



PERGAMON



Atmospheric Environment 36 (2002) 3429–3443

ATMOSPHERIC  
ENVIRONMENT

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# Mixing ratios of volatile organic compounds (VOCs) in the atmosphere of Karachi, Pakistan

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Received 18 November 2001; accepted 17 April 2002

## Abstract

Mixing ratios of carbon monoxide (CO), methane (CH<sub>4</sub>), non-methane hydrocarbons, halocarbons and alkyl nitrates (a total of 72 species) were determined for 78 whole air samples collected during the winter of 1998–1999 in Karachi, Pakistan. This is the first time that volatile organic compound (VOC) levels in Karachi have been extensively characterized. The overall air quality of the urban environment was determined using air samples collected at six locations throughout Karachi. Methane (6.3 ppmv) and ethane (93 ppbv) levels in Karachi were found to be much higher than in other cities that have been studied. The very high CH<sub>4</sub> levels highlight the importance of natural gas leakage in Karachi. The leakage of liquefied petroleum gas contributes to elevated propane and butane levels in Karachi, although the propane and butane burdens were lower than in other cities (e.g., Mexico City, Santiago). High levels of benzene (0.3–19 ppbv) also appear to be of concern in the Karachi urban area. Vehicular emissions were characterized using air samples collected along the busiest thoroughfare of the city (M.A. Jinnah Road). Emissions from vehicular exhaust were found to be the main source of many of the hydrocarbons reported here. Significant levels of isoprene (1.2 ppbv) were detected at the roadside, and vehicular exhaust is estimated to account for about 20% of the isoprene observed in Karachi. 1,2-Dichloroethane, a lead scavenger added to leaded fuel, was also emitted by cars. The photochemical production of ozone (O<sub>3</sub>) was calculated for CO and the various VOCs using the Maximum Incremental Reactivity (MIR) scale. Based on the MIR scale, the leading contributors to O<sub>3</sub> production in Karachi are ethene, CO, propene, *m*-xylene and toluene. © 2002 Elsevier Science Ltd. All rights reserved.

**Keywords:** VOCs; Urban air quality; Vehicular emission; Tropospheric ozone; Gas chromatography

## 1. Introduction

Urban air pollution is a problem in most megacities. Volatile organic compounds (VOCs) coupled with nitrogen oxides (NO<sub>x</sub>) are the most important chemical precursors of tropospheric ozone (O<sub>3</sub>) formation. Non-methane hydrocarbons (NMHCs) are especially important among VOCs in urban areas because their reaction with the hydroxyl radical (OH) plays a critical role in

atmospheric photochemical reactions (Derwent, 1995; Finlayson-Pitts and Pitts, 1999). The production of VOCs and NO<sub>x</sub> in urban environments is often dominated by vehicular emissions involving gasoline distribution, evaporation and automobile exhaust (Watson et al., 2001). Ethene and acetylene are characteristic products of internal combustion engines, while C<sub>5</sub>–C<sub>8</sub> NMHCs are generally associated with unburned vehicular emissions (Mayrsohn and Crabtree, 1976). Alkanes are emitted from gasoline evaporation, liquefied petroleum gas (LPG) leakage and natural gas leakage (e.g., Blake and Rowland, 1995; Chen et al., 2001).

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Natural biological sources of hydrocarbons and leakage of fossil fuels other than gasoline can also be important contributors for some species (Roselle et al., 1991; Benjamin et al., 1997). In order to determine the relative importance of various hydrocarbons to  $O_3$  production, detailed NMHC speciation in urban atmospheres is necessary, particularly in developing countries (Haszpra, 1991; Mohan et al., 1997; Sharma, 1997; Singh et al., 1997; Grosjean et al., 1998a, 1999; Hao et al., 2000; Padhy and Varshney, 2000; Sharma et al., 2000).

In this study, detailed NMHC speciation was performed to determine the overall sources and types of emissions for Karachi, southeastern Pakistan. The city of Karachi has a rapidly expanding population of over 14 million and a large industrial base including oil-fired power plants, cement factories, a steel mill, textile plants, two major refineries, heavy petrochemical industries and several light industries. A recent study reports one of the highest total suspended particulate (TSP) loadings recorded in any megacity of the world, with an average daily TSP concentration range of  $627\text{--}938\ \mu\text{g m}^{-3}$  (Parekh et al., 2001). Air pollution has reached alarming levels in major cities of Pakistan and the city dwellers are being continuously exposed to its harmful effects.

A major focus of this study is the contribution of vehicular emissions to air pollution in Karachi. Vehicular traffic can be classified into three categories: gasoline fueled (e.g., cars, jeeps), diesel fueled (e.g., buses, trucks), and vehicles with two-stroke engines (e.g., motor rickshaws). The number of vehicles in Pakistan (1 per 143 people in 1997) has swelled in recent years from 1.1 million in 1980 to 4.2 million in 1999 (Federal Bureau of Statistic, Government of Pakistan, 1990; Turner, 2001). Although the per capita vehicle usage is still well below that of the US (1 per 1.3 people), the average Pakistani vehicle emits 25 times as much carbon monoxide (CO) as the average US vehicle, and about 20 times more NMHCs (United States Energy Information Administration, 2000). A major problem is that most of the vehicles in Pakistan are old, ill-maintained and they have poor or no pollution control devices. Furthermore, the lead concentrations in gasoline in Pakistan are in the range of  $1.5\text{--}2.0\ \text{g/l}$  (Murley, 1991), which is well above the WHO maximum allowable concentration of  $0.15\ \text{g/l}$ .

Thirty percent of Pakistan's automobile traffic is concentrated in Karachi. While Karachi is about 50 km across, the location of commercial and business areas that have the greatest impact on transportation has remained the same since the 1970s. The peak hour vehicle speed has fallen from 15 km/h in 1983 to 10 km/h today. Numerous traffic lights lead to frequent stop/start traffic patterns which in turn result in poor and incomplete combustion. Gases and particulates originating in automobile engine emissions are among the most

significant sources of air pollution in the congested and poorly ventilated streets of the city. Certain areas (e.g., M.A. Jinnah Road) are badly affected by automotive exhaust. The projected increase in the use of gasoline and diesel powered automobiles will further increase this problem.

## 2. Experimental

Karachi is situated on the Arabian Sea ( $25^\circ\text{N}$ ;  $67^\circ\text{E}$ ; 22 m elevation), with a subtropical climate and little rainfall (mean annual rainfall 169 mm). Between 10 December 1998 and 11 January 1999, two sets of whole air samples were collected in evacuated 21 electropolished stainless steel canisters throughout the city of Karachi. The sampling height was about 1.5 m above the ground. The preparation and pre-conditioning of the canisters prior to sampling is described in Blake et al. (1994).

In the first sampling campaign, 28 air samples were collected at the side M.A. Jinnah Road (Fig. 1). M.A. Jinnah Road is located in the most crowded business district in the downtown area and it is crossed by several streets with high traffic flow. There are no industrial plants near the M.A. Jinnah Road, and air samples from this area should strongly reflect vehicular emissions in the Karachi urban area. Samples were collected approximately every 6 h for 7 days beginning at 17:00 on Thursday, 10 December 1998 and ending at 14:05 on Thursday, 17 December 1998 (all times are local). 10–12

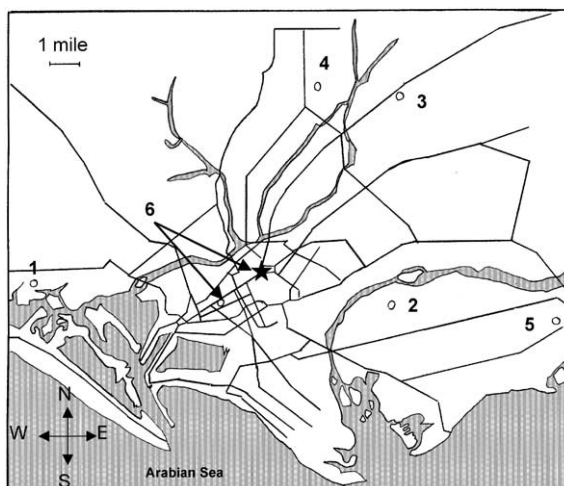


Fig. 1. Map of Karachi metropolitan area and sampling sites: 1—Mauripur; 2—National Fiber Company, Korangi; 3—University of Karachi; 4—North Karachi; 5—Dawood Chaurangi, Landhi; 6—M.A. Jinnah Road. The star and open circle denote the sampling sites for the first and second campaigns, respectively.

and 14–17 December were normal working days and 13 December was Sunday, a non-working day in Pakistan. Heavy traffic is expected on all working days on the M.A. Jinnah Road, in particular during the commuting hours of 07:30–10:30 and 15:00–20:00. During the sampling period the weather was average for that time of year (15–31°C and cloudless). All of the samples were collected at the same location, close to the traffic. The purpose was to have a detailed time series to define which compounds are primarily emitted from Karachi's motor vehicles and to determine their daily and weekly variations.

In the second sampling campaign, Karachi was divided into grids in order to determine the overall CO and hydrocarbon mixing ratios in the Karachi urban area. Fifty samples were collected at six sampling sites located throughout the city: two industrial areas (Landhi industrial area and Korangi), three sites relatively well separated from local sources (Karachi University area, North Karachi and Mauripur) and the M.A. Jinnah Road (Fig. 1). The first sample from each site was collected at 00:00 on Saturday, 9 January 1999. Samples were then collected every 4 h beginning at 04:00 on Sunday, 10 January 1999 and ending at 08:00 on Monday, 11 January 1999.

During sampling the canister valve was slightly opened, allowing about 2 min for the collection of the "integrated" samples. The canisters were then shipped to our laboratory at the University of California, Irvine (UCI) and analyzed for CO, methane (CH<sub>4</sub>), NMHCs, halocarbons and alkyl nitrates. Carbon monoxide analyses were carried out using a gas chromatograph (HP 5890) equipped with a flame ionization detector (FID) and a 3 m molecular sieve column. The samples were injected and then converted to CH<sub>4</sub> in a catalyst (2% coating of nickel on Chromosorb G) after the chromatographic separation. Methane was also analyzed using an HP 5890 GC equipped with an FID detector. The samples were injected into an 1/8" stainless steel 0.9 m column packed with 80/100 mesh Spherocarb.

The analytical system used to analyze NMHCs, halocarbons and alkyl nitrates involved the cryogenic pre-concentration of 217 cm<sup>3</sup> of air sample in a stainless steel loop (1/4" O.D.) filled with 3 mm glass beads and immersed in liquid nitrogen (–196°C). The pre-concentrated sample was subsequently vaporized with hot water and split into five different streams directed to three GCs (all HP 6890). The first GC was equipped with two different detector/column combinations: (1) a 60 m, 0.32 mm I.D., 1 µm film thickness, 1701 column (Restek) output to an ECD for the detection of halogenated hydrocarbons and C<sub>1</sub>–C<sub>4</sub> alkyl nitrates, and (2) a GS-Alumina PLOT, 30 m, 0.53 mm I.D. (J&W Scientific) output to an FID measuring C<sub>2</sub>–C<sub>7</sub> NMHCs. The second GC was equipped with a 60 m, 0.32 mm I.D.,

1 µm film thickness, DB-1 column (J&W Scientific) output to an FID providing data on C<sub>3</sub>–C<sub>10</sub> hydrocarbons. The third GC was equipped with two different detector/column combinations: (1) a 60 m, 0.25 mm I.D., 0.5 µm film thickness, DB5-MS column (J&W Scientific) output to a quadrupole mass spectrometer detector (HP-5973) working in selected ion monitoring (SIM) mode, and (2) a 30 m, 0.25 mm I.D., 0.5 µm film thickness, DB-5 column (J&W Scientific) output to an ECD for the detection of halocarbons and C<sub>1</sub>–C<sub>4</sub> alkyl nitrates. Additional analytical details are given by Blake et al. (2001) and Colman et al. (2001).

The measurement precision, detection limits and accuracy vary by compound and are quantified for each species in Colman et al. (2001). Briefly, the detection limit is 5 ppbv for CO, 3 pptv for NMHCs, 0.02 pptv for alkyl nitrates, and 0.01–10 pptv for halogenated species (CH<sub>4</sub> is always above its detection limit). The accuracy of our measurements is 1% for CH<sub>4</sub>, 5–7% for CO, 5% for NMHCs, 10–20% for alkyl nitrates, and 2–20% for halogenated species. The measurement precision is 2 ppbv for CH<sub>4</sub>, 4 ppbv for CO, and ranges from 0.5–16% for NMHCs, 1–2% for alkyl nitrates, and 0.7–9% for halogenated species. The measurement precision improves with increasing mixing ratio, and the precision of measurements reported in this city study is expected to be better than those reported for less polluted air by Colman et al. (2001).

### 3. Results and discussion

#### 3.1. Composition of Karachi's urban air

The samples collected at the six urban sampling sites throughout the city were used to make a detailed characterization of the composition of Karachi's urban air (Table 1). Methane (77% of total measured compounds) and CO (19.5%) were dominant among the gases. The remainder comprised alkanes (2.6%), alkenes (0.4%), alkynes (0.2%), aromatic compounds (0.2%), halogenated hydrocarbons and alkyl nitrates (<0.1%). We note that oxygenated compounds (e.g., alcohols, aldehydes and ketones) were not measured during this study. As will be shown in Section 3.3, a compound's concentration coupled with its reactivity determines its contribution to O<sub>3</sub> production in the city.

Comparison with NMHC mixing ratios from other cities indicates that Karachi has some of the highest NMHC mixing ratios of anywhere in the world (Table 2). In particular, CH<sub>4</sub> (6.3 ppmv) and ethane (93 ppbv) levels in Karachi are substantially elevated compared to other cities that have been studied, and propane mixing ratios are also high (41 ppbv). For these three compounds, a decrease in their mixing ratios was observed during the daytime, leading to a midafternoon

Table 1

Mean, minimum and maximum mixing ratios for the compounds identified in the Karachi urban area. Correlation coefficients ( $R^2$ ) with CO and acetylene are also shown. SD—standard deviation

Compound	Units	Mean		Minimum	Maximum	Correlation ( $R^2$ )	
		Total	SD			CO	Acetylene
CO	ppmv	1.6	1.3	0.3	6.0	—	0.89
Methane		6.3	4.7	1.9	28	0.27	0.34
Ethane	ppbv	93	84	2.8	411	0.25	0.30
Propane		41	35	0.7	163	0.30	0.34
<i>n</i> -Butane		19.8	16.9	0.4	80	0.62	0.66
<i>i</i> -Butane		11.0	9.1	0.2	40	0.44	0.50
<i>n</i> -Pentane		13.4	13.9	0.15	60	0.72	0.79
<i>i</i> -Pentane		12.1	11.6	0.16	45	0.70	0.79
<i>n</i> -Hexane		7.5	8.1	0.07	39	0.67	0.75
2,3-Dimethylbutane		0.5	0.5	0.02	2.5	0.68	0.77
2,2-Dimethylbutane		0.6	0.4	0.02	1.8	0.59	0.69
2-Methylpentane		4.7	5.1	0.06	23.9	0.68	0.77
3-Methylpentane		3.1	3.3	0.06	15.5	0.66	0.76
<i>n</i> -Heptane		3.9	4.5	0.06	22.3	0.69	0.76
2,4-Dimethylpentane		0.3	0.3	0.02	1.4	0.69	0.76
2,3-Dimethylpentane		0.5	0.5	0.02	2.6	0.66	0.73
2-Methylhexane		1.8	2.0	0.07	10.3	0.66	0.73
<i>n</i> -Octane		1.1	1.0	0.02	3.8	0.67	0.71
2,2,4-Trimethylpentane		0.5	0.5	0.03	2.4	0.72	0.69
<i>n</i> -Nonane		0.7	0.6	0.02	2.2	0.57	0.56
<i>n</i> -Decane		0.7	0.6	0.03	2.3	0.60	0.59
Ethene		19.0	17.0	0.45	67	0.92	0.89
Propene		5.5	5.3	0.06	19.9	0.83	0.70
<i>i</i> -Butene		1.2	1.1	0.02	4.8	0.71	0.54
1-Butene		1.1	1.2	0.007	4.5	0.78	0.65
<i>cis</i> -2-Butene		0.2	0.2	0.007	1.0	0.71	0.55
<i>trans</i> -2-Butene		0.3	0.3	0.01	1.4	0.68	0.52
<i>cis</i> -2-Pentene		0.1	0.1	0.003	0.5	0.75	0.68
<i>trans</i> -2-Pentene		0.3	0.3	0.01	1.1	0.78	0.72
Isoprene		0.8	1.1	0.02	6.0	0.03	0.03
1,2-Propadiene		0.2	0.2	0.02	1.0	0.94	0.93
1,3-Butadiene		0.8	0.8	0.03	3.4	0.89	0.87
Acetylene		18.0	16.2	1.3	69	0.89	—
Propyne		0.4	0.4	0.04	1.6	0.93	0.93
Benzene		5.2	4.5	0.34	19.3	0.64	0.51
Toluene		7.1	7.6	0.19	37	0.62	0.70
Styrene		0.4	0.4	0.02	2.1	0.27	0.14
<i>n</i> -Propylbenzene		0.2	0.2	0.02	0.8	0.73	0.77
<i>i</i> -Propylbenzene		0.05	0.0	0.006	0.2	0.52	0.37
2-Ethyltoluene		0.4	0.3	0.04	1.4	0.70	0.71
4-Ethyltoluene		0.4	0.3	0.04	1.3	0.69	0.77
1,3,5-Trimethylbenzene		0.4	0.4	0.04	1.5	0.67	0.74
1,2,4-Trimethylbenzene		1.0	0.8	0.10	3.5	0.65	0.71
<i>o</i> -Xylene		1.1	1.0	0.08	4.5	0.63	0.69
<i>m</i> -Xylene		2.1	2.0	0.16	9.0	0.65	0.74
<i>p</i> -Xylene		1.0	0.9	0.08	4.2	0.62	0.71
Methylnitrate	pptv	6.9	1.9	4.0	13.3	0.41	0.37
Ethylnitrate		11.8	2.2	6.8	17.9	0.24	0.24
<i>n</i> -Propylnitrate		4.7	0.9	2.8	6.9	0.08	0.07
<i>i</i> -Propylnitrate		21.1	4.6	13.1	34	0.16	0.15
2-Butylnitrate		26.0	7.1	15.1	45	0.13	0.12
CFC-11		298	32.9	264	465	0.12	0.11
CFC-12		650	121.6	547	1070	0.61	0.50
CFC-113		83	2.8	80	96	0.09	0.12

Table 1 (continued)

Compound	Units	Mean		Minimum	Maximum	Correlation ( $R^2$ )	
		Total	SD			CO	Acetylene
CFC-114		14.0	1.2	11.7	16.8	0.0001	0.0035
Halon 1211		4.8	1.6	3.7	9.6	0.02	0.02
H-2402		0.5	0.0	0.4	0.5	0.00	0.00
HCFC-141b		16.4	7.5	10.2	47	0.09	0.07
HCFC-142b		13.6	4.2	7.0	26.6	0.01	0.01
HFC-134a		23.1	31.1	6.4	186	0.09	0.01
HCFC-22		295	267	100	1360	0.43	0.28
Methyl chloride		2720	1546	1063	8940	0.21	0.10
Methyl bromide		21.8	6.8	11.1	48	0.50	0.49
Methyl iodide		1.5	1.0	0.5	4.5	0.09	0.05
1,2-Dichloroethane		10.0	6.4	2.6	34.0	0.86	0.87
Methylene chloride		329	630	24.1	3000	0.16	0.12
Methylene bromide		1.5	0.3	1.2	2.8	0.02	0.03
Bromoform		2.4	1.2	1.2	7.2	0.05	0.07
Chloroform		241	559	11.4	2720	0.01	0.00
Methyl chloroform		74.5	3.4	69	86	0.18	0.16
Carbon tetrachloride		131	43.4	100	361	0.26	0.14
Tetrachloroethylene		68	147	7.8	1010	0.19	0.07

minimum (16:00) and an early morning maximum (04:00) (data not shown). Assuming a constant emission during the 24 h, the accumulation of these species during the night is likely the result of the low-level inversion layer, while the mixing ratio reduction from morning until early afternoon is caused by the daytime boundary layer expansion. The main candidate for explaining the high levels of  $\text{CH}_4$  in Karachi is continuous leakage from natural gas, of which  $\text{CH}_4$  is the main constituent. A sample of natural gas used in Karachi in January 1999 confirms that  $\text{CH}_4$  dominates the natural gas composition (99.9%), followed by ethane (0.06%) and propane (0.01%).

Whereas natural gas is the main source of  $\text{CH}_4$  in Karachi, the source of the elevated ethane throughout Karachi is less clear. Because natural gas in Karachi contains only 0.06% ethane, natural gas leakage can only account for a few of the 93 ppb of ethane observed in Karachi (Table 2). A second known source of light alkanes is the leakage of unburned LPG from household uses (Blake and Rowland, 1995; Chen et al., 2001). In Karachi, the hydrocarbon composition of LPG samples reveals *n*-butane as main constituent (43.4%), followed by propane (28.9%), *i*-butane (15.1%),  $\text{CH}_4$  (7.8%) and ethane (2.9%). However, in all 50 samples collected at the six different urban locations, the ethane mixing ratio was always found to be higher than propane (ethane/propane ratio of  $2.3 \pm 0.4$ ), even though ethane is a minor component of LPG compared to propane. That is, natural gas and LPG leakage do not explain the high levels of ethane found in Karachi, suggesting either an additional

unknown source, or that the natural gas source sample was not representative of ethane levels normally found in Karachi's natural gas. In the latter case, natural gas containing a maximum of 1.5% of ethane would be required to explain the observed levels of ethane in Karachi.

Although the  $\text{CH}_4$  and ethane levels in Karachi are much higher than in other cities (Table 2), Karachi shows lower levels of propane (41 ppbv) and *n*-butane (20 ppbv) compared to Mexico City (158 and 70 ppbv, respectively; Blake and Rowland, 1995) and Santiago (137 and 27 ppbv, respectively; Chen et al., 2001). For example, whereas ethane is the most abundant NMHC in Karachi (Table 2), propane was found to be the most abundant NMHC in Santiago's air (Chen et al., 2001). These results highlight the lesser importance LPG leakage on NMHC levels in Karachi compared to cities such as Mexico City and Santiago. By contrast, the very high levels of  $\text{CH}_4$  in Karachi show the strong influence of natural gas leakage in Karachi compared to other cities.

Benzene, ethylbenzene, *n*-hexane, toluene, xylenes (*meta*-, *para*- and *ortho*-) and 1,3-butadiene are in the Urban Air Toxics list of the Clean Air Act of the United States, as amended in 1990. The regulatory limit for benzene in several countries is  $10 \mu\text{g}/\text{m}^3$  (3.1 ppbv) and sometimes less. In Pakistan, air quality standards have not yet been set for organic pollutants. However, the maximum benzene mixing ratio measured in Karachi (19.3 ppbv; Table 1) exceeds the 3.1 ppbv regulatory limit in other countries, indicating that high benzene levels are a concern in Karachi.

Table 2  
Mean mixing ratios for selected hydrocarbons measured in the Karachi urban area and in other cities (units are ppbv unless otherwise specified)

Compound	Karachi	Kathmandu <sup>a</sup>	Mexico City <sup>b</sup>	Santiago <sup>c</sup>	Athens <sup>d</sup>	Taipei <sup>e</sup>	Osaka <sup>f</sup>	Hamburg <sup>g</sup>	Sydney <sup>h</sup>	Chicago <sup>i</sup>	London <sup>j</sup>
CO (ppmv)	1.6			3.1							
Methane (ppmv)	6.3		2.6	2.2							
Ethane	93	7.7	14	9.4		8.3			7.5	6.4	4.2
Propane	41	6	158	137.5	1.2	6.4	8.9	2.1	5.9	3.2	2
<i>n</i> -Butane	19.8	42.2	70.4	27.0	2.1	5.2	11	7.8	7.5	6	3.2
<i>i</i> -Butane	11	16.4	33.1	16.1	1.1	2.4	5.1	3.8	4.7	1.2	1.4
<i>n</i> -Pentane	13.4	24.8	14.4	6.6	4.2	4.3	7.7	5.1	5	3.8	0.6
<i>i</i> -Pentane	12.1	25.9	19.4	14.2	11.7	12.8	10.6	6.4	9	4.1	2.6
<i>n</i> -Hexane	7.4	13.8	12.2	4.1	1.6	2.3	5.5	3.8	2.1	2	0.2
2-Methylpentane	4.7	16.1	8.1	4.8	3.3		3.9		2.6	2.4	
3-Methylpentane	3.1	13.4	5.3	2.8	2.3		3.1		1.6	2.4	
<i>n</i> -Heptane	3.9		3.4	2.8	2.4		2				0.1
<i>n</i> -Octane	1.1			1.1							
Ethene	19	48.4	21.6	29.4		14.1	23.3	5.3	12.5	3.5	3.4
Propene	5.5	12.8	5	8.0	3.9	4.6	6.1	2.9	7.4	1.4	1.4
<i>i</i> -Butene	1.2		1.8	2.8		2.7			1.4		
1-Butene	1.1	2.5	2.1	2.4	0.9	0.9			1		0.2
Isoprene	0.8	0.3	0.1	0.5							0.1
1,3-butadiene	0.8			1.5							
Acetylene	18	36	31.6	25.9		15.1		8.8	10.1	4.1	4.6
Benzene	5.2		4.6	6.0	5		5.1	3.2	2.6	2.4	1.1
Toluene	7.1		21	21.8	14.3		31.1	8.2	8.9	3.8	2.2
1,3,5-Trimethylbenzene	0.4			1.4			1.2		0.5		
1,2,4-Trimethylbenzene	1.0			3.1			2.9		1.3		
<i>o</i> -Xylene	1.1			3.8	3.7		2.8	1.8	1.5	0.4	0.4
<i>m</i> -Xylene	2.1			7.0			5.4				
<i>p</i> -Xylene	1.0			3.3			2.3			1.5	

<sup>a</sup>Sharma et al. (2000).

<sup>b</sup>Blake and Rowland (1995).

<sup>c</sup>Chen et al. (2001).

<sup>d</sup>Moschonas and Glavas (1996).

<sup>e</sup>Ding and Wang (1998).

<sup>f</sup>Tsujino and Kuwata (1993).

<sup>g</sup>Bruckmann et al. (1988).

<sup>h</sup>Nelson et al. (1982).

<sup>i</sup>Aronian et al. (1989).

<sup>j</sup>Derwent et al. (2000).

Significant levels of isoprene were detected in Karachi's urban area (Table 1). The mean isoprene mixing ratio (0.8 ppbv) is higher than that reported in Kathmandu (0.3 ppbv; Sharma et al., 2000) and Mexico City (0.1 ppbv; Blake and Rowland, 1995) (Table 2). A correlation plot of isoprene versus CO is shown for the 50 samples collected throughout the urban area in Fig. 2a. The crosses correspond to samples collected at sites well removed from downtown and the main traffic artery. In these samples, no correlation exists between isoprene and CO, suggesting that biogenic isoprene emissions are significant. By contrast, samples collected at the other four sampling sites throughout Karachi correlate well with CO, suggesting an anthropogenic source (Section 3.2).

Most of the hydrocarbons identified in the Karachi urban area correlate well with CO and acetylene, two markers for vehicular fuel combustion (Table 1). These results suggest that vehicular exhaust is an important source for numerous hydrocarbons in Karachi, though we note that if two sources have nearly parallel time patterns of usage in a city, then correlations may not be useful for discriminating between sources (Blake and

Rowland, 1995). The poorer correlations of isoprene, CH<sub>4</sub>, ethane, propane and *i*-butane with CO and acetylene in the urban area samples suggest other/additional sources. The lack of correlation for the reported alkyl nitrates and the halogenated hydrocarbons, with the exception of 1,2-dichloroethane, indicates that these gases have primary sources other than vehicular emissions. Although the alkyl nitrate and halocarbon data are presented here for completeness, their sources are not discussed in this paper.

### 3.2. Composition of Karachi's roadside air

Karachi vehicular emissions were characterized using the air samples collected at the side of M.A. Jinnah Road, the busiest route in Karachi. Time series of toluene, benzene and *i*-pentane illustrate the daily and weekly mixing ratio trends (Fig. 3). In particular, traffic levels and pollutant concentrations were significantly lower on Sunday (13 December). The working day hydrocarbon mixing ratios show the strongest increases during the evening rush hour (15:00–20:00), despite the expanded boundary layer at this time of day. Smaller

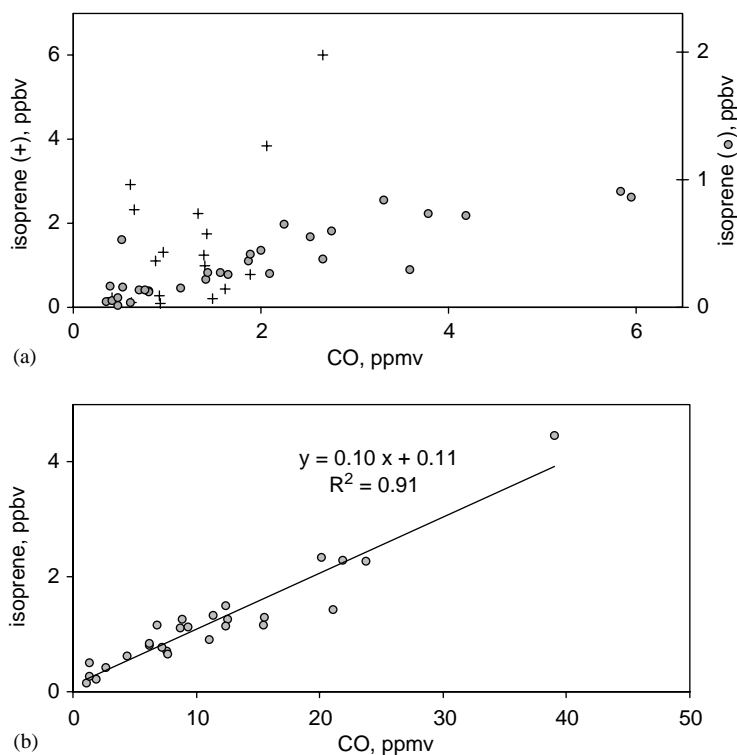


Fig. 2. (a) Correlation plot of isoprene with CO for the Karachi urban area. Crosses (+) represent samples collected at sites well removed from downtown (near the University of Karachi and North Karachi sector). Solid circles represent samples collected in the other four locations throughout Karachi (see text). (b) Correlation plot of isoprene versus CO for the samples collected at the M.A. Jinnah Road.

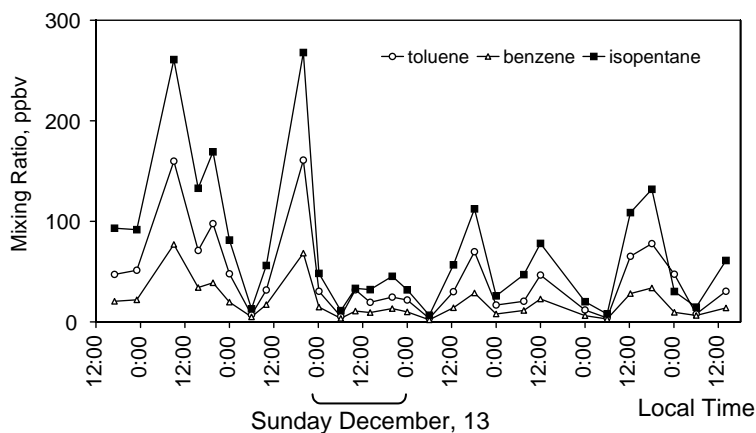


Fig. 3. Time series mixing ratio of toluene (open circles), benzene (triangles) and *i*-pentane (solid squares) observed at the M.A. Jinnah road, close to the roadside.

increases were observed during the morning rush hour (07:30–10:00), with the exception of 11 December in which the peak diurnal value occurred during the morning rather than afternoon commute. The day-to-day variations in the NMHC mixing ratio levels and patterns are expected to reflect changes in meteorology and vehicle traffic density.

The mean diurnal (24 h), daytime (07:30–20:00) and nocturnal (20:00–07:30) mixing ratios of the traffic samples are shown in Table 3, together with correlations of all the measured compounds with CO and acetylene. The most abundant measured gases were CO (65%) and CH<sub>4</sub> (29%), followed by alkanes (3.2%), alkenes (1.2%), alkynes (0.7%), aromatic compounds (0.5%), and halogenated hydrocarbons (<0.1%). Most of the hydrocarbons identified, with the exception of CH<sub>4</sub>, ethane and propane, showed strong correlations with CO and acetylene ( $R^2 > 0.8$ ), suggesting that vehicular emissions contribute to their observed mixing ratios in Karachi.

Mixing ratios of the most abundant hydrocarbons in both the Karachi urban area and M.A. Jinnah Road samples are shown in Fig. 4. With the exception of CH<sub>4</sub>, ethane and propane, the M.A. Jinnah Road samples show similar pattern compared to the Karachi urban area samples, again suggesting that vehicular emissions are important sources of each of these gases in Karachi. By contrast, CH<sub>4</sub>, ethane and propane are not enhanced in the M.A. Jinnah road samples, showing that vehicular emissions are not a source of these gases.

The number of vehicles in Karachi equipped with catalytic converters is quite small. The ethene/acetylene ratio is well-known to be an indicator of the presence of a catalytic device: emissions from non-catalyst vehicles have an ethene/acetylene ratio close to 1 (Hoekman, 1992), while catalyst equipped cars have a ratio of 3 or

greater (Duffy and Nelson, 1996). In addition, benzene/toluene ratios of about 0.4 have been reported for non-catalyst cars, whereas a ratio of about 2 indicates cars equipped with catalytic converters (Hebb et al., 2000). Plots of ethene versus acetylene and of benzene versus toluene are shown for the 28 samples collected beside the M.A. Jinnah road in Figs. 5a–b. Ethene/acetylene and benzene/toluene ratios were 0.95 ( $R^2 = 0.88$ ) and 0.43 ( $R^2 = 0.97$ ), respectively, reflecting the high number of vehicles without catalytic converters.

Karachi's gasoline contains high levels of lead (United States Energy Information Administration, 2000), and 1,2-dichloroethane (1,2-DCE, a known carcinogenic and mutagenic agent) is a leaded gasoline additive that is added on a mole-to-mole basis with lead (Clark et al., 1984). Among the halogenated hydrocarbons that were measured in the M.A. Jinnah Road samples, only methyl bromide (CH<sub>3</sub>Br) and 1,2-DCE correlated well with both CO and acetylene, suggesting that vehicular emissions contribute to elevated levels of these gases in Karachi (Table 3). Other studies have also found a small global source of CH<sub>3</sub>Br resulting from vehicular emissions (e.g., Thomas et al., 1997; Baker et al., 1998; Chen et al., 1999).

Isoprene mixing ratios in Karachi's urban area suggested the presence of both biogenic and anthropogenic sources (Fig. 2a; see Section 3.1). For the traffic samples collected along the M.A. Jinnah road, a strong correlation was found between isoprene and both CO and acetylene ( $R^2 = 0.91$  and 0.78, respectively). Moreover, the diurnal variations of isoprene were similar to other hydrocarbons with vehicular sources, showing a higher mean daytime value (1.6 ppbv) with a peak during the late afternoon from 18:00 to 20:00, and a lower mixing ratio at night (0.7 ppbv) (Table 3). The main known source of isoprene is biogenic (Khalil and



Table 3

Mean diurnal (24 h), daytime (07:30–20:00 local time) and nocturnal (20:00–07:30) mixing ratios for the compounds identified in samples collected at the side of the M.A. Jinnah Road, Karachi. Correlations with CO and acetylene are also shown. SD—standard deviation

Compound	Units	Mean				Correlation ( $R^2$ )	
		Total (24 h)	SD	Daytime	Nocturnal	CO	Acetylene
CO	ppmv	12.3	10.6	17.5	6.2	—	0.90
Methane		5.5	3.6	4.2	6.9	0.09	0.03
Ethane	ppbv	83	81	63	106	0.15	0.08
Propane		40	36	34	48	0.21	0.15
<i>n</i> -Butane		73	65	103	39	0.92	0.83
<i>i</i> -Butane		24.9	21.3	31.7	17.1	0.84	0.68
<i>n</i> -Pentane		102	98	154	43	0.93	0.90
<i>i</i> -Pentane		74	69	109	33	0.94	0.89
<i>n</i> -Hexane		71	70	108	27.4	0.93	0.90
2,3-Dimethylbutane		4.3	4.4	6.6	1.7	0.92	0.89
2,2-Dimethylbutane		2.5	2.3	3.6	1.3	0.91	0.85
2-Methylpentane		39	38	59	15.8	0.93	0.90
3-Methylpentane		25.9	25.5	39	10.4	0.93	0.90
<i>n</i> -Heptane		39	39	60	15.1	0.93	0.90
2,4-Dimethylpentane		2.5	2.5	3.8	1.0	0.94	0.90
2,3-Dimethylpentane		4.8	4.9	7.4	1.9	0.93	0.90
2-Methylhexane		18.1	18.2	27.7	7.0	0.93	0.90
<i>n</i> -Octane		7.0	6.7	10.0	3.5	0.89	0.81
2,2,4-Trimethylpentane		3.9	3.8	5.9	1.7	0.92	0.89
<i>n</i> -Nonane		1.6	1.4	2.0	1.1	0.67	0.67
<i>n</i> -Decane		1.2	1.1	1.4	0.9	0.44	0.52
Ethene		129	110	185	65	0.98	0.88
Propene		39	33	56	20.6	0.91	0.82
<i>i</i> -Butene		7.3	5.9	10.3	4.0	0.93	0.86
1-Butene		8.4	7.2	11.9	4.3	0.86	0.80
<i>cis</i> -2-Butene		1.3	1.1	1.8	0.6	0.91	0.84
<i>trans</i> -2-Butene		1.8	1.5	2.6	0.9	0.90	0.84
<i>cis</i> -2-Pentene		0.7	0.6	1.0	0.3	0.92	0.86
<i>trans</i> -2-Pentene		1.3	1.2	1.9	0.6	0.91	0.86
Isoprene		1.2	0.9	1.6	0.7	0.91	0.78
1,2-Propadiene		2.0	1.6	2.8	1.0	0.97	0.85
1,3-Butadiene		6.6	5.4	9.2	3.6	0.87	0.78
Acetylene		109	89	164	49	0.90	—
Propyne		2.9	2.6	4.2	1.5	0.97	0.91
Benzene		19.7	18.0	28.7	9.3	0.97	0.91
Toluene		44	41	64	21.2	0.93	0.87
Styrene		0.9	0.8	1.2	0.5	0.93	0.81
<i>n</i> -Propylbenzene		1.3	1.3	1.9	0.6	0.94	0.89
<i>i</i> -Propylbenzene		0.2	0.2	0.3	0.1	0.94	0.88
2-Ethyltoluene		1.9	1.7	2.7	1.0	0.93	0.88
4-Ethyltoluene		2.3	2.1	3.3	1.1	0.95	0.90
1,3,5-Trimethylbenzene		2.4	2.1	3.3	1.2	0.93	0.89
1,2,4-Trimethylbenzene		6.5	5.8	9.2	3.2	0.94	0.91
<i>o</i> -Xylene		12	15	15	9.2	0.95	0.90
<i>m</i> -Xylene		23	25	28	16	0.95	0.90
<i>p</i> -Xylene		11	11	13	7.4	0.94	0.87
Methylnitrate	pptv	10.6	4.1	12.2	8.8	0.86	0.75
Ethylnitrate		15.5	4.6	16.6	14.2	0.44	0.20
<i>n</i> -Propylnitrate		5.0	1.6	5.2	4.9	0.10	0.0004
<i>i</i> -Propylnitrate		21.0	7.6	21.8	20.2	0.20	0.01
2-Butylnitrate		25.1	12.8	27.3	22.6	0.27	0.02
CFC-11		312	62	318	305	0.11	0.15
CFC-12		957	620	1126	761	0.07	0.17

Table 3 (continued)

Compound	Units	Mean				Correlation ( $R^2$ )	
		Total (24 h)	SD	Daytime	Nocturnal	CO	Acetylene
CFC-113		84	1.0	84	84	0.00	0.07
CFC-114		14.4	1.6	14.6	14.2	0.12	0.19
Halon 1211		4.0	0.6	4.0	4.1	0.07	0.02
H-2402		0.5	0.04	0.5	0.5	0.16	0.09
HCFC-141b		15.8	9.2	15.3	16.4	0.003	0.001
HCFC-142b		180	277	209	152	0.02	0.002
HFC-134a		16.8	7.9	15.9	18.0	0.13	0.10
HCFC-22		456	372	502	411	0.16	0.31
Methyl chloride		1921	529	1800	2061	0.01	0.00
Methyl bromide		76	43	97	50	0.90	0.77
Methyl iodide		1.1	0.4	1.0	1.2	0.04	0.01
1,2-Dichloroethane		63	62	104	23.1	0.93	0.89
Methylene chloride		173	167	151	199	0.04	0.09
Methylene bromide		1.3	0.3	1.3	1.2	0.20	0.10
Bromoform		1.7	1.4	1.6	1.9	0.06	0.004
Chloroform		81	67	68	96	0.03	0.04
Methyl chloroform		76	3.8	76	75	0.10	0.11
Carbon tetrachloride		172	122	132	218	0.004	0.01
Tetrachloroethylene		122	150	147	92	0.05	0.07

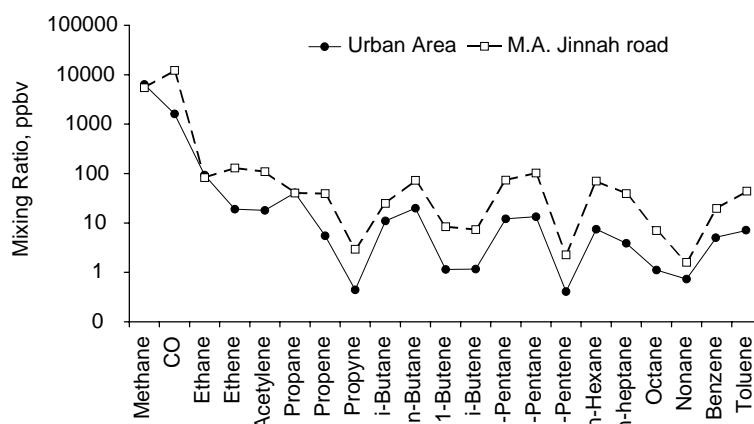


Fig. 4. Mixing ratios of major hydrocarbons detected alongside the M.A. Jinnah Road (open squares) during the first sampling campaign and throughout Karachi (solid circles) during the second sampling campaign. Note that methane, ethane and propane are not elevated in the M.A. Jinnah road samples compared to the Karachi urban area.

Rasmussen, 1992; Guenther et al., 1993; Jobson et al., 1994) but the above observations help confirm that isoprene is also emitted during combustion (Jonsson et al., 1985; McLaren and Singleton, 1996; Starn et al., 1998). The percentage contribution of isoprene from vehicular exhaust can be estimated from the slope of isoprene versus CO for the samples collected at the M.A. Jinnah Road (0.1 ppbv/ppmv, Fig. 2b) and the mean CO value throughout Karachi (1.6 ppmv; Table 1). We estimate that about 20% of the observed 0.8 ppbv mean isoprene comes from vehicular exhaust.

*i*-Butane and CO were better correlated in the M.A. Jinnah roadside samples compared to the Karachi urban area (Figs. 6a–b). The same behavior was found for *n*-butane, which showed an excellent correlation with CO for the samples collected at the M.A. Jinnah Road ( $R^2 = 0.96$ ) and a much weaker correlation for the samples collected throughout Karachi ( $R^2 = 0.67$ ). From this we conclude that an additional source of butanes must be considered. The average *i*-butane/*n*-butane ratio calculated for the samples collected at the M.A. Jinnah Road was 0.36, while the ratio for air

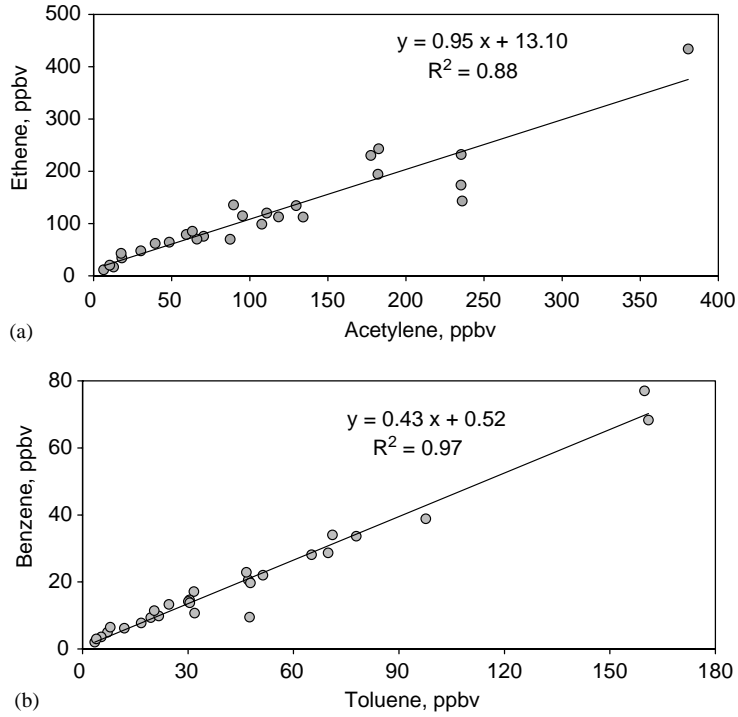


Fig. 5. Correlation plot of (a) ethene versus acetylene and (b) benzene versus toluene for the roadside samples collected at the M.A. Jinnah Road.

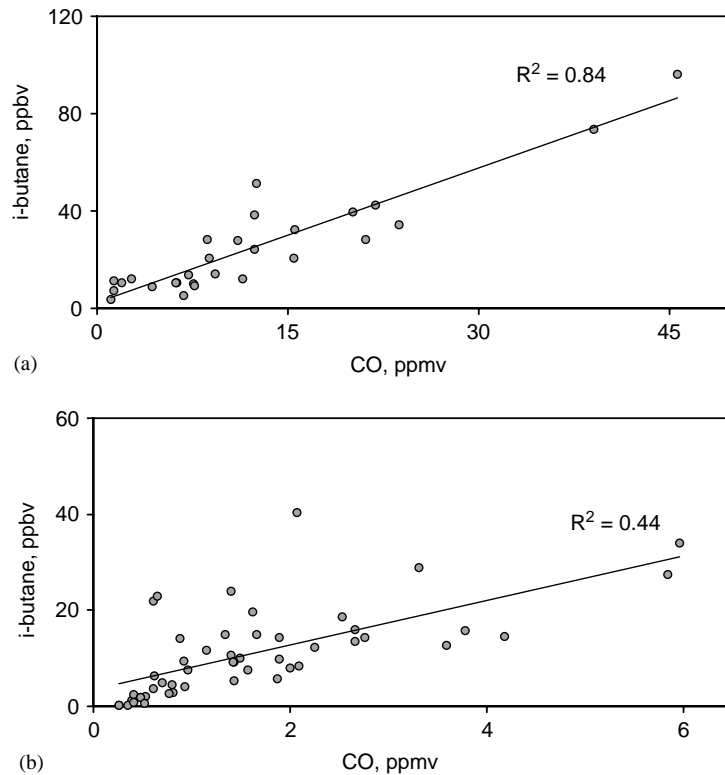


Fig. 6. Correlation plot of *i*-butane with CO at (a) the M.A. Jinnah roadside ( $R^2 = 0.84$ ) and (b) the Karachi urban area ( $R^2 = 0.44$ ).

samples collected throughout Karachi was 0.53. From source samples, the ratio of *i*-butane/*n*-butane from natural gas leakage is 1. However, natural gas in Karachi contains <0.03% butanes (Section 3.1), and the leakage of butanes from natural gas can contribute only minimally to the observed butane levels in Karachi. Butanes are a major component of LPG in Karachi (Section 3.1), and LPG leakage is expected to be a source of butanes in Karachi. However, LPG leakage does not explain the higher ratio of *i*-butane/*n*-butane in Karachi compared to the M.A. Jinnah road samples, because the *i*-butane/*n*-butane ratio for LPG (0.35) is almost the same as that for vehicular emissions (0.36). Instead, because *n*-butane reacts more quickly with OH than does *i*-butane (Atkinson, 1997), the higher ratio of *i*-butane/*n*-butane throughout Karachi could be in part the result of preferential removal *n*-butane during oxidation in more aged Karachi air, as compared to a lower ratio for fresh vehicular emissions along the M.A. Jinnah Road.

### 3.3. Photochemical reactivity

To estimate the amount of O<sub>3</sub> produced in Karachi by CO and each VOC, all reactions following the initial OH attack on CO or the VOC must be considered. In this study, the contributions of CO and each hydrocarbon to local O<sub>3</sub> production was approximated using the Maximum Incremental Reactivity (MIR) estimates of Carter (1994). This dimensionless coefficient (grams of O<sub>3</sub> produced per gram of VOC added to an initial VOC-NO<sub>x</sub> mixture), multiplied by the measured VOC concentration gives the expected contribution of each compound to local ozone formation (Grosjean et al., 1998b; Table 2). When applying the MIR scale, it is important to be aware that it does not perfectly fit the Karachi situation, and we use these calculations to assess the general significance of our Karachi observations.

Based on the MIR scale, the largest contributors to O<sub>3</sub> production in Karachi are ethene, CO, propene, *m*-xylene and toluene (Table 4). Ethene and propene are characteristic emissions from vehicular exhaust, and vehicular emissions are seen to be a leading source of O<sub>3</sub> production in Karachi. Methane, usually a very minor contributor to urban O<sub>3</sub> production, is sixth overall in Karachi. The wintertime mixing ratios of CH<sub>4</sub> in Karachi (6.3 ppmv) are more than triple current background levels (Dlugokencky et al., 2001; Simpson et al., 2002), and they are by far the highest levels we have measured in a wintertime city study (Blake and Rowland, 1995; Chen et al., 2001; Table 2). A reduction in natural gas emissions would benefit Karachi air quality and have a positive effect on both local and regional scales.

Table 4  
Photochemical ozone production by VOCs and CO for samples collected in the Karachi urban area

Compound	Ozone formation <sup>a</sup>
Ethene	161.2
CO	100.0
Propene	89.3
<i>m</i> -Xylene	74.9
Toluene	71.7
Methane	62.5
<i>i</i> -Pentane	49.4
<i>n</i> -Butane	48.2
1,2,4-Trimethylbenzene	43.8
<i>n</i> -Pentane	41.3
Propane	35.2
<i>i</i> -Butane	31.6
<i>o</i> -Xylene	31.1
<i>p</i> -Xylene	28.7
Ethane	28.5
<i>n</i> -Hexane	25.8
2-Methylpentane	25.0
1-Butene	23.3
1,3,5-Trimethylbenzene	21.4
Isoprene	20.3
1,3-Butadiene	19.3
3-Methylpentane	16.4
<i>i</i> -Butene	14.2
<i>n</i> -Heptane	12.9
Ethyne	9.6
Benzene	7.0
<i>n</i> -Octane	3.1

Note: See text for calculation details. VOC—volatile organic compound; MIR—Maximum Incremental Reactivity.

<sup>a</sup>[VOC] × MIR coefficient ([VOC] units, μg m<sup>-3</sup>; MIR units, dimensionless, gram of ozone produced per additional gram of VOC).

## 4. Conclusions

Two sampling campaigns were conducted in Karachi from December 1998 to January 1999. The first campaign characterized vehicular emissions next to the busiest thoroughfare in Karachi (the M.A. Jinnah Road), and the second campaign included air sampling throughout the Karachi urban area. This is the first time that VOC levels in the urban environment in Pakistan have been extensively characterized.

Many of the detected hydrocarbons were emitted from vehicular exhaust, as suggested by linear regression analysis carried out on the samples collected at the M.A. Jinnah Road and throughout the city. About 20% of the isoprene observed in Karachi was found to come from vehicular emissions. During working days, hydrocarbon mixing ratios typically showed the strongest increase during the afternoon commute (15:00–20:00) rather than in the morning. Much lower daytime mixing ratios were

observed along the roadside on Sunday, a non-working day in Pakistan.

The measurements taken throughout the Karachi urban area allow us to compare differences in NMHC emissions and abundances among various cities. In Karachi, CH<sub>4</sub> and ethane levels were much higher than in other cities that have been studied, highlighting the strong influence of natural gas leakage on Karachi's hydrocarbon composition. LPG leakage was found to contribute to the propane and butane burden in Karachi, though propane and butane levels in Karachi were less than in other cities such as Mexico City and Santiago. Benzene levels in Karachi sometimes exceeded recommended levels in other countries, suggesting that high benzene levels are of concern for Karachi air quality.

The VOC data were used to estimate the amount of O<sub>3</sub> produced in Karachi by each VOC. Based on the Maximum Incremental Reactivity (MIR) scale, the leading contributors to O<sub>3</sub> production in Karachi are ethene, CO, propene, *m*-xylene and toluene. Ethene and propene are signature gases from vehicular exhaust, and vehicular emissions are a leading source of O<sub>3</sub> production in Karachi. In addition to photochemical reactivity and O<sub>3</sub> production calculations, the VOC data obtained in this study will serve as inputs to toxicity (human exposure) and air quality and fuel policy related studies of air pollution control in the urban centers of Pakistan. Improvement in fuel quality and implementation of emission controls are needed in order to significantly improve Karachi air quality.

### Acknowledgements

We are grateful to Mr. Kevin Gervais, Mr. Adam Hill, Mr. Brent Love, Mr. Murray McEachern and Mr. Jason Paisley for technical support (University of California, Irvine). The authors would like to thank Drs. Ronaq R. Naqvi, Abdul Malik and Khalid Khan, and Ghazanfar Hussain and Amjad A. Mahmood (Chemistry Department and HEJ Institute of Chemistry, University of Karachi) for host institutes and help in sampling. One of the authors (Dr. Haider A. Khwaja) is deeply indebted to the United Nations Development Program (UNDP-TOKTEN) and to the National Talent Pool of the Government of Pakistan for providing financial assistance without which this work would not have been possible.

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