. However, the seasons of both campaigns were different. It is recommended that CO be measured during the winter as in the study conducted in 1991 to evaluate air quality policies.

5. Conclusions

Commuters' exposure to $PM_{2.5}$, CO and benzene was measured in minibuses, buses and Metro in Mexico City

during morning and evening rush hours. Minibuses measured the highest concentrations for all the pollutants during morning rush hours. For $PM_{2.5}$, chemical speciation was carried out for all modes of transport. Carbon was identified as the main component of the total composition of $PM_{2.5}$. Carbon monoxide was lower by a factor of between 2.2 and 3.8 in 2002 compared with a campaign conducted in 1991. An integrated sampling technique was used to sample benzene during morning and evening rush hours. Low-wind speed was identified as a major factor that contributes to high concentrations of $PM_{2.5}$ and CO in-vehicle for minibuses and buses. Further measurements are needed to determine if minibuses consistently give higher exposure to air pollution in the morning rush hour, and if this trend is reversed for some pollutants in the evening, as appears to be the case in this study, and to investigate possible reasons for this. Further measurements are also needed to quantify exposure to the main individual components of $PM_{2.5}$, possibly focusing on a larger number of elemental and chemical analyses on minibuses as a mode of transport used by the largest number of commuters and which appears to give the highest exposure under some conditions. Winter measurements should be made for comparison with earlier work, to understand the extent to which change in mode of transport might negate some of the exposure benefits arising from improved efficiency of combustion and emissions abatement. Such useful and reliable scientific evidence is required by local and federal authorities to continue to improve the quality of air to which commuters are exposed in Mexico City.

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References

Adams, H.S., Nieuwenhuijsen, M.J., Colvile, R.N., McMullen, M.A., Khandelwal, P., 2001a. Fine particle ($PM_{2.5}$) personal exposure levels in transport microenvironments, London, UK. The Science of The Total Environment 279, 29–44.

Adams, H.S., Nieuwenhuijsen, M.J., Colvile, R.N., 2001b. Determinants of fine particle ($PM_{2.5}$) personal exposure levels in transport microenvironments, London, UK. Atmospheric Environment 35, 4557–4566.

Adams, H.S., Kenny, L.C., Nieuwenhuijsen, M.J., Colvile, R.N., Gussman, R.A., 2001c. Design and validation of a high-flow personal sampler for $PM_{2.5}$. Journal of Exposure Analysis and Environmental Epidemiology 11, 5–11.

Adams, H.S., Nieuwenhuijsen, M.J., Colvile, R.N., Older, M.J., Kendall, M., 2002. Assessment of road users' elemental carbon personal exposure levels, London, UK. Atmospheric Environment 36, 5335–5342.

Aldape, F., Flores, M.J., Garcia, G.R., Nelson, J.W., 1996. PIXE analysis of atmospheric aerosols from a simultaneous three site sampling during the autumn of 1993 in Mexico City. Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms 109–110, 502–505.

Borja-Aburto, V.H., Castillejos, M., Gold, D.R., Bierzwinski, S., Loomis, D., 1998. Mortality and ambient fine particles in Southwest Mexico City 1993–1995. Environmental Health Perspectives 106 (12), 849–855.

Bravo, H., Sosa, R., Sanchez, P., Bueno, E., Gonzalez, L., 2002. Concentrations of benzene and toluene in the atmosphere of the Southwestern area at the Mexico City metropolitan zone. Atmospheric Environment 36, 3843–3849.

Brice, R.M., Roesler, J.F., 1966. The exposure to carbon monoxide of occupants of vehicles moving in heavy traffic. Journal of Air Pollution Control Association 16, 597–600.

CARB, 1992. Standard operating procedure for analyzing anions from ambient air particulate samples from the California Acidic Dry Deposition Monitoring Network. California Air Resource Board Monitoring and Laboratory Division. S.O.P. No. 044. 12-11-1992, California, Report.

Castillejos, M., Borja-Aburto, V.H., Dockery, D.W., Gold, D.R., Loomis, D., 2000. Airborne coarse particles and mortality. Inhalation Toxicology 12, 61–72.

CENICA, 2002. Manual de procedimientos de Preparación y pesaje de filtros en el monitoreo atmosférico de bajo volumen. Clave. CENICA/PT-APF-01, Centro Nacional de Investigación y Capacitación Ambiental, Ciudad de México, Report.

Chan, L.Y., Liu, Y.M., 2001. Carbon monoxide levels in popular passenger commuting modes traversing major commuting routes in Hong Kong. Atmospheric Environment 35, 2637–2646.

Chan, C.C., Spengler, J.D., Ozkaynak, H., Lefkopoulou, M., 1991a. Commuter exposures to Vocs in Boston, Massachusetts. Journal of the Air and Waste Management Association 41, 1594–1600.

Chan, C.C., Ozkaynak, H., Spengler, J.D., Sheldon, L., 1991b. Driver exposure to volatile organic-compounds, Co, Ozone, and NO_2 under different driving conditions. Environmental Science and Technology 25 (5), 964–972.

Chan, L.Y., Lau, W.L., Lee, S.C., Chan, C.Y., 2002a. Commuter exposure to particulate matter in public transportation modes in Hong Kong. Atmospheric Environment 36, 3363–3373.

Chan, L.Y., Lau, W.L., Zou, S.C., Cao, Z.X., Lai, S.C., 2002b. Exposure level of carbon monoxide and respirable suspended particulate in public transportation modes while

commuting in urban area of Guangzhou, China. Atmospheric Environment 36, 5831–5840.

Chow, J.C., Watson, J.G., Pritchett, L.C., Pierson, W.R., Frazier, C.A., Purcell, R.G., 1993. The DRI thermal optical reflectance carbon analysis system—description, evaluation and aplications in the United States air quality studies. Atmospheric Environment Part A—General Topics 27, 1185–1201.

Chow, J.C., Watson, J.G., Edgerton, S.A., Vega, E., 2002. Chemical composition of $PM_{2.5}$ and PM_{10} in Mexico City during winter 1997. The Science of The Total Environment 287, 177–201.

Clifford, M.J., Clarke, R., Riffat, S.B., 1997. Drivers' exposure to carbon monoxide in Nottingham, UK. Atmospheric Environment 31, 1003–1009.

Colvile, R.N., Hutchinson, E.J., Mindell, J.S., Warren, R.F., 2001. The transport sector as a source of air pollution. Atmospheric Environment 35, 1537–1565.

DETR, 1999. Source Apportionment of Airborne Particulate Matter in the United Kingdom. Airborne Particles Expert Group, Report.

Duffy, B.L., Nelson, P.F., 1997. Exposure to emissions of 1,3-butadiene and benzene in the cabins of moving motor vehicles and buses in Sydney, Australia. Atmospheric Environment 31, 3877–3885.

Edgerton, S.A., Bian, X., Doran, J.C., Fast, J.D., Hubbe, J.M., Malone, E.L., Shaw, W.J., Whiteman, C.D., Zhong, S., Arriaga, J.L., Ortiz, E., Ruiz, M., Sosa, G., Vega, E., Limon, T., Guzman, F., Archuleta, J., Bossert, J.E., Elliot, S.M., Lee, J.T., McNair, L.A., Chow, J.C., Watson, J.G., Coulter, R.L., Doskey, P.V., Gaffney, J.S., Marley, N.A., Neff, W., Petty, R., 1999. Particulate air pollution in Mexico City: a collaborative research project. Journal of the Air and Waste Management Association 49, 1221–1229.

Fernandez-Bremauntz, A.A., Ashmore, M.R., 1995. Exposure of commuters to carbon monoxide in Mexico City—I. Measurement of in-vehicle concentrations. Atmospheric Environment 29, 525–532.

GDF, Gobierno del Distrito Federal, Secretaria del Medio Ambiente, 2001a. Informe Anual de la Calidad del Aire y Precipitación Ácida en el Valle de México 2000, Report.

GDF, Secretaria de Ecologia del Estado de Mexico, Secretaria de Medio Ambiente y Recursos Naturales, 2001b. Inventario de Emisiones Zona Metropolitana del Valle de Mexico 1998, Mexico, Distrito Federal, (Report).

GDF (Gobierno del Distrito Federal), Gobierno del Estado de México, Secretaría del Medio Ambiente y Recursos Naturales, Secretaria de Salud, 2002. Programa para Mejorar la Calidad del Aire en el Valle de México, 2002–2010.

Holguin, F., Cortez, M., Tellez, M., Romieu, I., Chow, J., Watson, J., Hernandez, M., 2001. Fine particulate matter $PM_{2.5}$ in air pollution is associated with cardiac autonomic dysfunction in an elderly cohort in mexico city. Epidemiology 12, 155.

Jo, W.K., Park, K.H., 1998. Exposure to carbon monoxide, methyl-tertiary butyl ether (MTBE), and benzene levels inside vehicles traveling on an urban area in Korea. Journal of Exposure Analysis and Environmental Epidemiology 8, 159–171.

Kingham, S., Meaton, J., Sheard, A., Lawrenson, O., 1998. Assessment of exposure to traffic-related fumes during the journey to work. Transportation Research Part D: Transport and Environment 3 (4), 271–274.

Maeda, T., Onodera, S., Ogino, H., 1995. On-site monitoring of volatile organic compounds as hazardous air pollutants by gas chromatography. Journal of Chromatography 710, 51–59.

Maeda, T., Funaki, K., Yanaguchi, Y., Ichioka, K., Suzuki, K., Yamamoto, N., Morita, M., 1998. On-site monitoring system for hazardous air pollutants using an adsorption thermal desorption capillary GC system equipped with a photoionization detector and an electrolytic conductivity detector. Hrc-Journal of High Resolution Chromatography 21, 471–474.

Meneses, F., Romieu, I., Ramirez, M., Colome, S., Fung, K., Ashley, D., Hernandez-Avila, M., 1999. A survey of personal exposures to benzene in Mexico City. Archives of Environmental Health 54, 359–363.

Miranda, J., Paredes-Gutierrez, R., Lopez-Suarez, A., Gonzalez, S., De Lucio, O.G., Andrade, E., Morales, J.R., Avila-Sobarzo, M.J., 1998. A study of atmospheric aerosols from five sites in Mexico City using PIXE. Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms 136–138, 970–974.

Ott, W., Switzer, P., Willits, N., 1994. Carbon monoxide exposures inside an automobile traveling on an urban arterial highway. Air and Waste: Journal of the Air and Waste Management Association 44, 1010–1018.

Ortiz, E., Alemon, E., Romero, D., Arriaga, J.L., Olaya, P., Guzman, F., Rios, C., 2002. Personal exposure to benzene, toluene and xylene in different microenvironments at the Mexico City metropolitan zone. The Science of The Total Environment 287, 241–248.

Riveros, H.G., Alba, A., Ovalle, P., Silva, B., Sandoval, E., 1998. Carbon monoxide trend, meteorology, and three-way catalysts in Mexico City. Journal of the Air and Waste Management Association 48, 459–462.

Rodes, C., Sheldon, L., Whitaker, D.A., Clayton, A.C., Fitzgerald, K., Flanagan, J, 1999. Measuring Concentrations of Selected Air Pollutants inside California Vehicles. California Air Resource Board, 1-6-1999. http://www.arb.ca.gov/research/indoor/in-vehsm.htm. Electronic Citation.

SETRAVI, 2002. Programa Integral de Transporte y Vialidad 2001–2006. Mexico City, Secretaria de Transporte y Vialidad, Report.

USEPA, 1977. Quality assurance handbook for air pollution measurement systems, volume II—Ambient air specific methods. US Environmental Protection Agency, Environmental Monitoring Systems Laboratory Research Triangle Park. EPA-600/4-77-027a, Report.

USEPA, 1999a. Determination of volatile organic compounds (VOCs) in air collected in specially prepared canisters and analyzed by gas chromatography/mass spectrometry (GC/MS). EPA/625/R-96/010b, Compendium of Methods for the Detection of Toxic Organic Compounds in Ambient Air, Report.

USEPA, 1999b. Determination of metals in ambient particulate matter using X-ray fluorescence (XRF) spectroscopy. EPA/625/R-96/010a, Report.

Van Wijnen, J.H., Verhoeff, A.P., Jans, H.W., Van Bruggen, M., 1995. The exposure of cyclists, car drivers and pedestrians to traffic-related air pollutants. International Archives of Occupational and Environmental Health 63, 187–193.

Vega, E., Mugica, V., Carmona, R., Valencia, E., 2000. Hydrocarbon source apportionment in Mexico City using the chemical mass balance receptor model. Atmospheric Environment 34, 4121–4129.

Zielinski, M., Rommelt, H., Fruhmann, G., 1997. Ambient air soot concentrations in Munich public transportation systems. The Science of The Total Environment 196, 107–110.