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Estimates for biogenic non-methane hydrocarbons and nitric oxide emissions in the Valley of Mexico

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Abstract

Biogenic non-methane hydrocarbons (NMHC), 2-methyl-3-buten-2-ol (methylbutenol or MBO) and nitrogen oxide (NO) emissions were estimated for the Valley of Mexico developing a spatially and temporally resolved emission inventory for air quality models. The modeling domain includes all the Metropolitan Mexico City Area, the surrounding forests and agriculture fields. The estimates were based on several sources of land use and land cover data and a biogenic emission model; the biomass density and tree characteristics were obtained from reforestation program data. The biogenic emissions depend also on climatic conditions, mainly temperature and solar radiation. The temperature was obtained from a statistical revision of the last 10 yr data reported by the Mexico City Automatic Atmospheric Monitoring Network, while the solar radiation data were obtained from measurements performed in a typical oak forest in the Valley and from sources of total solar radiation data for Mexico City. The results indicated that 7% of total hydrocarbon emissions in Mexico Valley are due to vegetation and NO emissions from soil contribute with 1% to the total NO_x emissions.

Keywords: Biogenic emissions; Non-methane hydrocarbons; Nitric oxide; Methylbutenol; Mexican pollution

1. Introduction

The Metropolitan Area of Mexico City (MAMC) is located in the Valley of Mexico, with a population of over 18 million and with heavy atmospheric pollution problems. In 1999, 75% of the days exceeded the Mexican air quality norm for ozone: 0.11 ppm in 1 h (NOM-020-SSA1-1993) (SEMARNAP et al., 2000). Many studies have proposed that Mexico Valley's atmospheric pollution comes primarily from vehicles and industries, subtracting importance to natural conditions from the Valley itself, such as temperature, wind, solar radiation, topography and vegetation. Natural conditions and the social characteristics of the MAMC should be considered to design efficient strategies to reduce harmful compound concentrations in the atmosphere.

The vegetation, as part of its metabolism, emits very reactive non-methane hydrocarbons (NMHC) which account for a large fraction of the total NMHC emitted in an airshed and even in low concentrations. Their high reactivity may have significant effects on the creation of ozone (Rusell et al., 1995). For example, it has been reported that isoprene, α-pinene and β-pinene, typical biogenic compounds, are more reactive than a weighted average of hydrocarbons emitted from antropogenic sources (Carter, 1994). As part of the nitrogen cycle, biogenic nitric oxide (NO) is emitted by soil microbial processes, exacerbated by soil fertilization activities (National Research Council, 1991). Both biogenic NMHC and NO emissions have a high importance in ozone formation, not only in rural areas, but also in urban areas, although biogenic emissions are smaller than antropogenic emissions.

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Recent studies have reported that 2-methyl-3-buten-2-ol (methylbutenol or MBO) is emitted from needles from diverse North American and Mexican pines (Harley et al., 1998; Goldan et al., 1993). The MBO emission rates can be 1 or 2 orders of magnitude greater than typical monoterpene emissions, and in some cases at rates comparable to isoprene emissions from high isoprene emitting tree species. The MBO in the troposphere reacts with OH contributing to regional O_3, and also MBO may be a significant source of acetone to the atmosphere, at least on a regional scale (Harley et al., 1998).

Mexico Valley is located at 2240 m above sea level in a subtropical region surrounded by mountains, covered by oak and pine forests in the west and south areas; agriculture fields, seasonal wetlands, arid and semi-arid shrublands in the north and east zones. With mild weather and temperatures of over 20°C all the year round, high biogenic emissions are predicted to occur, with important contributions to the formation and transportation of ozone into the MAMC. The annual climate in Mexico Valley can be divided in three climatic seasons, dry-warm season from March to May, raining season from June to October and dry-cold season from November to February.

In the last 12 yr, three biogenic emission inventories for Mexico Valley have been developed (SEMARNAP et al., 1996; Secretaria del Medio Ambiente del Distrito Federal, 1998; Ruiz-Suarez et al., 1999). Only two have been included in the total emission inventory for the MAMC. The first, performed in 1994, as part of the Air Quality Program for the Metropolitan Zone of Mexico Valley 1995–2000 (SEMARNAP et al., 1996), estimated the annual average of total biogenic NMHCs in 38,909 ton yr^{-1}. The 1994 emission inventory only used the dry-warm season as reference for all the annual emissions. The biogenic emissions inventory of 1996 (Secretaria del Medio Ambiente del Distrito Federal, 1998) estimated the NMHC and NO emissions using the US Environmental Protection Agency's second version of the Biogenic Emissions Inventory System (BEIS2). Considering the three climatic seasons of the Mexico Valley, the biogenic NMHC emissions were estimated in 131,077 ton yr^{-1} and the NO emissions in 1,279 ton yr^{-1}.

The goal in this research was to develop a spatially and temporally resolved biogenic emissions inventory to introduce its results into photochemical models to determine the ozone formation and transportation in the MAMC. The NMHCs estimated were isoprene, monoterpene, other volatile hydrocarbons (OVOC) (*n*-alkenes, alkenes, alcohols, acetates, aldehydes, ketones, ethers, esters, sesquiterpenes, in general oxygenated hydrocarbons with a lifetime shorter than 1 day), MBO and NO. As a secondary goal, the vegetation and soil annual average contributions were estimated.

2. Methodology

In this research, the most available information was used regarding land use, land cover, forest characteristics, agriculture fields, and local climatology. A biogenic emission model was used to estimate the emissions from vegetation and soil. The result was an emissions inventory as a function of the spatial position, time of day, month and percentage of cloud coverage. In this section, a complete description of the biogenic emissions modeling is provided, followed by a description of the input data.

2.1. Modeling domain

The modeling domain covers a rectangular area of $75 \times 83\,\mathrm{km}^2$ divided in 6225 cells of $1 \times 1\,\mathrm{km}^2$, located between 19°00′ and 19°40′ north latitude and 98°45′ and 99°28′ longitude. This region covers all the metropolitan area and all the forests in the Valley including the Federal District completely, a part of Mexico State and the north of Morelos State, as shown in Fig. 1.

The time scale used was hourly, considering time periods of 1 month, meaning that during all days of a month, the climatic conditions are the same.

2.2. Land use and land cover analysis

In general, the biogenic NMHC emissions are estimated using the following equation:

$$E = A_t \rho_b A_r I_e, \qquad (1)$$

where E is the emission ($\mu g_{NMHC}\,h^{-1}$), A_t is the covered area by trees (m^2), ρ_b is the biomass density ($g_{biomass}\,m^{-2}$) and I_e is the emission factor ($\mu g_{NMHC}\,g_{biomass}^{-1}\,h^{-1}$).

A land use and land cover analysis was made to obtain the distribution and location of the areas covered by trees, agriculture fields, suburbs, etc., using topographic maps (INEGI, 1998), urban maps (Guia Roji, 1998), LANDSAT images (Plan de Desarrollo Urbano, 1991), aerial photographs (Comision de Conurbacion Centro del Pais, 1993), and the Reforestation Forest Register Program (GDF, 1995). Although some sources are not recent (e.g., LANDSAT images and aerial photographs), their data helped to describe the study domain. Table 1 summarizes the aerial extent of the 17 land cover categories used in this research. The total area covered by any kind of forest represents one-third of the total modeling domain, while agriculture field, almost one-fourth and the urban area one-fifth.

Fig. 2 depicts the spatial distribution of five land cover categories presented in Table 1: urban area, agriculture fields, pine forests, pine and alder mixed forest and oak forest. As shown in Fig. 2a, the urban area is located in the middle of the Valley; the primary agriculture fields

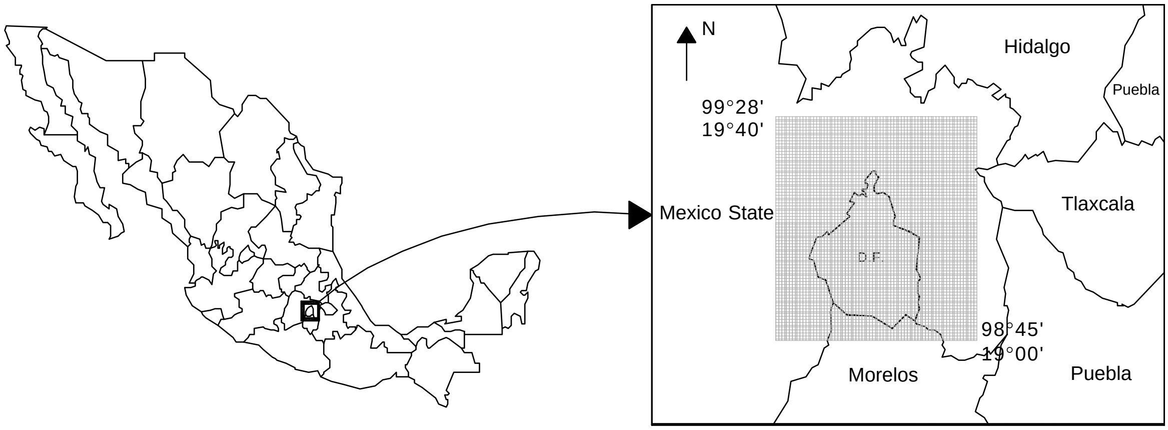

Fig. 1. Modeling domain and $1 \times 1\,\mathrm{km}^2$ grid cells used.

Table 1
Extents of different land cover categories within the modeling domain

Land cover category	Total area (km^2)	Percentage of the total study area
Urban area	1295.95	20.8
Industrial area	75.84	1.218
Urban parks	126.15	2.03
Arid areas	194.3	3.12
Lakes	35.81	0.575
Agriculture fields	1535.56	24.67
White cedar forest (*Cupressus*)	8.3	0.1333
Fir forest (*Abies*)	67.7	1.087
Pine forest (*Pinus*)	653.01	10.49
Oak forest (*Quercus*)	471.17	7.57
Alder forest (*Alnus*)	58.8	0.944
Oak and pine mixed forest	319.85	5.14
Pine and alder mixed forest	140.85	2.26
Pine and fir mixed forest	69.3	1.113
Oak and alder mixed forest	49.65	0.797
Grassland	1028.66	16.53
Temporal wet land	87.3	1.402
Total	6225	100

are located in the north and east, around the urban area, as in the southwest downhill (Fig. 2b); the pine forests are located in the southwest mountains (Fig. 2c); the pine and elder mixed forests are located in the highest south mountains (Fig. 2d); and the oak forests are located in the northwest and southeast of the modeling domain.

Table 2 summarizes the distribution of species for land cover categories with 2 or more species; for mixed forests, an equal cover for each species was considered. Current information about vegetation in the urban area for Mexico City does not exist. Thirteen years ago, it was estimated at 12.2% of total urban area (JICA, 1988). For this research it was assumed that urban vegetation is composed by 3% pines as the representative conifer, 3% eucalyptus as the representative broadleaf tree, and 6% grassland. Vegetation in urban parks was assumed to be 33% pine, 33% eucalyptus and 34% grasslands. Although eucalyptus is not a native species from Mexico Valley, previous urban reforestation programs, due to its easy and quick growth, it was considered as the principal urban species. There are many typical agriculture species in the Valley, e.g., corn, bean, pumpkin, amaranth, lettuce, maguey, cactus, among others. However, there is not specific information of its distribution because farmers often change their cultivated species. Besides, their covered areas are not very large, except for corn (INEGI et al., 1999), which is the main species and which was assigned as the representative agriculture species in this research. Vegetation in industrial areas is very scarce, so it was not included herein.

2.3. Biogenic emission model

The biogenic NMCH emissions estimate is based on the algorithm developed by Guenther et al. (1993) used by the US Environmental Protection Agency's second version of the BEIS2. This algorithm corrects the effects of temperature and solar radiation on biogenic NMCH emissions. The NO emissions from microbial soil processes are based on the model developed by Williams et al. (1992).

The emission factor, I_e in Eq. (1) is obtained from standard emission rates corrected for temperature and photosynthetically active radiation (PAR) for isoprene emissions, and only for temperature, for monoterpenes and OVOC. For isoprene emissions, I_e is calculated as

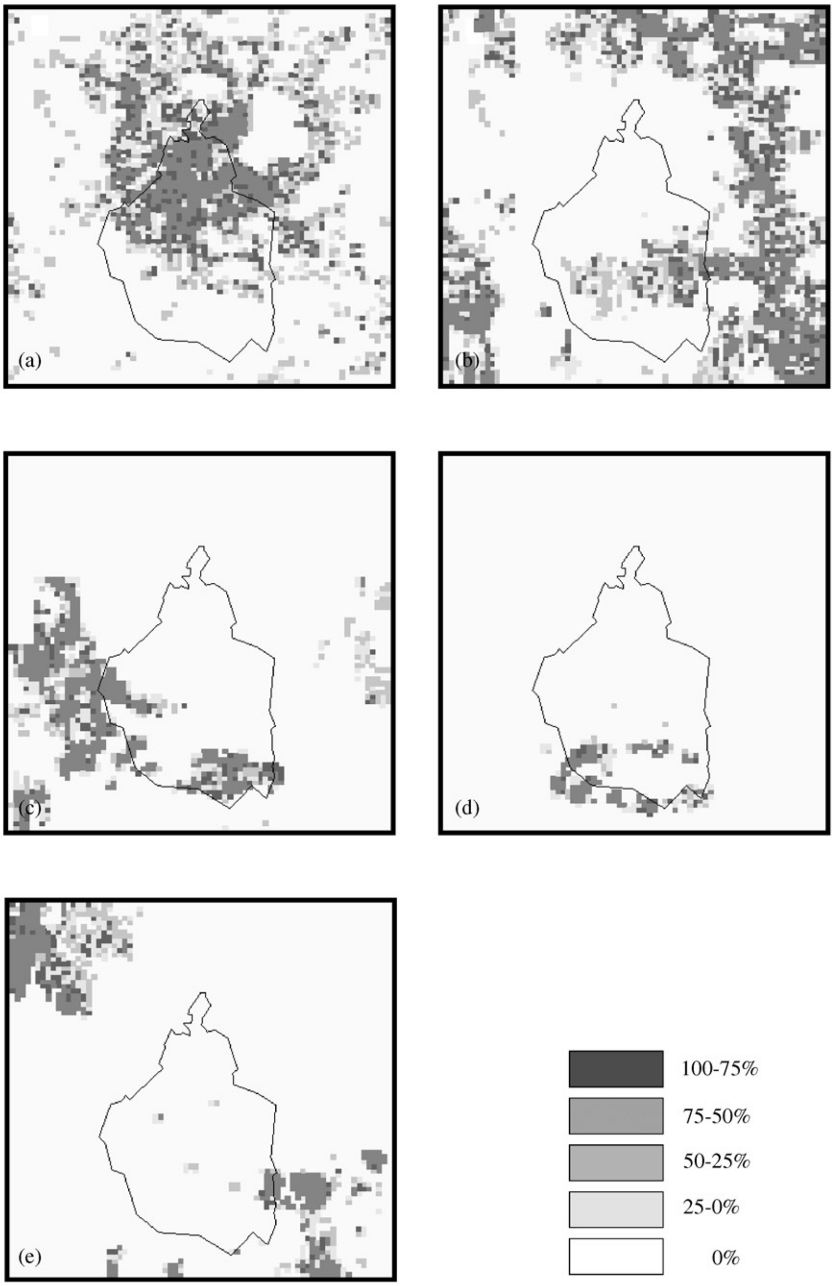

Fig. 2. Distribution analysis examples: (a) urban area, (b) agriculture fields, (c) pine forest, (d) pine and alder forest, and (e) oak forest.

follows:

$$I_e = I_S C_L C_T, \tag{2}$$

$$C_L = \frac{\alpha C_{L1} L}{(1 + \alpha^2 L^2)}, \tag{3}$$

$$C_T = \frac{\exp C_{T1}(T - T_S)/RT_S T}{1 + \exp C_{T2}(T - T_M)/RT_S T}, \tag{4}$$

where I_S is the species-specific emission flux at 30°C and $1000\,\mu\mathrm{mol\,m^{-2}\,s^{-1}}$, C_L is the light intensity correction factor, C_T is the temperature correction factor, C_{L1} and α are empirical coefficients derived from emission rate measurements (Guenther et al., 1993), L is the PAR flux ($\mu\mathrm{mol\,m^{-2}\,s^{-1}}$), T is the leaf temperature (taken to be the environmental temperature) (K), T_S is the normalizing temperature (303 K), R is the ideal gas constant and T_M, C_{T1}, and C_{T2} are empirical coefficients derived by fit to species of several genera (Guenther et al., 1993).

In the case of monoterpenes and OVOC, the emission factor, I_e is given by

$$I_e = I_S \exp(\beta(T - T_S)), \quad (5)$$

where β is an empirical coefficient derived by fit species of several genera (Guenther et al., 1993).

Finally, NO emissions are calculated using the next equation (Williams et al., 1992):

$$E_{NO_x} = A_r I_{NO}, \quad (6)$$

where A_r is the studied area (m^2) and I_{NO} is the emission index ($ng\,m^{-2}\,s^{-1}$), which is obtained by the model developed by Williams et al. (1992), given as

$$I_{NO} = A \exp(BT_{soil}), \quad (7)$$

where A is a factor associated with the use land (Williams et al., 1992), B is an empirical parameter derived from emission rate measurements ($^\circ C^{-1}$) and T_{soil} is the soil temperature which is dependent on land use ($^\circ$C). T_{soil} is calculated as

$$T_{soil} = T_1 T_e + T_2, \quad (8)$$

where T_1 is an empirical parameter derived from emissions rate measurements, T_2 is a land use specific soil temperature adjustment factor ($^\circ$C), and T_e is the environmental temperature. Table 3 presents the different values for A, T_1 and T_2 for each land cover category used here.

Considering MBO emissions respond to changes in both light and temperature, as the isoprene emissions, the algorithm developed by Guenther et al. (1993) described above can be successfully applied to calculate these emissions. For this case, the empirical correcting factors for PAR and temperature developed by Harley et al. (1998) could be used.

2.4. Solar radiation and temperature data

Leaf temperature and PAR are primary driving forces for vegetation emissions, as can be observed in the algorithm developed by Guenther et al. (1993). Leaf temperature was assumed to be equal to the environmental temperature. The hourly and monthly temperature averages ware obtained from a statistical analysis of data reported by the Mexico City Automatic

Table 2
Percent distribution in areas with more than one species

Kind of area	Species 1	Species 2	Species 3
Pine and fir mixed forest	50% pine	50% fir	—
Pine and oak mixed forest	50% pine	50% oak	—
Pine and alder mixed forest	50% pine	50% alder	—
Oak and alder mixed forest	50% oak	50% alder	—
Urban parks	33% pine	33% eucalyptus	34% grassland
Urban area	3% pine	3% eucalyptus	6% grassland

Table 3
Standardized emission rates, foliar mass and leaf area indexes used for the species in the Valley

Species	Foliar mass[a]	LAI[a]	HCNM emission rates[b] ($\mu g\ g_{biom.}^{-1}\ h^{-1}$)			NO emission rate[c] ($ng\,m^{-2}\,s^{-1}$)		
	($g_{biom}\,m^{-2}$)	($m^2\,m^{-2}$)	Isoprene	Monterpenes	OVOC	A	T_1	T_2
Vegetation in arid areas	150	0.00	0.433	0.630	0.378	0.90	0.66	8.8
Agriculture fields (corn)	1500	577.6	0.00	0.472	1.889	9.00	0.72	5.8
White cedar (*cupressus*)	700	4.5	0.10	1.60	1.50	0.07	0.84	3.6
Oyameles (*abies*)	1500	4.5	0.1133	3.4	1.85	0.07	0.84	3.6
Pine (*pinus*)	700	4.5	0.1132	3.4	1.85	0.07	0.84	3.6
Oak (*quercus*)	375	4.5	79.3	0.227	1.848	0.07	0.84	3.6
Alder (*alnus*)	375	4.5	0.1133	0.1133	1.85	0.07	0.84	3.6
Grassland	150	0.00	0.1120	0.280	0.1680	0.90	0.66	8.8
Vegetation in wet land	500	0.00	0.1120	0.280	0.1680	0.003	0.92	4.4
Eucalyptus (*eucalliptus*)	375	4.5	79.3	3.40	1.85	0.05	0.84	3.6

[a] (Geron et al., 1994).

[b] Standardized HCNM emission rates in ($\mu g\,g_{biom}^{-1}\,h^{-1}$) at 1000 $\mu mol\,m^{-2}\,h^{-1}$ and 30°C. For forest tree emission rates (Guenther et al., 1993, 1994; Geron et al., 1994) and for agriculture (Lamb et al., 1993).

[c] NO emission rates in ($ng\,m^{-2}\,s^{-1}$) and air-to-soil temperature conversion formulae for land cover categories (Williams et al., 1992).

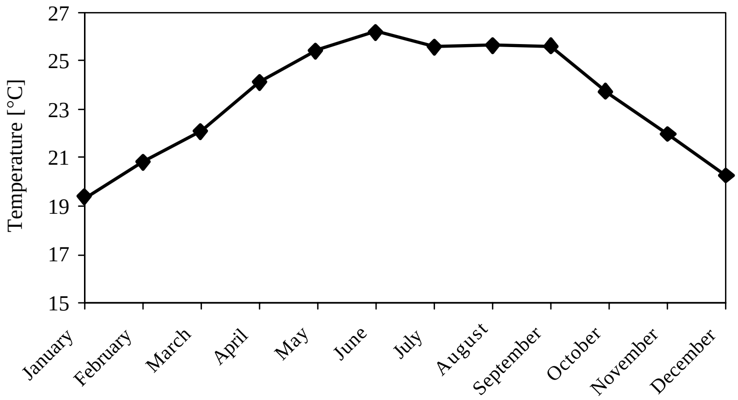

Fig. 3. Environmental average temperature in Mexico Valley at 15:00 h.

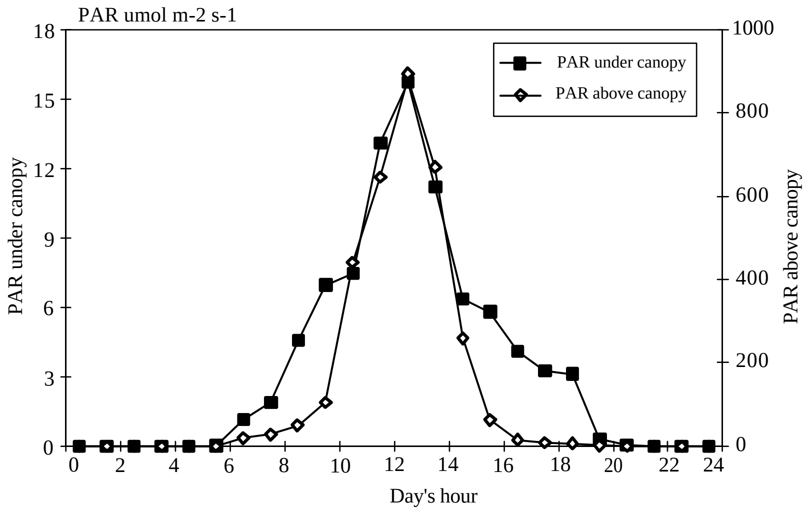

Fig. 4. PAR measurement under and above canopy in Chapa de Mota oak forest, Mexico State, from 16 to 22 April 2000.

Atmospheric Monitoring Network, from 1986 to 1998 (RAMA, 1998). The maximum daily temperature during all the year is always reported at 15:00 h, as can be observed in Fig. 3.

For Mexico Valley, there are only few short time PAR measurement studies. Ramos-Vazquez and Barradas (1998) measured PAR in the southwest of the Valley, registering $836 \pm 36.92\,\mu\text{mol}\,\text{m}^{-2}\,\text{s}^{-1}$ between 11:00 and 14:00 h, during the dry-warm season. In the present research, during an April week, PAR measurements in an oak forest at the northwest of the Valley (Chapa de Mota, 19°48′, 99°30′) were made using an IL1700 radiometer–photometer of International Light Inc. April was the month selected because of the month with less cloud cover percentage in Mexico Valley. Fig. 4 depicts the results, the maximum PAR measured was $883\,\mu\text{mol}\,\text{m}^{-2}\,\text{s}^{-1}$ at 13:00 h, which is 5.5% higher than the measured, by Ramos-Vazquez and Barradas (1998). Using as a reference, the PAR measured in April in this work and total solar radiation data for Mexico Valley (Almaya and Lopez, 1975), the monthly PAR was obtained.

The cloud cover attenuates the clear sky total and partial solar intensities to more closely represent actual conditions present in the atmosphere. To quantify its effect for isoprene emissions, the algorithm developed by Kaston and Czeplak (1980) was used, given as

$$\mathrm{PAR}_{\mathrm{attenuated}} = \mathrm{PAR}(1 + c(\mathrm{skyt}^{D})), \tag{9}$$

where $c = -0.75$, $D = 3.4$ and skyt is the fraction of the sky covered by clouds. This algorithm was used only to quantify specific scenarios.

2.5. Forest characteristics

In the Forest Register (DDF, 1995), 218 different forested areas are considered. The data required to estimate the biogenic emissions, covered area, species distribution, diameter at breast height, and average tree height and density was also obtained from this reference (DDF, 1995).

The covered area, A_t, in Eq. (1), for each species in the forested areas is calculated through

$$A_t = \rho_t \left(\frac{\pi \, \mathrm{crwd}^2}{4} \right) A_r, \tag{10}$$

where ρ_t is the tree density (number of trees/area), A_r is the studied area (in this case one cell of $1 \times 1\,\mathrm{km}^2$) and crwd is the crown width for trees, assuming as circular the total crown area. The model defined by Minckler and Gingrich (1970) was used to calculate the crwd, for conifer trees Eq. (11a) was used, and for broadleaf trees Eq. (11b)

$$\mathrm{crwd}\,(\mathrm{m}) = 0.47 + 0.166\,\mathrm{dbh}\,(\mathrm{cm}), \tag{11a}$$

$$\mathrm{crwd}\,(\mathrm{m}) = 1.13 + 0.205\,\mathrm{dbh}\,(\mathrm{cm}). \tag{11b}$$

The leaf biomass was calculated as the product of the covered area for each species multiplied by its foliar mass, which was assigned by genus from Geron et al. (1994) data. Information about Mexican trees foliar mass does not exit. In this work, the foliar mass for areas throughout North America were assumed to be applicable to the vegetation in Mexico Valley. Table 3 summarizes the foliar mass constants used for each land cover category.

For the biogenic NMHC emissions estimation, the biomass density for each kind of forest and cultivation is needed for Eq. (1). The forest biomass density was taken from Guenther et al. (1994) while the cultivation density was obtained from SAGAR (2000) and Iowa State University of Science and Technology (1993). The biomass density variation across the year is neglected because mostly Mexican tress are evergreens, meanwhile cultivation biomass density has important variations from April to September, coinciding with the crop season. The biomass tree distribution changes in the vertical, being an important factor for the emissions. To quantify this effect, two distributions were used, one for conifers and the other for broadleaf trees, as proposed by Mayenkar et al. (1992).

2.6. Canopy model

Several canopy models have been used in biogenic emission models, from the very simple "look-up table" models that reduce the solar radiation and temperature by fixed amounts as the canopy is penetrated (Guenther et al., 1993; Geron et al., 1994), to complex energy balance models that calculate the temperature based on many meteorological variables (Vogel et al., 1995). Lamb et al. (1996) evaluated forest canopy models to estimate isoprene emissions, observing little practical difference between the temperature and solar radiation profiles developed by simple and complex canopy models. Therefore, in this work the simple scaling functions of Lamb et al. (1993) were used to correlate the vertical profiles of environmental temperature, relative humidity and wind speed in the canopy to the existing above canopy conditions. Meanwhile, the PAR vertical profiles were estimated using the algorithm developed by Geron et al. (1994). It is much more important to accurately estimate the species composition and leaf biomass density of each forest; compared to these parameters, the choice of canopy model does not affect the accuracy of the biogenic emission estimation (Lamb et al., 1996; Wiedinmyer et al., 2000).

In order to corroborate the canopy models used in this work, additional temperature and PAR measurements were made above and under canopy during the PAR measurements in an oak forest at the northwest of the Valley (Velasco-Saldaña, 2001). The measurements above were made in an open space without tree interferences. The under canopy measurements were compared to the estimated, using the characteristics of that specific forest. The estimated relation between under and above canopy PAR was 2.73% and the measured 3.15%; therefore, the estimated PAR under the canopy was approximately underestimated by $3.7\,\mu\mathrm{mol\,m^{-2}\,s^{-1}}$ at 13:00 h in an April day.

3. Results

Using the methodology and input data described above, a special software was developed to calculate the biogenic emissions in Mexico Valley. The user only needs to define the cloud cover percentage, the month and the hour. The software gives the spatial distribution of the biogenic emissions in ($\mathrm{kg\,h^{-1}\,km^{-2}}$) for each $1 \times 1\,\mathrm{km}^2$ cell as a result. As an example, Fig. 5 presents the biogenic emissions estimations for a day in June at 14:00 h considering a 10% of cloud cover. Fig. 5a–e depict the estimated biogenic emissions for each compound analyzed (monoterpenes, isoprene, OVOC, NO and MBO). For these climatic and seasonal conditions, the total biogenic NMHC emissions in the modeling domain are $13.44\,\mathrm{ton\,h^{-1}}$ (76% of isoprene, 13% of monoterpenes and 10% of OVOC); while NO emissions reach $356\,\mathrm{kg\,h^{-1}}$. The major monoterpenes's emission is located in the southwest of the domain (Fig. 5a), coinciding with the principal areas covered by pine and fir forests (Fig. 2c). This area has historically reported the highest ozone concentrations in the Valley, where biogenic emissions are not the primary cause; the wind transports all the urban emissions to this area, increasing the ozone potential formation (SEMARNAP et al., 2000). Fig. 5b depicts the isoprene emission, which is the major compound emitted by biogenic sources in Mexico Valley. It is emitted principally by oak forests, located in the northwest and south of the Valley. The OVOC emissions (Fig. 5c) are located from the northwest to the southwest and in the south of the Valley, the emissions in the northwest emitted by oaks are smaller than the emissions emitted by conifers in the southwest. The NO emissions from soil are heavily emitted in agriculture areas (Fig. 5d), located mainly in the east and north of the Valley (Fig. 2b). Biogenic emissions are considerably lower in grasslands and arid areas in the

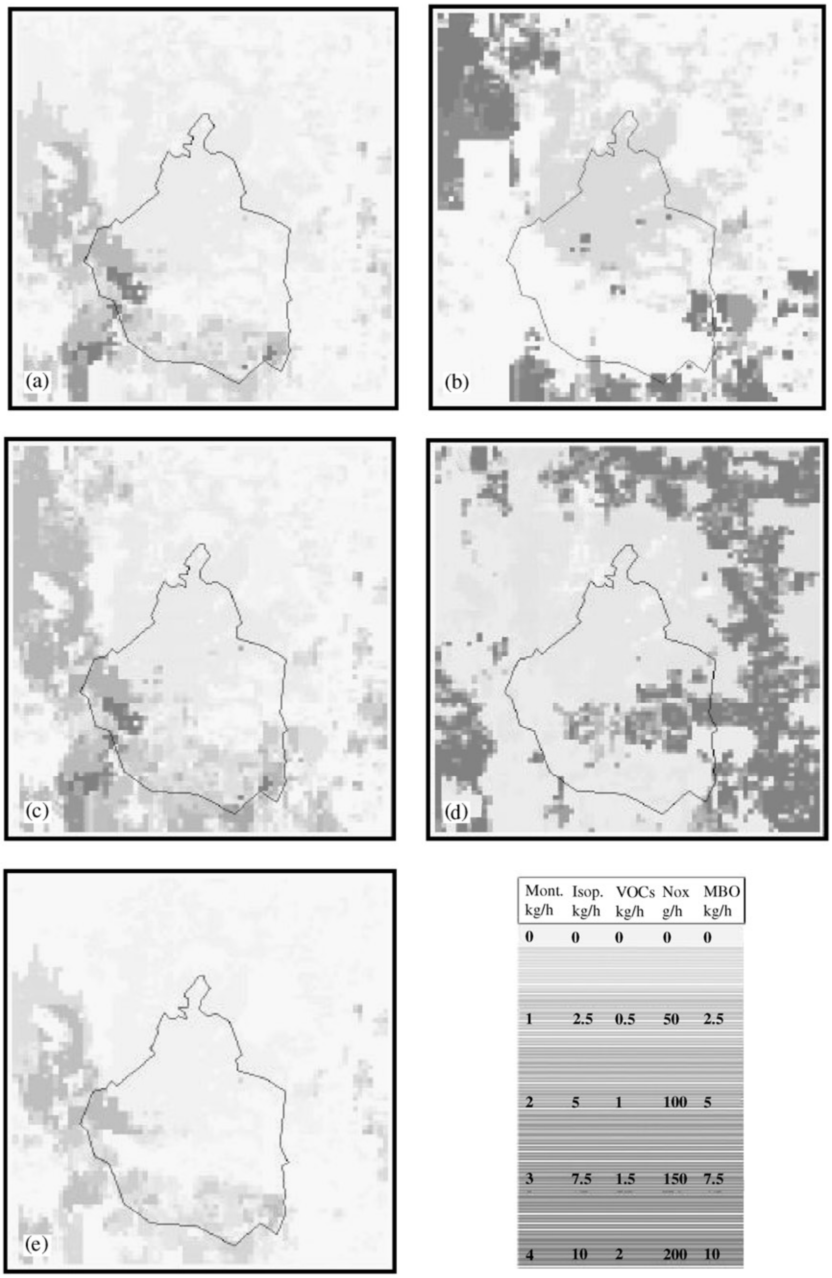

Fig. 5. Spatial distribution of biogenic emissions using $1 \times 1\,km^2$ grid cells for monoterpenes (a), isoprene (b), OVOC (c) and MBO (e) emissions in ($kg\,h^{-1}$), and for NO (d) emissions in ($g\,h^{-1}$), using the climatic conditions of a June day at 14:00 h with 10% of cloud cover.

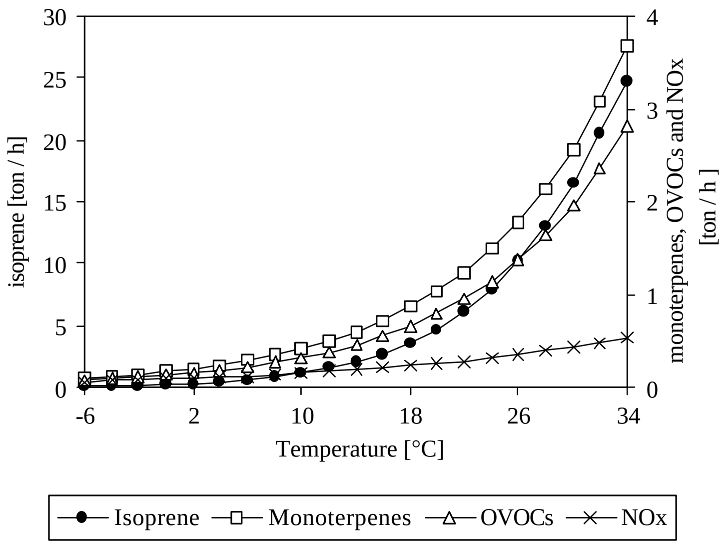

Fig. 6. Biogenic emissions for Mexico Valley as a function of the temperature in (ton h^{-1}), considering a constant PAR of 800 μmol m^{-2} s^{-1} and 0% of cloud cover.

north and east of the modeling domain, as well as in urban areas, where the green areas are small (less than 12.2% of the total urban area) (JICA, 1988). In the north and east of the Valley, grasslands and arid areas prevail, emitting few isoprene and monoterpenes.

Kirstine et al. (1998) found that emissions from pasture are high in oxygenated hydrocarbons including methanol, ethanol, propanone, butanone and ethanal, while isoprene and monoterpenes were found to be minor components of the grass emission. The grass species analyzed in the Kirstine's study were different from Mexican species, but they could be used to estimate these compounds from Mexican pastures in future works.

Monoterpenes, OVOC and NO emissions depend only on environmental temperature, while isoprene emissions depend on temperature and PAR. Fig. 6 shows the total emissions for Mexico Valley as a function of the temperature. The maximum temperatures appear in summer, reaching an average of 26°C at 15:00 h; in winter at the same hour, the average temperature is 20°C.

The biogenic isoprene emissions are a function of temperature and PAR. The PAR is affected by the cloud cover percentage. With 50% of cloud cover in the Valley, the isoprene emissions are reduced to 4.4%, in contrast, with 100% they are reduced to 67%. The cloud cover effect is shown in Fig. 7.

Fig. 8 presents the hourly biogenic emissions for a September day. It can be observed that between 13:00 and 15:00 h, the highest emissions are present, coinciding with the highest day temperatures. Monoterpenes, OVOC and NO are present during all the daytime and nighttime, whereas isoprene are present only during daytime, reaching the highest emission at 14:00 h. Fig. 9 presents the monthly emissions for each analyzed compound. It can be observed that September is the month with the highest biogenic NMCH emissions: 3898 ton $month^{-1}$, and OVOC and monoterpenes emissions reach their highest emissions in this month, 1860 and 1066 ton $month^{-1}$, respectively. The highest monthly emissions of these two compounds can be expected in June, coinciding with the highest environmental temperatures, although agriculture fields present the highest biomass density in September, when the crop is ready; OVOC and monoterpenes agricultural fields annual contribution are 60% and 11% of OVOC, respectively. Isoprene emissions have the highest emissions in May, the month with the highest PAR, being emitted principally by oak forests. The NO emissions do

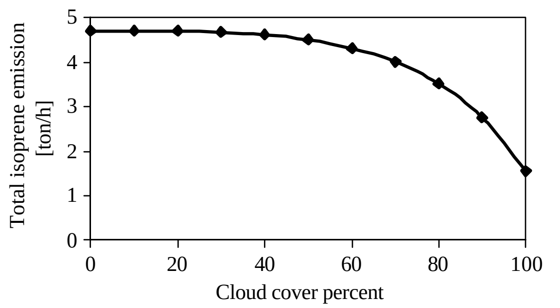

Fig. 7. Isoprene emissions in Mexico Valley as a function of the cloud cover percentage, and considering a constant PAR of 800 μmol m^{-2} s^{-1} and an environmental temperature of 20°C.

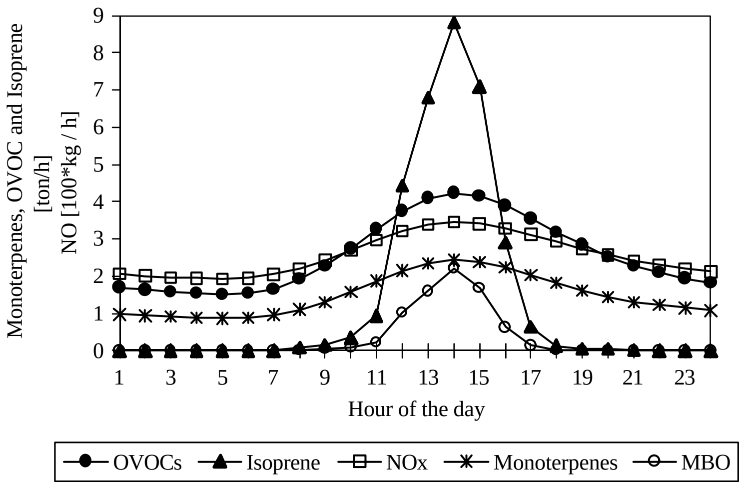

Fig. 8. Hourly emissions during a September day for Mexico Valley. Monoterpenes, OVOC, MBO and isoprene emissions in (ton h^{-1}), NO emissions in ($100 \times kg\,h^{-1}$).

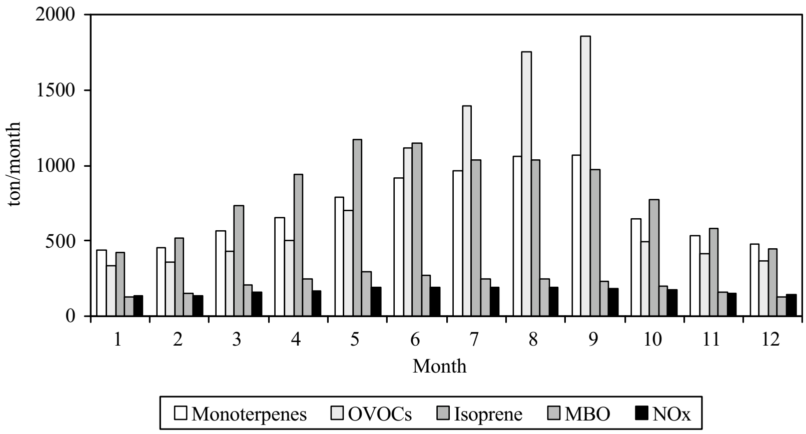

Fig. 9. Monthly emissions for Mexico Valley. Emissions are in (ton $month^{-1}$).

not present important differences during all the year, the highest emissions are during summer months with an average of 190 ton $month^{-1}$. Table 4 summarizes the annual emissions of NO and biogenic NMHC, which contribute each one approximately with a third of the total biogenic NMHC emissions.

The main pine species in the Valley of Mexico are *P. montezumae*, *P. ayacahuite*, *P. hartwagii*, *P. teocote*, *P. oocarpae*, *P. michoacana*, *P. leiophylla*, *P. rudis*, *P. pseudostrobus*, and *P. patula* (SAGARPA, 2002; SARH, 1994). Harley et al. (1998) determined the MBO emission rates of 34 species of pines, including *P. montezumae*, *P. pseudostrobus* and others of the subsection *oocarpae*, which were located in the modeling domain of this emission inventory. An estimation using the emission rate of 25 μg C $g^{-1}\,h^{-1}$ corrected to 30°C and 1000 μmol $m^{-2}\,s^{-1}$ calculated by Harley et al. (1998) was made with the assumption that Mexican pine species are similar to *P. ponderosa*. Fig. 5e presents the spatial distribution of MBO for a day in June at 14:00 h considering 10% of cloud cover. For these climatic conditions, the total MBO emissions in the modeling domain were 2.59 ton h^{-1}. Spatial distribution is similar to monotoerpenes, the highest emissions are located in the pine forests (Figs. 2c and d). The hourly profile of MBO emissions during a September day can be observed in Fig. 8, which is similar to the isoprene; meanwhile Fig. 9 depicts the monthly MBO emissions. Table 4 shows that annual MBO emissions are 71%, 74% and 74% lower than monoterpenes, OVOC and isoprene emissions, respectively.

Using as a reference the mobile (vehicles, buses, etc.), point (industries) and area (services, residences, etc.) source emission data from the emissions inventory for

Table 4
Annual emission for each biogenic compound for Mexico Valley

Compound	Annual emission (ton yr^{-1})
Monoterpenes	8562
OVOC	9718
Isoprene	9800
Total NMHC	28,080
Methylbutenol	2508
NO	2013

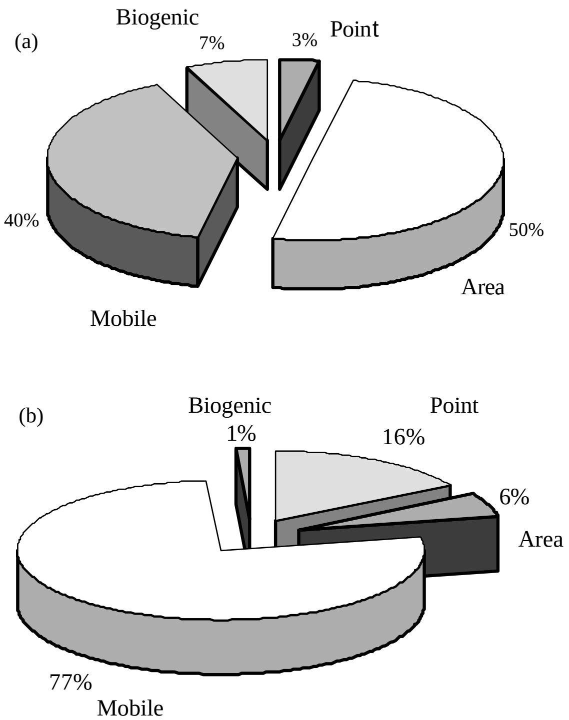

Fig. 10. Contribution of sources to the emission inventory for Mexico Valley. Point (industries), mobile (vehicles, buses, etc.) and area (services, residences, etc.) source data are from the emission inventory for the Metropolitan Area of Mexico Valley of 1996. (a) Total hydrocarbon emissions, 466,101 ton yr^{-1}, (b) NO_x emissions, 174,754 ton yr^{-1}.

the Metropolitan Area of Mexico Valley of 1996 (SEMARNAP et al., 1996), and adding the biogenic emissions estimated here, it was found that biogenic emissions contribute with 7% of total hydrocarbon emissions, without considering MBO emissions, and 1% for NO emissions (Fig. 10).

The 1994 emission inventory (SEMARNAP et al., 1996) determined that biogenic NMHC emissions contributed with 3.79% of the total hydrocarbons emissions in the Valley of Mexico. The biogenic emissions obtained in the present study were 38% lower. The biogenic NMHC emissions estimated in the 1996 emission inventory (Secretaria del Medio Ambiente del Distrito Federal, 1998) were 4.6 times higher than the estimated in this study, while its contribution to the total hydrocarbons emissions was 3 times higher. The soil NO emissions estimated in 1996 were 50% lower than this study, but its contribution to the total NO_x emission was similar (1%). A comparison between these inventories and our results is difficult, since the modeling domains, the climatic conditions, and the forest's data used were different. However, according to our results, previous emission inventories had overestimated the biogenic emissions.

4. Conclusions

In this research, a new biogenic emission inventory was developed for Mexico Valley, proving that with the data available, generated with other purposes and scarce economic resources, it is possible to obtain input data to be used in photochemical models for the assessment of air quality. For Mexico Valley, it is the first time that characteristics of the trees are used to estimate biogenic NMHC, including all forest and cultivations in a $1 \times 1\,km^2$ grid area, with a time distribution of 1 h and considering constant climatic conditions each month. Considering biogenic emissions contribution to the total mass emissions in the Valley of Mexico and more important, their high reactivity, ozone formation studies must consider natural emissions data.

In this work, MBO emissions from trees for the Valley of Mexico were estimated for the first time. This estimation is a first approach, and results can be overestimated or underestimated since emission rates for the majority of Mexican pine species are unknown, emission data of *P. Ponderosa* was used as one of the highest emitters among pines (Harley et al., 1998). Emission factors for Mexican trees should be determined in future studies.

As final conclusion, the knowledge about biogenic emissions in Mexico Valley have to be improved. In order to reduce atmospheric pollution, environmental decision makers must consider the emissions from vegetation and soil as an important source.

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