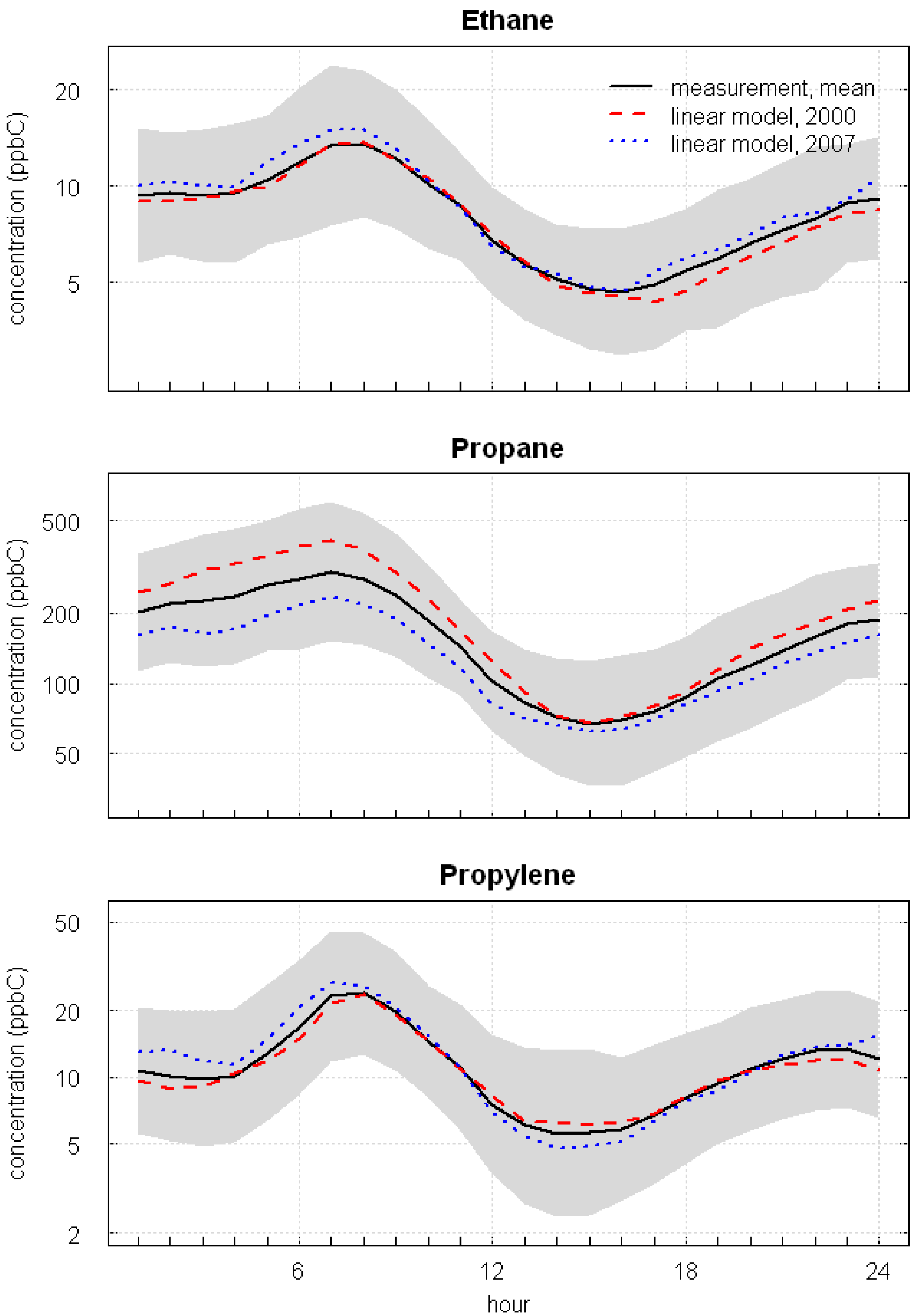
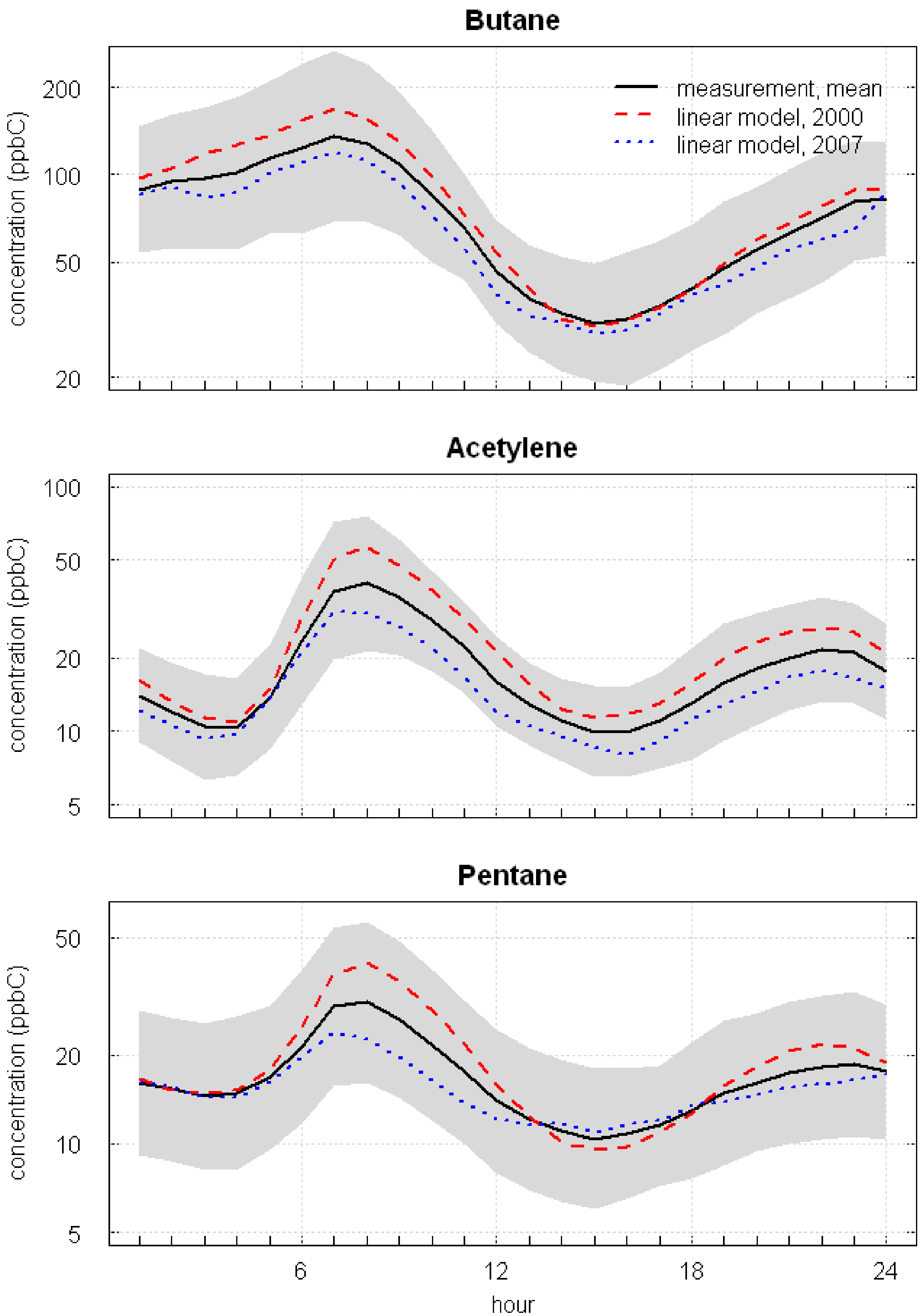
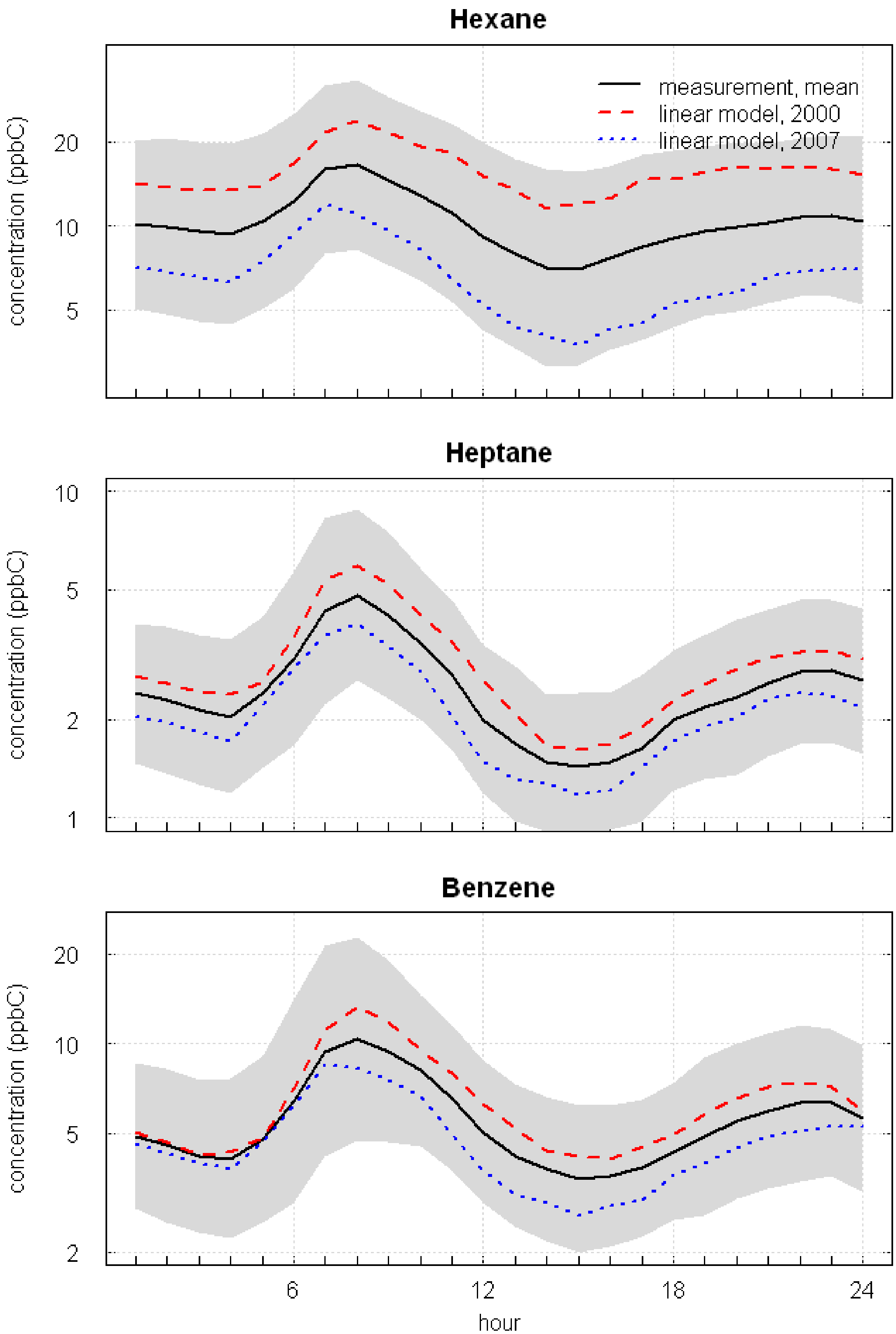
Measurements and receptor modeling of volatile organic compounds in Southeastern Mexico City, 2000 – 2007

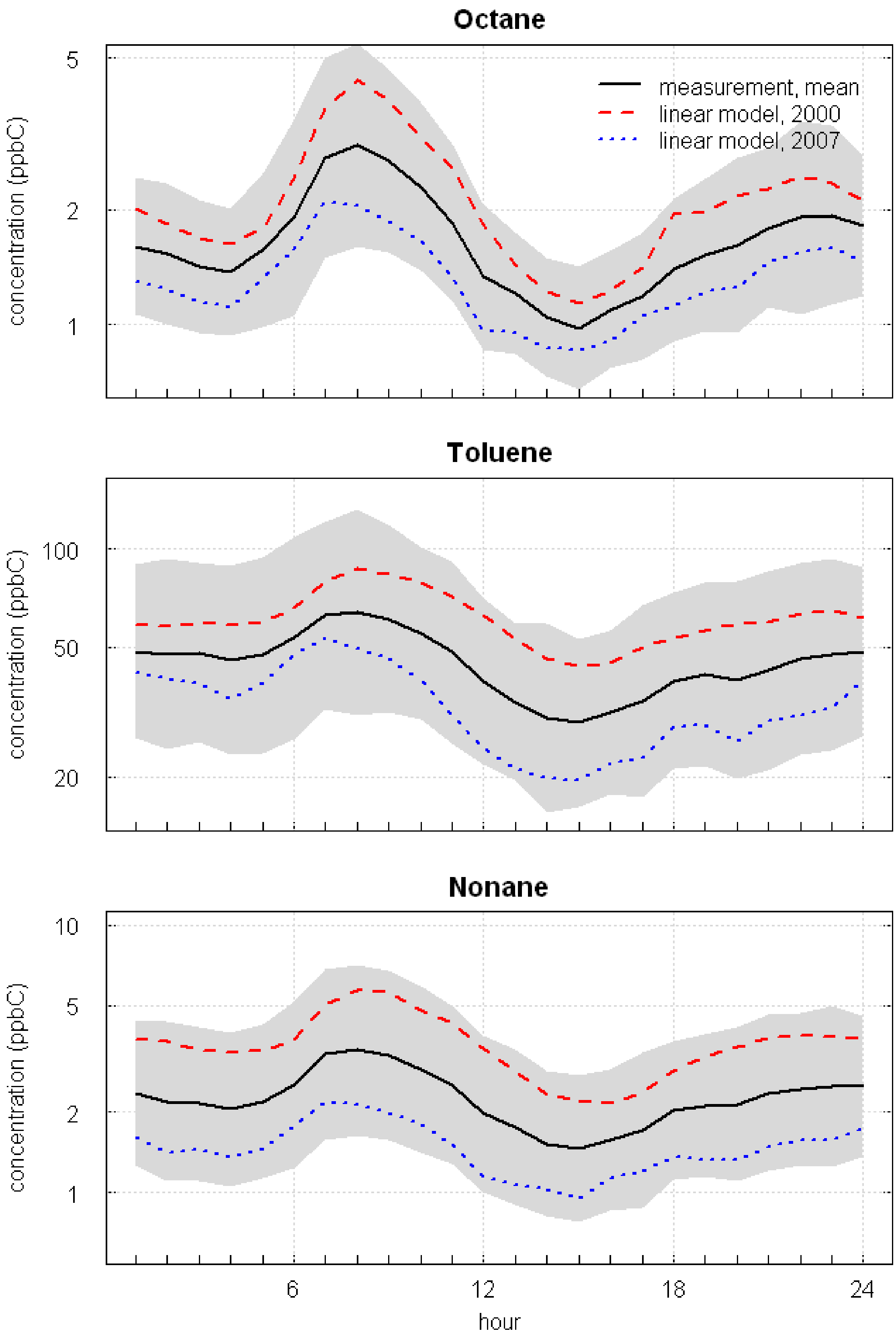
Supplementary Information

1. Diurnal variation of 13 VOC species




Butane
measurement, mean
linear model, 2000
linear model, 2007
concentration (ppbC)
200
100
50
20
Acetylene
concentration (ppbC)
100
50
20
10
5
Pentane
concentration (ppbC)
50
20
10
5
6
12
18
24
hour


Hexane
measurement, mean
linear model, 2000
linear model, 2007
concentration (ppbC)
20
10
5
Heptane
concentration (ppbC)
10
5
2
1
Benzene
concentration (ppbC)
20
10
5
2
6
12
18
24
hour


Octane
measurement, mean
linear model, 2000
linear model, 2007
concentration (ppbC)
5
2
1
Toluene
concentration (ppbC)
100
50
20
Nonane
concentration (ppbC)
10
5
2
1
6
12
18
24
hour

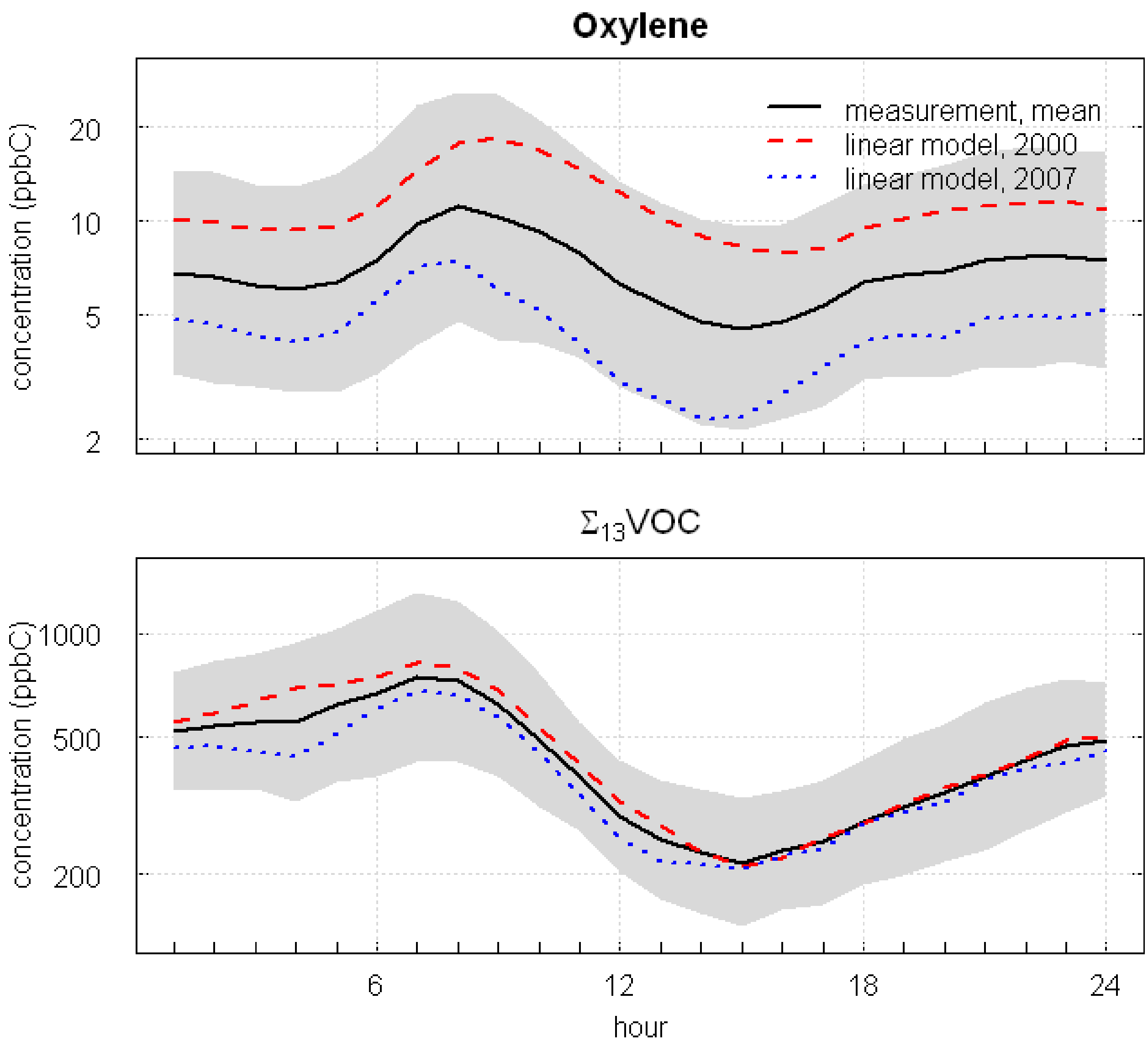


Figure 1. Diurnal variation of ethane, propane, propylene, butane, acetylene, pentane, hexane, heptane, benzene, octane, toluene, nonane, o-xylene, and Σ_{13}VOC. Shown are the measured log-transformed averages with their standard deviations (solid line with grey shadow), as well as the modelled values for mid 2000 and mid 2007 (dotted lines).

2. New vehicular source profiles determined in Guanajuato, Mexico

Vehicular source profiles, including 13 VOC species, were determined in a tunnel study in the City of Guanajuato, Mexico, during November 2008 (Figure 2). Two tunnels were selected, the Barretero tunnel and the Subterránea, in which samples were taken with SUMMA stainless steel canisters. Additionally to a sampling site at the center of each tunnel, a sampling site was established at the entrance of the Barretero tunnel, in order to account for non-vehicular emissions entering the tunnel from outside. The time for each sample was 2 hours. During sampling, also a traffic count was done. Table 1 shows the characteristics of each tunnel. The resulting vehicular source profiles (EXHTG1 for the Barretero tunnel and EXHTG2 for the Subterránea) and their uncertainties are given in Table 2 and Table 3, respectively.

Table 1. Characteristics of tunnels during the Guanajuato tunnel study.

	El Barretero	Subterránea
Length of unventillated section	800 m	160 m
Sampling site 1	400 m from entrance	80 m from entrance
Sampling site 2	50 m from entrance	--
Number of samples	18	8
Traffic count	Total: 673 vehicles per hour Gasoline vehicle (car, pickup): 91% Diesel vehicle (truck / bus): 4% motor bike: 5%	Total: 362 vehicles per hour Gasoline vehicle (car, pickup): 86% Diesel vehicle (truck / bus): 11% motor bike: 3%

Figure 2. Fotos from inside the Subterránea (left and middle panel), and the entrance of the Barretero tunnel (right panel)

3. Source profiles and uncertainties used for CMB analysis.

Table 2. Source profiles in ppbC%, normalized to 100% contribution of all 13 species. Vinylic paint (VINPA), liquefied petroleum gas (LPG), hot soak (HOTS), vehicle exhaust (EXHTI and EXHTN) from Mugica et al. (2002). Varnish (VARNISH) from Vega et al. (2000). Vehicle exhaust (EXHTG1 and EXHTG2) from Instituto Nacional de Ecologia, unpublished.

	SOLVENT		LPG	HOTSOAK	EXHAUST			
	VINPA	VARNISH	LPG	HOTS	EXHTI	EXHTN	EXHTG1	EXHTG2
Ethane	0.000	0.000	0.011	0.004	0.033	0.017	0.029	0.034
Propane	0.001	0.000	0.792	0.013	0.097	0.165	0.339	0.314
Propylene	0.000	0.000	0.005	0.005	0.055	0.044	0.158	0.150
Butane	0.010	0.003	0.191	0.130	0.087	0.120	0.064	0.080
Acetylene	0.000	0.000	0.000	0.016	0.225	0.160	0.134	0.150
Pentane	0.003	0.004	0.000	0.412	0.075	0.080	0.042	0.040
Hexane	0.153	0.006	0.000	0.150	0.059	0.064	0.049	0.050
Heptane	0.007	0.001	0.000	0.034	0.025	0.024	0.020	0.027
Benzene	0.014	0.002	0.000	0.068	0.068	0.059	0.020	0.019
Octane	0.002	0.001	0.000	0.013	0.017	0.012	0.002	0.002
Toluene	0.773	0.959	0.000	0.116	0.189	0.199	0.124	0.115
Nonane	0.001	0.002	0.000	0.007	0.016	0.009	0.002	0.004
o-Xylene	0.036	0.022	0.000	0.033	0.053	0.046	0.017	0.017

Table 3. Source profile uncertainties (standard deviations of replicates), scaled to normalized source contributions. Vinylic paint (VINPA), liquefied petroleum gas (LPG), hot soak (HOTS), vehicle exhaust (EXHTI and EXHTN) from Mugica (1999). Varnish (VARNISH) estimated from VINPA. Vehicle exhaust (EXHTG1 and EXHTG2) from Instituto Nacional de Ecologia, unpublished.

	SOLVENT		LPG	HOTSOAK	EXHAUST			
	VINPA	VARNISH	LPG	HOTS	EXHTI	EXHTN	EXHTG1	EXHTG2
Ethane	0.000	0.000	0.013	0.001	0.020	0.001	0.011	0.006
Propane	0.000	0.000	0.090	0.004	0.031	0.014	0.106	0.087
Propylene	0.000	0.000	0.003	0.002	0.005	0.009	0.030	0.023
Butane	0.003	0.001	0.047	0.020	0.013	0.012	0.028	0.024
Acetylene	0.000	0.000	0.000	0.005	0.039	0.054	0.096	0.058
Pentane	0.000	0.001	0.000	0.032	0.010	0.000	0.028	0.010
Hexane	0.022	0.001	0.000	0.004	0.008	0.006	0.024	0.011
Heptane	0.000	0.000	0.000	0.000	0.002	0.001	0.014	0.022
Benzene	0.006	0.001	0.000	0.002	0.006	0.005	0.013	0.008
Octane	0.000	0.000	0.000	0.001	0.007	0.000	0.002	0.001
Toluene	0.031	0.039	0.000	0.013	0.016	0.013	0.035	0.027
Nonane	0.000	0.000	0.000	0.001	0.014	0.001	0.001	0.001
o-Xylene	0.007	0.005	0.000	0.006	0.011	0.004	0.004	0.004

4. Example for CMB model output (version implemented in "R").

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===============================================
Chemical Mass Balance Version R-CMB 0.3
Report date and time: Mon Jun 21 20:54:44 2010
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Best fit out of 612
Runtime = 0.11 minutes

INPUT OPTIONS:
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Input file: data/Data_VOC_ppbC_evening.txt
Size: VOC_evening
ID: 404
Date: 14/5/2002

Fitting species and sources:
 Potential fitting species: Eth Pro But Ace Pen Hex Hep Ben Oct Tol Non
 Allowed number of species: 10 11
 Potential fitting Sources: VINPA VARNISH LPG HOTS EXHTI EXHTN EXHTG1 EXHTG2
 Allowed number of sources: 2 3 4 5

Eligible space criteria:
 Maximum uncertainty 20 %
 Minimum Projection 0.95

MAIN REPORT:
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Performance measures:
 R2:             0.982
 Chi2:           0.83
 Mass%:          81.2
 FracEst:        1
 Deg. Freedom:   6

Source contribution estimates:
   Source SCE(ppbC) Std.Err. SCE(%) TStat Estim
1   VINPA      41.3      6.5   14.2   6.4  TRUE
2     LPG     154.9     17.5   53.3   8.9  TRUE
3    HOTS      17.8      8.8    6.1   2.0  TRUE
4   EXHTI      76.4     13.8   26.3   5.5  TRUE

ELIGIBLE SPACE:
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Eligible space dim. = 4 for maximum uncertainty = 71.54 ppbC (20% of total measured mass)
 1 / Singular Values: 5.29 8.08 14.46 17.71

 Number of estimable sources: 4 for minimum projection = 0.95
   Source Projection
1   VINPA          1
2     LPG          1
3    HOTS          1
4   EXHTI          1
```

SPECIES CONCENTRATION:

Calculated over measured species concentrations

	Species	Fit	Measured	Calculated	Calc./Meas.
1	Total		357.7	290.2	0.81
2	Eth	*	7.2	4.3	0.60
3	Pro	*	118.4	130.4	1.10
4	Pre		17.2	5.1	0.29
5	But	*	52.3	39.0	0.74
6	Ace	*	17.5	17.5	1.00
7	Pen	*	13.1	13.2	1.01
8	Hex		65.0	13.5	0.21
9	Hep	*	3.7	2.8	0.76
10	Ben	*	5.3	7.0	1.32
11	Oct	*	1.5	1.6	1.08
12	Tol	*	48.5	48.4	1.00
13	Non	*	1.6	1.4	0.87
14	Oxy		6.4	6.1	0.96

Eliminated species: Hex

SOURCE CONTRIBUTION TO MEASURED SPECIES:

	Species	VINPA	LPG	HOTS	EXHTI
1	Total	0.115	0.433	0.050	0.214
2	Eth	0.000	0.237	0.173	0.042
3	Pro	0.000	1.036	0.055	0.008
4	Pre	0.000	0.045	0.049	0.022
5	But	0.008	0.566	0.083	0.190
6	Ace	0.000	0.000	0.091	0.070
7	Pen	0.009	0.000	0.023	2.404
8	Hex	0.097	0.000	0.004	0.176
9	Hep	0.078	0.000	0.029	0.702
10	Ben	0.109	0.000	0.181	0.981
11	Oct	0.055	0.000	0.047	0.663
12	Tol	0.658	0.000	0.024	0.183
13	Non	0.026	0.000	0.022	0.334
14	Oxy	0.232	0.000	0.053	0.394

5. References for Supporting Information

Mugica, V.: Determinación de los perfiles de emisión de compuestos orgánicos volátiles en la ZMVM y su aplicación en el modelo CMB, Ph.D. Thesis, Universidad Nacional Autónoma de México, Mexico, 1999.

Mugica, V., Watson, J., Vega, E., Reyes, E., Ruiz, M. E. and Chow, J.: Receptor Model Source Apportionment of Nonmethane Hydrocarbons in Mexico City, The Scientific World, 2, 844-860, 2002.

Vega, E., Mugica, V., Carmona, R. and Valencia, E.: Hydrocarbon source apportionment in Mexico City using the chemical mass balance receptor model. Atmos. Environ., 34, 4121-4129, 2000.