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# Photochemical reactivity and sources of individual VOCs in Mexico City

V. Mugica[1], E. Vega[2], H. Ruiz[1], G. Sánchez[2], E. Reyes[2] & A. Cervantes[2]

[1] *Universidad Autónoma Metropolitana-Azcapotzalco. Química Aplicada*
[2] *Instituto Mexicano del Petróleo, México D.F.*

## Abstract

Volatile organic compounds (VOCs) play a very important role in the photochemical production of atmospheric ozone. To developing cost-effective strategies aimed reducing ozone levels, the CMB model has been used to estimate the source contribution to the presence of total VOCs. Nevertheless, the photochemical importance and the origin of VOCs are not the same for all of them. In this paper, the relative contribution of VOCs to photochemical formation of ozone was examined in three sites of the Mexico City by ranking the VOCs according to their average concentration and the maximum incremental reactivity coefficients of each species. The most important compounds in the ozone formation in order of decreasing importance were: *meta/para* xylene, ethylene, toluene, 3methyl1butene, *iso*pentane, 124 trimethylbenzene, propene, *ortho*xylene, toluene, *n*butane, propane, 135 trimethylbenzene, and 1 butene. On the other hand, an assessment of the contribution of different sources to the observed concentration of the most abundant individual VOC was made by the application of the CMB model. Exhaust of gasoline and diesel powered vehicles were the most important sources to acetylene, ethylene, pentanes, *n*hexane, toluene and xylenes, although evaporative gasoline emissions contributed with more of 20% of *n*pentane and *iso*pentane. The major contributor to propane, nbutane and *iso*butane was the handling and distribution of LP gas. Food cooking contributed also to the presence of acetylene, ethylene, propane and butanes. Painting operations were emitters of toluene and *n*hexane. The results also showed that asphalting operation was an important source of xylenes and toluene.

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## 1 Introduction

Despite of the strict environmental controls established in Mexico City since 1990, local ozone air quality standard is still exceeded frequently. Ozone is a primary constituent of urban smog, although it is not emitted directly. Ozone is formed from the interaction of volatile organic compounds (VOC) and oxides of nitrogen (NOx) in the presence of sunlight. Of the hundreds of different VOC compounds emitted into the atmosphere, each has a different impact in the ozone levels, which is related with the rate, reaction mechanisms, conditions of the system reacting and how these reactions promote or inhibit ozone formation [1,2].

There are a number of ways to quantify a VOC effect on ozone formation, but probably the most direct quantitative measure for air quality impact assessment is its “incremental reactivity”. This is defined as the actual change in ozone formation in the airshed produced by the addition of a VOC in that airshed [2, 3, 4]. Due to the air pollution regulations, fuels and solvents with low ozone formation potentials could have a much greater chance to be widely used than those with high values [5]. For that reason some studies both in smog chambers as well as real world have been conducted with the aim to determine the VOC reactivities. [4, 5, 6, 7, 8].

Once the most reactive volatile organic compounds are known, next step is to know and control their sources. CMB model has been utilised as a powerful tool for the source apportionment of particulate matter and hydrocarbons [9]. In recent years the CMB model has been applied to the apportionment of non-methane organic compound sources in Mexico City [10, 11, 12]. These studies revealed that the main sources of these compounds are the gasoline vehicle exhaust, followed by diesel vehicle exhaust, handling and transportation of liquefied petroleum gas, asphalting operations, fuel vapours, food cooking, and use of solvents in painting and graphic arts. CMB model can be also utilised to determine the source contribution of individual organic compounds in order to focus the control strategies on those sources that emit the most reactive and toxic organic compounds [9, 13].

In this research, the main objective was to obtain specific information about the concentration, atmospheric reactivity, and source apportionment of the most abundant individual organic volatile compounds. The findings presented here were obtained as part of a larger air quality research that includes field campaigns, chemical analysis and modelling studies conducted by the Metropolitan University of Mexico City, the Mexican Petroleum Institute and the Desert Research Institute.

## 2 Methodology

### 2.1 Sampling and analytical methods

An intensive campaign was carried out in Mexico City during March 1997 at three monitoring stations, installed in three sites with different land uses

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(commercial, industrial and residential). Three hour integrated morning samples (6:00-9:00 A.M) were collected in stainless steel canisters [10, 11]. On the other hand, 9 two-hour integrated samples of vehicle emissions were obtained in a tunnel study during March 1998 [14]. Samples were analysed for $C_2$-$C_{12}$ hydrocarbons by gas chromatography with flame ionization detector (GC-FID) after previous cryogenic concentration of VOCs according to the EPA protocol of [11, 15, 16]. In this paper VOC refers to $C_2$-$C_{12}$ light hydrocarbons collected in canisters and measured by GC-FID. Compounds such as carbonyl, carbon dioxide and carbon monoxide are excluded.

### 2.2 Photochemical reactivity estimates

The relative contribution of 54 hydrocarbons to photochemical formation of ozone in Mexico City was estimated for both ambient air VOC concentrations as well as VOC tunnel concentrations using the dimensionless maximum incremental reactivity coefficients (MIR) developed by Carter [3]. The product of every average volatile organic compound concentration and its MIR was used to estimate the effects of individual VOC on ozone formation and to obtain a ranking of that. The MIR scale has been used in California, to quantify the reactivity of alternatively fueled vehicles, scaled to the reactivity of exhaust emissions from a vehicle using standard gasoline [1]. Grosjean *et al* [7] also utilised the MIR to assess the volatile organic compounds reactivity in the urban area of Porto Allegre City, Brazil.

### 2.3 Individual volatile organic compounds source apportionment

As was mentioned above, CMB model has been applied in Mexico City to the apportionment of total non-methane organic compounds. The CMB receptor model consists of a least-squares solution to a set of mass-balance equations that express each receptor chemical concentration as a linear sum of products of source profile abundances and source contributions. The sources profile abundances (i.e. the mass fraction of a chemical or other property in the emissions from each source type) and the receptor concentration with appropriate uncertainty estimates, serve as CMB input data. CMB calculates values for the contributions from each source type and the uncertainties of those values [9]. In the present study the CMB8 receptor modelling computer program was utilised to estimate the source contributions to each of the mass balance individual organic compounds [17].

## 3 Results and Discussion

Differences between average ambient air and tunnel concentrations of 54 volatile organic compounds can be observed in Table 1. The most abundant species for the three sites (commercial. Industrial and residential) were in decreasing order:

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**Table 1. Photochemical reactivity of VOC in Mexico City, March 1997**

| Specie | Ambient air | | | Tunnel | | |
|---|---|---|---|---|---|---|
| | Concentration µg/m³ | Ozone Formation (a) | Rank | Concentration µg/m³ | Ozone Formation (a) | Rank |
| Ethane | 16.53 | 4.1 | 49 | 48.01 | 12.0 | 48 |
| Ethylene | 32.40 | 239.7 | 2 | 201.38 | 1490.2 | 2 |
| Acetylene | 48.69 | 24.3 | 23 | 380.79 | 190.4 | 13 |
| Propene | 14.92 | 140.3 | 7 | 103.45 | 972.5 | 3 |
| Propane | 258.60 | 124.1 | 10 | 215.83 | 103.6 | 24 |
| Ibutane | 58.04 | 70.2 | 13 | 58.88 | 71.2 | 29 |
| Ibutene | 11.21 | 59.4 | 14 | 106.6 | 564.9 | 6 |
| 1-Butene | 10.56 | 94.0 | 12 | 0.0 | 0.0 | 53 |
| 13Butadiene | 0.2 | 2.2 | 54 | 29.8 | 324.8 | 9 |
| NButane | 133.19 | 135.9 | 9 | 180.02 | 183.6 | 15 |
| t2Butane | 3.26 | 32.6 | 20 | 13.54 | 135.4 | 21 |
| c2Butane | 3.86 | 38.6 | 19 | 11.50 | 115.0 | 23 |
| 3Methyl1butene | 29.35 | 182.0 | 4 | 23.58 | 146.2 | 19 |
| IPentane | 125.78 | 173.6 | 5 | 379.92 | 524.3 | 7 |
| 1Pentene | 2.87 | 17.8 | 28 | 11.37 | 70.5 | 30 |
| 2Methyl 1butene | 5.19 | 25.4 | 22 | 19.74 | 96.7 | 25 |
| NPentane | 43.26 | 45.0 | 17 | 152.21 | 158.3 | 17 |
| Isoprene | 1.63 | 14.8 | 32 | 0.00 | 0.0 | 54 |
| 2Methyl2butene | 7.41 | 47.4 | 15 | 44.39 | 284.1 | 10 |
| 22Dimethylbutene | 5.63 | 4.6 | 46 | 3.15 | 2.6 | 51 |
| Cyclopentene | 2.37 | 18.3 | 27 | 11.55 | 89.0 | 27 |
| 23Dimethylbutane | 3.37 | 3.6 | 51 | 41.87 | 44.8 | 37 |
| 2Methylpentane | 30.01 | 45.0 | 16 | 155.67 | 233.5 | 11 |
| 3Methylpentane | 11.55 | 17.3 | 30 | 92.58 | 138.9 | 20 |
| NHexane | 31.22 | 30.6 | 21 | 120.67 | 118.3 | 22 |
| t2Hexene | 1.38 | 9.2 | 35 | 6.82 | 45.7 | 36 |
| c2Hexene | 1.11 | 7.4 | 39 | 4.06 | 27.2 | 42 |
| Methylterbuthyleter | 30.32 | 18.8 | 26 | 275.34 | 170.7 | 16 |
| Metcyclopentane | 6.76 | 18.9 | 25 | 5.50 | 15.4 | 47 |
| 24Dimethylpentane | 3.43 | 5.1 | 45 | 38.81 | 58.2 | 32 |
| Benzene | 17.66 | 7.4 | 40 | 119.74 | 50.3 | 35 |
| Cyclohexane | 2.00 | 2.6 | 52 | 43.88 | 56.2 | 33 |
| 2Methylhexane | 9.04 | 9.8 | 34 | 51.19 | 55.3 | 34 |
| 23DiMethylpentane | 4.25 | 5.6 | 44 | 45.16 | 59.2 | 31 |
| 3Methylhexane | 11.39 | 15.9 | 31 | 56.65 | 79.3 | 28 |
| 224TrimethylPentane | 22.60 | 21.0 | 24 | 233.67 | 217.3 | 12 |
| NHeptane | 10.33 | 8.4 | 37 | 49.17 | 39.8 | 38 |
| Methylcyclohexane | 4.06 | 7.3 | 41 | 19.09 | 34.4 | 40 |
| 234TriMethylPentane | 10.96 | 17.5 | 29 | 93.90 | 150.2 | 18 |
| Toluene | 79.92 | 215.8 | 3 | 347.73 | 938.9 | 4 |
| 2Methylheptane | 4.06 | 3.9 | 48 | 21.88 | 21.0 | 44 |
| 3Methylheptane | 4.05 | 4.0 | 47 | 25.00 | 24.8 | 43 |
| NOctane | 6.21 | 3.7 | 50 | 28.08 | 16.8 | 46 |
| 25Dimethylheptane | 3.57 | 5.7 | 43 | 4.76 | 7.6 | 49 |
| Ethylbenzene | 15.46 | 41.7 | 18 | 69.71 | 188.2 | 14 |
| m/p-Xylene | 55.95 | 458.8 | 1 | 233.51 | 1914.8 | 1 |
| Styrene | 3.59 | 7.9 | 38 | 13.30 | 29.3 | 41 |
| o-Xylene | 21.05 | 136.8 | 8 | 90.19 | 586.2 | 5 |
| AnNonane | 4.42 | 2.4 | 53 | 2.32 | 1.3 | 52 |
| IPropBenzene | 4.64 | 10.2 | 33 | 8.35 | 18.4 | 45 |
| a-Pinene | 2.64 | 8.7 | 36 | 2.19 | 7.2 | 50 |
| NPropylbenzene | 3.11 | 6.5 | 42 | 18.79 | 39.5 | 39 |
| 135Trimethylbenzene | 10.17 | 102.7 | 11 | 35.16 | 355.1 | 8 |
| 124Trimethylbenzene | 16.32 | 143.6 | 6 | 10.50 | 92.4 | 26 |

(a) Products of mean individual VOC concentration and MIR coefficient

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propane, nbutane, *iso*pentane, toluene, *iso*butane, m/p xylene, acetylene, *n*pentane, ethylene, hexane and methylterbutyleter (MTBE); meanwhile the abundance of the organic species for the tunnel emissions had the following order: acetylene, *iso*pentane, toluene, MTBE, 224trimethylpentane, m/p xylene, propane, ethylene, and 2methylpentane, all of them associated with vehicular exhaust.

Table 1 also compiles the estimation of relative contribution of the VOCs to photochemical formation of ozone in the city area. The contributions were estimated for the three sites but, as the results were quite similar, only the values calculated for the average concentration are presented. The most important differences among sites were in the cases of propane, nbutane and isobutane which had a lower ranking in Xalostoc than the average ranking (10, 9 and 13 respectively) and acetylene which had the rank 18 in Pedregal. The ten most important hydrocarbons from the ambient air for production of ozone include four aromatics, three alkenes and three alkanes: *m/p*xylene (calculated for *m* xylene), ethylene, toluene, 3Methyl1-butene, *iso*pentane, 124 trimethylbenzene, propene, *o*xylene, *n*butane and propane. It is significant to highlight that the presence of high quantities of *n*butane and propane sometimes has been minimized because these compounds have small MIR coefficients, 0.48 and 1.02 respectively, that are very ineffectual compared with *m*xylene or 124 trimethylbenzene which have MIR coefficients of 8.2 and 8.8. Although the *n*butane and propane's reactivity coefficients are small, the elevated concentrations of these compounds are too elevated, and for that reason they play an important role in the formation of ozone in Mexico City. Making a comparison with Porto Allegre´s study [7], *n*butane and propane ranked 29 and 31 respectively for production of ozone.

On the other hand, the most important organic species from vehicle exhaust emissions in the tunnel for production of ozone had include four aromatic compounds, four alkenes, one diene and one alkane: *m/p* xylene, ethylene, propene, toluene, *o*xylene, *iso*butene, *iso*pentane, 135trimethylbenzene, 13butadiene, and 23dimethylbutene. *M/p*xylene and ethylene ranks 1 and two in both cases. In general, the alkenes ranks were higher in tunnel emission than in the ambient air. Despite of its high abundance, acetylene ranks 24 in ambient air and 13 in vehicular emissions due to its low reactivity (MIR coefficient = 0.5). The 124 trimethylbenzene ranks 6 for photochemical reactivity, but ranks only 26 for tunnel emissions, suggesting that this compound is emitted from a different source than vehicular exhaust. Finally, the presence of high quantities of 13butadiene into the tunnel emissions has a big concern not only for its toxicity but also due to its high photochemical reactivity.

The source contributions to the presence of the most abundant and photochemical reactive organic compounds in the ambient air at the three sites of Mexico City are presented in Figure 1. Except for propane, *n*butane and *iso*butane, which are emitted principally by handling and distribution of LP gas, the major source of volatile organic compounds in the atmosphere is the gasoline exhaust followed by diesel exhaust. Gasoline vapors have an important contribution to the presence of *iso*pentane, *n*pentane and *n*hexane. On the other hand the presence of atmospheric toluene, xylenes and nhexane is due also to asphalting operations.

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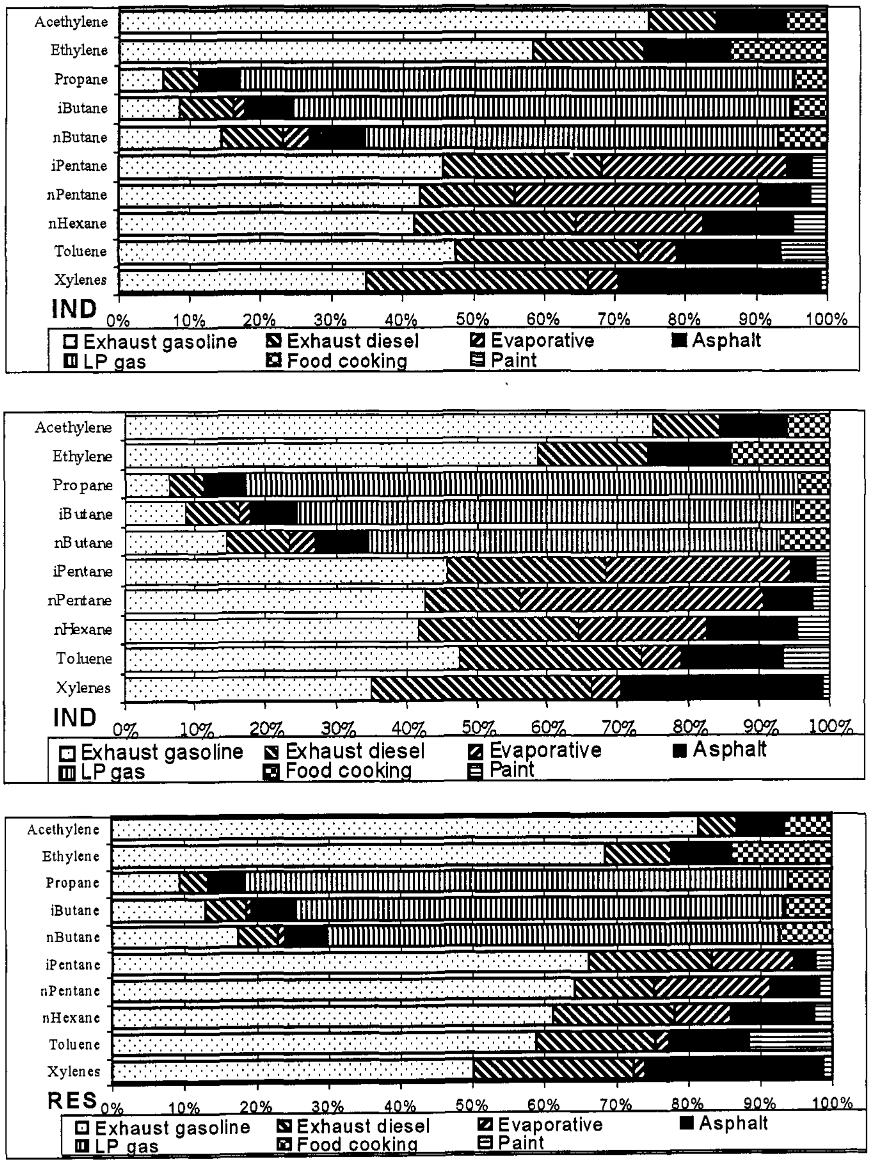

**Figure 1. Individual volatile organic compounds source apportionment**
COM: commercial site; IND: Industrial site; RES: Residential site

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Landfill had contribution only in the commercial place to toluene, butanes, propane and xylenes. Architectural coatings, painting and graphic arts contribute with around 10% of atmospheric toluene and had small contributions to *n*hexane, *n*pentane, *iso*pentane and xylenes. The apportionment of 124trimethylbenzene could not be done due to model estimations apportioned only 40%. This means that there is another unknown source of this compound, which is consistent with tunnel emissions measurements that reported small quantities emitted by vehicular sources.

Food cooking contributed to the presence of acetylene, ethylene, propane, isobutane and butane with 5, 12, 5, 6, and 7% in average, respectively. The presence of two carbon compounds in the ambient air has been always attributed to vehicle source, but the results obtained in this study suggest that the food cooking is also a source of these compounds. Although the results at three sites are similar, some differences were detected, for example the contribution of vehicular sources was smaller in the industrial site than in the other two. In opposite the contribution of fuel vapors were higher in the industrial site, maybe due to the use of petroleum distillates in that area.

## 4 Conclusions

The implementation of cost-effective control strategies of ozone control which take into account differences among the volatile organic species such as their ozone formation potentials or their toxicity require more knowledge of the photochemical reactivity of the organic compounds present in Mexico City as well as of their specific sources.

The ranking of VOC photochemical reactivities has been calculated for ambient air concentration at three sites of Mexico City as well as for tunnel emissions finding that in all sites xylenes, ethylene, toluene, propene and isopentane are into the ten most important compounds that contributes to ozone formation. In addition *n*butane and propane ranks 9 and 10 in ambient air due to their high abundance, while in tunnel emissions, *iso*butene, 13butadiene and 23dimethylbutene ranks into the first ten compounds with high ozone formation potentials. The results obtained in this research suggest that although propane and butanes are not very reactive on ozone formation, the emissions are so big that there is a significant contribution of these compounds in the atmospheric photochemical reactions, which conducts to ozone formation.

CMB model was applied to estimate the contribution of different sources to the presence of the most abundant and reactive VOCs. Results showed that handling and transportation of LP gas was the most important source of propane, nbutane and *iso*butane, although vehicular exhaust and food cooking had also a contributions. In general vehicular exhaust was the main source of most of the other organic compounds, especially gasoline exhaust. Diesel exhaust and asphalting operations were important sources of toluene and xylenes, while fuel vapours were important contributors of *iso*pentane and *n*pentane.

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