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Vertical distribution of ozone and VOCs in the low boundary layer of Mexico City

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Abstract

The evolution of ozone and 13 volatile organic compounds (VOCs) in the boundary layer of Mexico City was investigated during 2000–2004 to improve our understanding of the complex interactions between those trace gases and meteorological variables, and their influence on the air quality of a polluted megacity. A tethered balloon, fitted with electrochemical and meteorological sondes, was used to obtain detailed vertical profiles of ozone and meteorological parameters up to 1000 m above ground during part of the diurnal cycle (02:00–18:00 h). VOCs samples were collected up to 200 m by pumping air to canisters with a Teflon tube attached to the tether line. Overall, features of these profiles were found to be consistent with a simple picture of nighttime trapping of ozone in an upper residual layer and of VOCs in a shallow unstable layer above the ground. After sunrise an ozone balance is determined by photochemical production, entrainment from the upper residual layer and destruction by titration with NO, delaying the ground-level ozone rise by 2 h. The subsequent evolution of the conductive boundary layer and vertical distribution of pollutants are discussed in terms of the energy balance, the presence of turbulence and the atmospheric stability.

1 Introduction

Air overlying a region has layers of diverse history and consequently diverse composition and chemistry, as well as complex vertical distributions of pollutants. These vertical distributions are result of the horizontal and vertical transport due to the effects of the winds and turbulence produced by thermal fluxes and surface friction. In practice, vertical profiles of pollutants are estimated by mathematical models. The drawback of these models is that they require ideal conditions; otherwise their predictions are more uncertain. In an urban area there are many buildings, which cause large inhomogeneities in the energy and wind profiles, and thus the vertical distributions of pollutants are difficult to model. A clear understanding of the evolution of air pollutants at different heights of

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the boundary layer over urban areas is an important factor to improve the air quality assessment of polluted cities, where the high concentrations of ozone and other toxic pollutants produce serious impacts on public health. For example, the characterization of nighttime accumulation of pollutants in the lowest layers and their subsequent interactions in the following morning as the nocturnal boundary layer begin to break up are necessary to evaluate the effectiveness of pollution control measures, such as limiting stationary emissions at night or instituting a later workday to shift the morning rush hour to later on after sunrise.

Despite the importance of the vertical distribution of pollutants in urban areas, data to characterize the lowest few hundred meters of the atmosphere are scarce, and the complex interactions between anthropogenic emissions and the evolving chemistry of secondary pollutants in the urban boundary layer are not yet well understood. This lack of information is accentuated in urban areas located in tropical regions, where much of the urban world population growth occurs. A good example of these urban centers is Mexico City, the second largest megacity and one of the most polluted urban areas of the world. Mexico City has a population of 19 millions, around 4 million vehicles and over 50,000 industries. It is situated in the Valley of Mexico, at a low latitude (19°25′ N) and at high altitude (2240 m), resulting in subtropical weather and intense solar radiation. In addition, the elevated anthropogenic emissions and the area's topography with mountains to the west, east and south of the valley produce high levels of photochemical pollutants on a daily basis (Molina and Molina, 2002). These characteristics have converted Mexico City into an ideal laboratory to perform field experiments to address the urban air pollution of the developing world. A number of extensive field campaigns have included upper layer measurements in Mexico City. The MARI initiative included upper air quality measurements using tethered balloons, rawinsondes, a lidar and an aircraft during the winter of 1991 (Streit and Guzman, 1996; Nickerson et al., 1992). During the take-offs and landings of the aircraft, vertical profiles of O_3, NO_x, CO and aerosols were acquired (Pérez-Vidal and Raga, 1998). The IMADA-AVER experiment in February and March of 1997 included diverse meteorological measurements to char-

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acterize the wind circulation and boundary layer of the Valley of Mexico (Doran et al., 1998). From 2000 to 2004 the National Center for Environmental Research and Training (CENICA) of the National Institute of Ecology (INE) of Mexico, with the support of the Japanese International Cooperation Agency (JICA), conducted tethered balloon measurements in selected days to improve the understanding of the vertical evolution of pollutants in the boundary layer of Mexico City. Measurements corresponding to 2002 and 2003 were part of the MCMA-2002 & 2003 field campaigns (Molina et al., 2007). Wöhrnschimmel et al. (2006) analyzed the 2003 measurements in terms of the impact of emission sources on the vertical profiles of pollutants. The recent MILAGRO (Megacitiy Initiative: Local and Global Research Observations) field campaign in Mexico City during March 2006 included a wide array of instruments located at ground sites and onboard aircraft to study the evolution of emissions from a megacity. It is expected that analysis of the data sets from MILAGRO will provide additional valuable information on the air pollution science of Mexico City.

This manuscript analyzes data obtained from tethered balloon measurements during 2000 to 2004. These measurements included vertical distributions of ozone and meteorology up to 1000 m above ground level (all heights hereafter are referenced to ground level), and for the first time, observations of concentrations of 13 selected VOCs (ethane, propane, propylene, butane, acetylene, pentane, hexane, heptane, benzene, octane, toluene, nonane and o-xylene) in the lowest 200 m of the atmosphere of Mexico City. These VOCs were selected since they are representative species of the VOC burden in the atmosphere of Mexico City (Velasco et al., 2007). They included alkanes, alkenes, alkynes and aromatic species. The objectives of this study were three-folds: 1) to investigate the diurnal vertical distribution and concentrations of ozone and VOCs in the urban boundary layer of a polluted megacity; 2) to determine the diurnal variations of these pollutants in terms of the evolution of the convective boundary layer; and 3) to provide vertical profiles as input data for air quality models.

Despite the particular characteristics of air pollution and meteorology of Mexico City, some features of the evolution of the boundary layer and vertical distribution of pollu-

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tants discussed in this article, have been observed in other places of the world using also tethered balloons (e.g., Lee et al., 2003; Glaser et al., 2003; Baumbach and Vogt, 2003; Chen et al., 2002; Aneja et al., 2000). The results presented here are expected to have wide applicability, in particular to other polluted megacities and large urban complexes of the world.

2 Experiment description

A total of 175 vertical profiles of ozone and meteorology were measured by a medium-sized tethered balloon (Vaisala TSB-9) over 28 selected days between 2000 and 2004. 94 profiles were over an altitude of 500 m with 40% reaching 1000 m. The wind conditions did not always allow the balloon to reach the desired altitude, mostly in the afternoons, when wind speed increased and the balloon's control became complicated. 35% of all profiles included speciation of the 13 VOC species mentioned above up to 200 m. Almost all profiles were measured during the dry-warm season from March to May and the dry-cold season from November to February of Mexico City, when convective processes are not as strong and pollutants accumulate in the boundary layer. During the rainy season (from June to October) it is difficult to launch the balloon; the pollutants are more efficiently removed from the boundary layer by wet deposition or simply by the strong vertical motions generated by the convective storms. The results presented here include profiles measured in February 2002 and April 2003 as part of the MCMA field campaigns (Molina et al., 2007).

The tethered balloon was launched at 3 different sites inside the urban core of Mexico City: 1) CENICA lab located at the southeast part of the city (W99°04′25″, N19°21′31.8″) in a mixed area surrounded by residences, light and medium industries, services and commerce. The traffic was heavy and composed of old and new vehicles. About 88% of the profiles were obtained at this site; they were measured from 02:00 to 19:00 h local time (all times hereafter are referenced to local time). 2) The sport facilities of the National Polytechnic Institute located at the northwest part of the city

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(W99°08′19.8″, N19°29′52.9″); 3) the practice stadium of the National Autonomous University of Mexico located at the southwest (W99°11′13.1″, N19°19′40″). Measurements at (2) and (3) were restricted from 09:00 to 16:00 h due to aeronautical activities. A comparison of the measured profiles at these three different sites during that period showed that they were similar.

Meteorological parameters, which included ambient temperature, atmospheric pressure, relative humidity, and wind speed and direction, were measured by a meteorological sonde (TS-5A-SP Tethersonde) tethered 10 m below the balloon. The data collected by the sonde were sent to ground by a radio transmitter. The height of the balloon was controlled by comparing atmospheric pressure readings from the sonde located next to the balloon to readings from the second sonde located at ground level (see Fig. 1). Ozone concentrations were measured by an electrochemical sonde (4Z ECC-O3-Sonde) tethered together with the meteorological sonde 10 m below the balloon.

Electrochemical sondes rely on the conversion of chemicals in a solution by ambient ozone to alter the electric conductivity of the solution (Parrish and Fehsenfeld, 2000). These sondes are very light and have been widely used to measure ozone profiles in the atmosphere. However, the measurements made by these sondes may suffer interferences from compounds other than ozone, such as SO_2, NO_2 and peroxyacetylnitrate (PAN) (Barnes et al., 1985; Grant and Wong, 1999) that contribute to the measurement uncertainty. Barnes et al. (1985) estimated these uncertainties to be between 6 and 10% from background current. For each day of measurements, the electrochemical sondes were prepared 24 h in advance and calibrated with a standard UV ozone monitor (Advanced Pollution Instruments, API 400) and/or verified by an ozone generator (Ozonizer KTU-2). The resulting calibration curves relating ozone concentrations and ozone sonde responses were applied to the measured profiles to minimize possible uncertainties caused by other oxidant species in the electrochemical sondes.

The time required for measuring a profile up to 1000 m of height in intervals of 50 m for 10 readings of ozone and meteorology was on average 60 min. For a typical profile

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including VOC speciation up to 200 m in 50-m intervals, the required time was 75 min. For the analysis of both types of profiles, quasi-stationary and quasi-homogeneity conditions were assumed in an ideal boundary layer. That is, the vertical distribution of pollutants and meteorology did not change over the course of one profile measurement. These measurement durations were within the recommended time range (10^3 to 10^4 s) for the analysis of micrometeorological observations, which depends on the height of observation, the boundary layer height, and stability (Arya, 2001). At nighttime the atmosphere is stable; therefore the atmospheric conditions as well as the vertical distribution of pollutants of the boundary layer change slowly. At daytime the boundary layer evolves faster and the time range in which atmospheric conditions can be considered stationary decreases.

Figure 1 shows the set up of the tethered balloon for measuring meteorological parameters, ozone profiles and VOC sampling. For the VOC sampling a Teflon tube of 5 mm of internal diameter (id) was attached to the balloon's tethered line with the inlet located at the same height of the electrochemical cell. The tube was connected to a diaphragm pump located at the ground. Samples were introduced into 6 L Summa electro-polished stainless-steel canisters for 4 min after flushing out the line from previous sampling for 10 min.

Before sampling, canisters were cleaned, evacuated and analyzed to verify the absence of VOCs. Sampled canisters were analyzed within 48 hours of sampling to avoid complication from storage before the analysis. Samples were analyzed by cryogenic pre-concentration with temperature programming using a gas chromatograph with flame ionization detection (GC-FID), following the DKK Corporation procedure designed by Maeda et al. (1998), which is equivalent to the TO-14a protocol (USEPA, 1999). The analytical set up consisted of a dynamic dilution system, a humidity controller, a sample concentrator, and a GC-FID. The humidity controller was operated at 25°C. Samples were preconcentrated in a multi-adsorbent trap. The trap, packed with tenax, activated alumina and activated charcoal, was cooled to 10°C by liquid carbon dioxide (industrial grade). The compounds were thermally desorbed at 250°C

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with helium as the carrier gas (flow: 5.98 ml min^{-1}) for 4 min. VOC separation was made with a Hewlett-Packard 6890 Series chromatograph, operated at constant flow of 5.98 ml min^{-1} and equipped with two columns connected in series, the first of alumina (id 0.53 mm, 30 m) and the second of methylsilicone (id 0.5 mm, 1.5 μm, 30 m). During sample loading, the oven remained at 40°C for 4 minutes; subsequently the oven temperature was raised at a rate of 8°C min^{-1} to reach 100°C, and then at 6°C min^{-1} to 240°C, the final temperature at which the oven was kept for 10 min. The total analysis time is one hour. Individual species are identified by retention times and responses of calibration standards (1 ppmv of each monitored species, SAAN Co.) with a ten-fold dilution mixture. The detection limit is calculated to be 0.1 ppbv.

3 Results

This section examines the vertical distribution of ozone and VOCs in the context of the boundary layer evolution to understand their temporal and vertical variation throughout the course of the day. Overall, the features of the observed profiles can be explained in terms of the development of a stable layer near the surface at night and the onset of convective mixing the following morning. To find out the characteristics of the vertical distribution of those pollutants and meteorological parameters, we have plotted the 175 measured profiles together in Fig. 2a–f. Each panel shows the vertical distribution for a different parameter and is discussed in the following sections. To increase the apparent resolution of the vertical distributions shown in those panels, we used the interpolation function of IGOR© based on a Delaunay triangulation to generate contour lines with a setting factor of 16. Despite these profiles were measured on different days, seasons and years, they show clearly the evolution of the low urban boundary layer of Mexico City.

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3.1 Vertical distribution of potential temperature and vertical mixing

In an urban environment, the vertical distribution of trace gases depends strongly on the atmospheric stability and the turbulence produced by the heat released from surface and the friction produced by winds in combination with surface. To analyze the stability of the atmosphere and the ease with which air parcels can mix vertically, we computed profiles of potential temperature and a modified bulk Richardson number. The potential temperature θ is defined by

$$\theta = T\left(p_0/p\right)^{R/C_p}, \quad (1)$$

where T is the ambient temperature in Kelvins, p is the ambient pressure, p_0 is a reference pressure usually taken as 100 kPa, C_p is the specific heat of air at constant pressure and R is the gas constant. For the dry conditions in Mexico City prevalent during the measurements, we used a value of 0.286 for the R/C_p ratio. The modified bulk Richardson number was calculated as

$$R_B = \frac{g\Delta\overline{\theta_v}\Delta z}{\overline{\theta_v}\left(\Delta U\right)^2}, \quad (2)$$

where g is the acceleration of gravity, $\overline{\theta_v}$ is the average virtual potential temperature over a specific depth Δz, $\Delta\overline{\theta_v}$ and ΔU are the differences in the virtual potential temperature and wind speed over Δz, respectively. Δz is the difference in meters between a specific height of the vertical profile and the lowest height at which the sonde tethered to the balloon collected data (between 10 and 50 m). We assumed that at the bottom height U≈0, and therefore ΔU=U. The term θ_v includes the buoyant effects of water vapor in the potential temperature; it is defined by

$$\theta_v = \theta\left(1 + 0.61r\right), \quad (3)$$

where r is the mixing ratio of water vapor; it is calculated from the partial pressure water term, which is obtained from the measured temperature, pressure and relative humidity (Stull, 1988).

To better observe the atmospheric stability through the θ vertical distribution, we have plotted in Fig. 2a the differences in θ at each height for each profile using θ at 100 m as reference ($\Delta\theta_{@100\,m} = \theta_i - \theta_{100\,m}$), instead of plotting the absolute θ values. A positive $\Delta\theta_{@100\,m}$ value indicates a stable stratified atmosphere, while a negative value indicates a neutral or unstable atmosphere. Figure 2b shows the vertical distribution of the modified bulk Richardson number described above. Large positive values of R_B indicate greater dynamic stability, while negative values or close to zero indicate a greater possibility of vertical mixing. There is no well-defined critical value of R_B above which turbulence ceases (Stull, 1988), but it has been accepted that for R_B greater than one, vertical mixing is suppressed. Note that the bulk Richardson number itself does not provide information about the intensity of turbulence; it only indicates the presence or absence of turbulence.

At nighttime the θ profile is characterized by nocturnal inversion, which is produced as a result of radiative cooling of the surface. The nocturnal boundary layer is usually stable in the absence of turbulence (R_B>1 and $\Delta\theta_{@100\,m}$>1) above 200 m until sunrise (~07:00 h). Below that altitude the turbulence is almost always present (R_B<1). At night the turbulence is maintained by the wind and roughness of the city, but mainly by the release of the heat stored in the buildings and urban surface during daytime. At daytime the term of the storage heat (ΔQ_s) in the energy balance represents 50% of the net radiation (Q^*) in the urban core of Mexico City (Velasco et al., 2007[1]). At nighttime the Q_s/Q^* ratio is positive and greater than one, which explains the turbulence presence in the surface layer. As reference, Fig. 3 shows the energy balance for a typical day of the dry-warm season in Mexico City measured recently during the 2006 MILAGRO field campaign. Although this energy balance was measured in a different site close to the center of the city, it gives insight of the nocturnal release of energy.

[1]Velasco, E., Pressley, S., Grivicke, R., Allwine, E., Westberg, H., Molina, L.T., and Lamb, B.: Flux measurements of trace gases and energy in an urban district of Mexico City, in preparation, 2007.

Shortly after sunrise, surface heating leads to an upward exchange of sensible heat and subsequent warming of the lowest layer due to heat flux convergence. After 07:00 h the surface boundary layer becomes warmer than the air above. Figure 2a shows this morning heating through positive $\Delta\theta_{@100\,m}$ values below 100 m. By 09:00 h the air at the surface layer is between 2 and 3°C warmer than the air at 100 m. This process progressively erodes the nocturnal inversion from below and replaces it with an unstable or convective boundary layer (CBL). The CBL is characterized by vigorous vertical mixing with constant or small negative $\Delta\theta_{@100\,m}$ values and R_B values below one. The depth of the CBL grows with time; Fig. 2a shows that negative $\Delta\theta_{@100\,m}$ values reach higher altitudes during the morning at a similar rate than R_B values below one appear at those altitudes in Fig. 2b. The boundary layer passes from ~200 m at 07:00 h to ~600 m by midday. The rate of growth of the CBL in Mexico City is not as fast as typically in other places, where the maximum rate of growth attains within a few hours after sunrise (Arya, 2001). The vertical distributions of $\Delta\theta_{@100\,m}$ and R_B show that the maximum rate of growth occurred between one and two hours after midday, when the boundary layer depth reached 1000 m. Our findings are consistent with those obtained from the IMADA-AVER boundary layer experiment (Doran et al., 1998; Whiteman et al., 2000) conducted during the dry season in Mexico City, in which the boundary layer grows slowly after sunrise to a depth under 1000 m before noon, and grows rapidly to heights of 3000 m or more within the subsequent few hours.

According to Whiteman et al. (2000), after the rapid growth stage of the boundary layer in Mexico City ending between 13:00 and 14:00 h, a quenching stage follows in which the rate of heating and growth are slowed during the next two hours. Then a rapid and deep cooling stage occurs with a collapse of the boundary layer. Because of the height limitations of our measurements, we could not observe these two stages of the boundary layer, nor determine its maximum growth. We only observed an unstable atmosphere and a vigorous vertical mixing in the 1000-m layer above the ground between 14:00 h and few minutes before 18:00 h. After 18:00 h positive values of $\Delta\theta_{@100\,m}$ started to appear above ~600 m, indicating the collapse of the CBL

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and the formation of a new residual layer. Although few measurements were made after 18:00 h, they were enough to show this event, which is related to the formation of ozone pool at that height and will be discussed later.

A detailed description of the evolution of the boundary layer in terms of the energy balance is given by Whiteman et al. (2000). They suggested that the falloff of the rate of heat storage from the energy balance between 13:00 and 14:00 h (see Fig. 3) could be interpreted as quenching of boundary layer growth caused by the leakage of cold air into the warm basin atmosphere from the colder surroundings of the valley where Mexico City is located. The formation of the residual layer around 18:00 h coincides when the heat storage term changes sign, and when the release of the stored heat in the urban surface begins.

3.2 Vertical profiles of wind speed and direction

Figure 2c shows the vertical profiles of the horizontal wind speed throughout the course of the day, and Fig. 2d shows the vertical distribution of the wind direction. Our measurements were not able to describe the wind diurnal and spatial variations of the boundary layer in Mexico City, but they provide a glimpse of the winds in the low boundary layer at the southeast of the city, when winds were within the speed range to safely launch the tethered balloon. Overall, weak northerly winds prevailed in the residual layer until few hours after the sunrise. Winds at the surface attain minimum values before the sunrise, and increase during the day reaching maximum values in the afternoon. As the CBL evolves during the morning and early afternoon, the wind speed becomes uniform in the 1000-m layer above the ground, excluding the surface layer, which is characterized by a strong gradient. After midday, the wind direction becomes more variable in the vertical profile during the next three hours, coinciding with the rapid growth stage of the boundary layer. This is due to the vigorous vertical mixing produced by the heating of the CBL. After this stage, wind tends again to blow from the north. Detailed descriptions of the wind diurnal variations in Mexico City are provided by Whiteman et al. (2000) and de Foy et al. (2005), in particular for the dry season,

when the bulk of our measurements were made. During this season Mexico City is normally under the influence of anticyclone weather with light winds above the valley and nearly cloudless skies.

3.3 Vertical distribution of humidity

To illustrate the vertical changes in the specific humidity (q) we normalized each profile to its maximum measured value in Fig. 2e. We observed that the evapotranspiration of the urban surface is enough to produce abrupt gradients throughout most of the day, from early morning to early afternoon. During early morning and few hours after sunrise, the turbulence and unstable conditions of the surface layer produce a layer of 350 m depth above the ground with uniform values of q. Within one to two hours after sunrise, q attains maximum values up to 12 g kg^{-1} in this layer. Sometimes this is enhanced by the water vapor condensation and deposition on the surface in the form of dew before sunrise when winds are weak and the surface temperature falls below the dew point temperature of the moist air near the surface. Before sunrise, the residual layer above 500 m shows nearly uniform profiles of q, between 30 and 45% lower than in the lowest layer. After sunrise, as the boundary layer evolves, the moisture in the lowest layer mixes with the air in upper layers, producing nearly uniform profiles within the CBL. Throughout the morning and early afternoon q decreases, attaining minimum values of 1 to 4 g kg^{-1} between 13:00 and 15:00 h, when the solar radiation is strongest. During the afternoon q rises slowly again, reaching values close to 6 g kg^{-1} by 18:00 h. This period coincides with the rapid and deep cooling stage that drives the decay of the boundary layer.

3.4 Vertical distribution of ozone

Figure 4a shows the diurnal variation of the surface level ozone concentration and other trace gases obtained at the CENICA supersite for a typical day of the dry season during the MCMA-2003 campaign (Molina et al., 2007). As expected, the ozone concentration

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shows a distinct diurnal pattern, a minimum in the morning and a maximum in the early afternoon. This diurnal pattern extends to the shallow unstable boundary layer at night and the CBL during daytime (Fig. 2f). Figure 5 shows the ozone vertical profiles normalized to their maximum concentrations in different periods of the day (only those profiles that reached at least 500 m are included).

At nighttime, the presence of the nocturnal inversion layer isolates the ground-level ozone from that of upper levels. Surface ozone is removed by deposition and titration with nitric oxide (NO) from evening traffic emissions. Since no ozone is produced in the absence of sunlight at night, ozone concentration decreases after sunset, attaining minimum values by sunrise, between 06:00 and 08:00 h. The ozone confined in the nocturnal stable boundary layer creates a residual layer of ozone shielded from NO and VOCs emissions. The beginning of this residual layer occurs at ~18:00 h of the previous day, when the release of the stored heat in the urban surface begins and the CBL starts to collapse. A clear and well-established residual layer is observed above 500 m. The ozone accumulation starts at 200 m, coinciding with the cut off of the nocturnal unstable layer, but in some cases it can start at 100 m. An interesting seasonal feature is that the ozone gradient from 200 to 500 m shows a relatively constant rate of ~0.1 ppbv m^{-1} during the dry-warm season; but during the dry-cold season no gradient is observed, the residual layer appears abruptly above 300 m as shown in Fig. 5a. However, more measurements are needed to confirm and explain this feature. The ozone concentration in the residual layer depends on the ozone level from the previous day and meteorological conditions; on average the observed ozone concentration in the residual layer was 35 ppbv and concentrations above 50 ppbv were typical. The maximum ozone concentration observed within the residual layer was 75 ppbv.

After sunrise, the height of the unstable boundary layer begins to increase as the surface is heated and the nocturnal inversion is destroyed. This results in downward mixing ozone from aloft. Surface ozone is also locally generated by reactions of nitrogen oxides with VOCs in the presence of sunlight. Consequently, one would expect a fast increase in the ozone concentration. However, during the next two hours after

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sunrise, ozone remains constant, even though it is being rapidly produced. Ozone production rates exceed 50 ppbv h^{-1} as early as one hour after sunrise (Shirley et al., 2006), but this production is not detectable because the fresh ozone and the mixed ozone downward from the residual layer are depleted by reaction with NO, forming NO_2 (see Figs. 4b and c). The available NO from nighttime emissions trapped in the shallow unstable boundary layer plus the fresh emitted NO during the morning rush period are enough to delay the rise of the ambient ozone concentration by about 2 h.

After the morning ozone balance determined by photochemical production, entrainment from the residual layer, and destruction by titration with NO, the ground-level ozone concentration jump up around 09:00 h, when NO had fallen to half its peak value (see Fig. 4b). As the CBL evolves during the subsequent hours, the ozone entrainment from upper layers continues, and adds up to new ozone formed by the combination of high levels of reactive VOCs, NO_x and strong solar radiation. Between 09:00 and 11:00 h, the accumulated ozone in the upper layers is still there, but at higher altitudes (Fig. 5c). Between 10:00 and 12:00 h, as a result of the accumulation of fresh ozone beneath the residual layer plus the mixed ozone downward, the ozone concentration within the CBL becomes at least 50% of the concentration in the remaining residual layer (Fig. 5d). After midday, during the next three hours the vertical ozone distribution is uniform (Fig. 5e) as a consequence of the efficient vertical mixing during the rapid growth stage of the boundary layer. Ozone attains maximum concentrations in this period, with concentrations between 120 and 150 ppbv, coinciding with the period of strongest solar radiation. Concentrations over 180 ppbv were observed in a pair of profiles. After 15:00 h, the intensity of sunlight diminishes (see Fig. 3), and thus the ozone production declines, resulting in a decrease of the ozone concentration. Besides, wind intensity increases in the afternoon enhancing the pollutants dispersion, which helps to reduce the ozone concentration and destroying the uniform profiles of ozone within the CBL (Fig. 5f). In the late afternoon, the cooling of the atmosphere and the collapse of the CBL drive the formation of a new ozone residual layer, beginning a few minutes before the sunset (Fig. 5g).

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The irregular features observed in the ozone profiles are caused by variations of the solar radiation strength due to absorption and scattering by clouds, local emissions of ozone precursors, efficiency of ozone production, and dispersion processes.

3.5 Vertical distribution of VOCs

Figure 6 shows the vertical distribution for each of the 13 VOCs monitored. The VOCs levels are uniform in the unstable boundary layer due to the efficient vertical mixing throughout the day. Overall, no differences were observed in the VOCs concentrations within the 200 m layer above the ground. The parcels with higher concentrations within this layer may be due to transport processes of local plumes, as well as artifacts from our measurements and/or of the interpolation method used for the figures. The chemical reactions with OH radical are slow to produce significant gradients in the vertical distribution. The turbulence mixes the VOCs in the unstable boundary layer much faster than the OH radical depletes them. For example, propylene, the most reactive of the 13 measured VOCs, has a lifetime of 1 h at midday, when OH attains maximum concentrations of 0.4 pptv (Shirley et al., 2006), compares to the average time of 4 min that an air parcel takes to travel from the surface to 200 m (information from turbulent flux measurements in Mexico City, Velasco et al., 2005).

The diurnal patterns of VOCs depend on the anthropogenic activities, photochemistry and meteorology. Figures 4d–f show the diurnal patterns of butane, benzene and olefins at ground level measured by continuous instruments during the MCMA-2003 field campaign. All VOCs reach their highest level during the morning period (05:00 to 10:00 h), when the boundary layer growth begins and the traffic is most intense. The shallow unstable boundary layer contributes also to the high morning VOCs levels.

The low molecular weight alkanes (ethane, butane and propane) show similar vertical and diurnal distributions. The high ambient concentrations of propane and butane are attributed mainly to liquefied petroleum gas (LPG) combustion and leakage during handling, distribution and storage. LPG is the main fuel for cocking and water heating in Mexican households. Although LPG powered vehicles represent less than

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1% of the total fleet, they are also important sources. The LPG fleet is composed mainly of vehicles used intensively (light and heavy duty trucks, and microbuses with 20-passenger capacity); 95% of them have emissions that exceed those required by local environmental regulations (Schifter et al., 2000). The LPG leaked at nighttime from households accumulates in the shallow unstable boundary layer and adds to the morning emissions from traffic and from LPG transmission systems. Since LPG is used by Mexican households to heat water for bathing and showering prior going to work in the morning, the emission of these alkanes is largest during this period of maximum LPG usage. After 09:00 h their ambient concentrations starts to decrease as the CBL evolves and the photochemistry increases. The ethane levels decreases slowly compared to propane and butane because of its lower reactivity with the OH radical, and because it is emitted also by other sources besides LPG use, such as vehicle exhaust and degreasing activities (Vega et al., 2000).

Velasco et al. (2007) demonstrated that VOCs levels in Mexico City depend strongly on traffic emissions. Acetylene is known to be a good marker for vehicular combustion and therefore is a good indicator to analyze the traffic influence in the vertical and diurnal distribution of VOCs. The morning rush-hour period is clearly identified between 05:00 and 10:00 h, when acetylene concentrations are at least 3 times higher than those before and after this period, but the most intense period of traffic is registered between 07:00 and 09:00 h, when acetylene reaches concentrations above 50 ppbv. Acetylene is the VOC species with the most uniform vertical profiles due to its unique source from vehicle emissions. Similar patterns are observed for other species emitted also by vehicle exhaust, such as propylene, o-xylene, pentane, octane and nonane, but with less uniform vertical distributions because of the contribution from other local emission sources; for example, o-xylene is emitted also during incineration of solid wastes. Hexane, benzene and toluene are emitted by vehicle exhaust, but also by the evaporation of gasoline in gas stations, usage of solvents, paints, adhesives, resins and degreasers. These additional emission sources drive extended periods of high concentrations, mainly during the morning. Heptane is the only VOC that does not

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show a clear vertical distribution. Heptane is emitted also by vehicle exhaust, with the highest emissions around 09:00 h, but peaking also in the afternoon, maybe due to local plumes emitted by factories close to the monitoring site.

4 Summary

Strong inversion layers occur during nighttime and early hours in the morning. The release of the heat stored in the urban surface is strong enough to maintain a 200-m unstable layer above the ground during nighttime. In this shallow layer, VOCs and other pollutants accumulate and add to the morning emissions that initiate the photochemical processes of the day. In contrast to VOCs, ozone is depleted within this layer by deposition and titration with NO from evening traffic emissions. But a fraction of the ozone from the previous day is carried over in the nocturnal stable layer. This layer forms a residual layer of ozone shielded from NO and VOCs emissions. The nocturnal stable layer starts at 200 m, but a clear and well established residual layer is observed at 500 m. The average ozone concentration in the residual layer is 35 ppbv, although it frequently exceeds 50 ppbv.

After sunrise, the CBL evolves as the surface is heated and the nocturnal inversion is destroyed. This results in downward mixing ozone from aloft, which adds to the fresh ozone produced by the high morning levels of VOCs and NO in the presence of sunlight. However, the ground-level ozone concentration does not rise until 09:00 h, even though the ozone production rate is high. This period is characterized by an ozone balance determined by photochemical production, entrainment from the residual layer and destruction by titration with NO.

A particular feature of the CBL in Mexico City is its slow evolution during the morning hours compared to other places. By noon the CBL reaches a height below 600 m, but grows rapidly to heights above 1000 m in the subsequent two hours. By this time the vertical distributions of ozone, VOCs and moisture are uniform as a consequence of the vigorous vertical mixing within the CBL. Around 14:00 h ozone attains maximum values

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above 120 ppbv, coinciding with the period of strongest solar radiation. After the rapid growth stage of the CBL ending at 14:00 h, a quenching stage follows in which the rates of heating and growth slow down during the next 2 h. Then a rapid and deep cooling stage occurs with the decay of the boundary layer and the formation of a new nocturnal stable layer a few minutes before sunset. The ozone concentration begins to decrease when the sunlight diminishes in the afternoon. The strong afternoon winds enhance the pollutants dispersion, contributing to the ozone reduction within the boundary layer.

5 Conclusions

Tethered balloons offer a direct way of probing into the urban atmosphere to study the complex interactions between trace gases and meteorological variables, and their influence on air quality. Of particular interest are the micrometeorological variables, such as turbulence and atmospheric stability, on which the vertical distribution of pollutants depends strongly. These parameters and vertical distributions of trace gases need to be reproduced by air quality models to reduce the discrepancies between measured and modeled concentrations of ozone and other secondary pollutants in the atmosphere of Mexico City.

Future studies should extend the number of chemical species to be determined such as NO_x, CO and a wider number of VOCs. Vertical profiles of NO and NO_2 will provide valuable information to understand better the photochemical processes; different NO and NO_2 sensors have been used successfully in tethered balloons (Pisano et al., 1997; Glaser et al., 2003). Also, the number of VOC species measured should increase, as well the altitude at which the samples are collected. The Teflon tube system is limited to certain height by its own weight; active charcoal cartridges is an alternative option to collect samples at higher altitudes (Glaser et al., 2003; Greenberg et al., 1999), or Teflon bags with small time-controlled pumps and immediate analysis of the samples (Chen et al., 2002).

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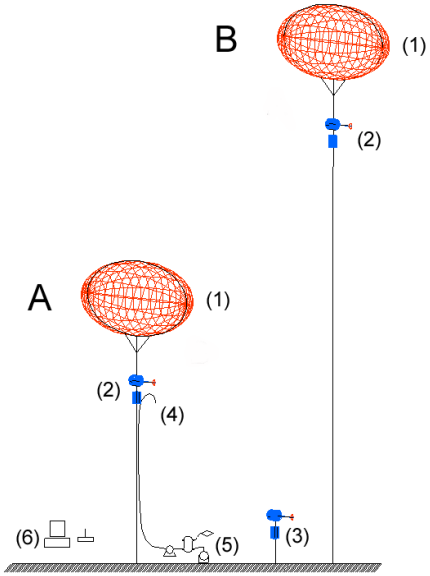

Fig. 1. Set up of the tethered balloon system. **(A)** Vertical profile measurements of VOCs, ozone and meteorology up to 200 m. **(B)** Vertical profile measurements of ozone and meteorology up to 1000 m. The tethered balloon system is composed of: (1) 9 m^3 balloon filled with helium, (2) meteorological sonde with the ozone electrochemical cell below the balloon, (3) meteorological sonde at ground level, (4) Teflon tube, (5) diaphragm pump and stainless-steel canister for the VOCs sampling, and (6) ratio receiver system.

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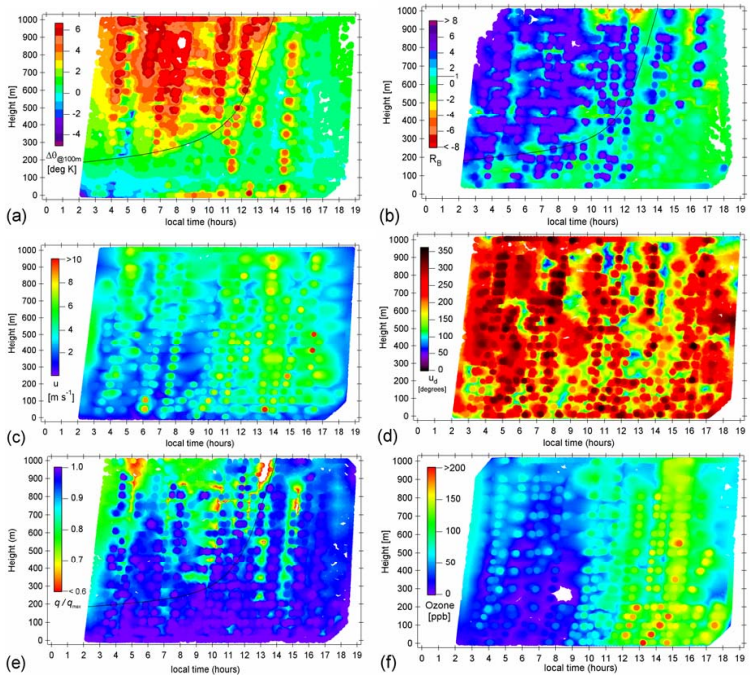

Fig. 2. Vertical distributions of different meteorological parameters and ozone throughout the course of the day. **(a)** Vertical distribution of the differences in θ at each height using as reference θ at 100 m ($\Delta\theta_{@100\,m}=\theta_i-\theta_{100\,m}$). Values of $\Delta\theta_{@100\,m}>0$ indicate a stable stratified atmosphere, while values of $\Delta\theta_{@100\,m}<0$ indicate a neutral or unstable atmosphere. **(b)** Vertical distribution of a modified bulk Richardson number. Values of $R_B<1$ indicate a high probability of vertical mixing, while values of $R_B>1$ indicate dynamic stability. **(c)** Vertical distribution of the wind speed. **(d)** Vertical distribution of the wind direction. **(e)** Vertical distribution of the normalized specific humidity (q/q_{max}). **(f)** Vertical distribution of ozone concentration. The black lines in Figs. 2a, b, e indicates the evolution of the CBL.

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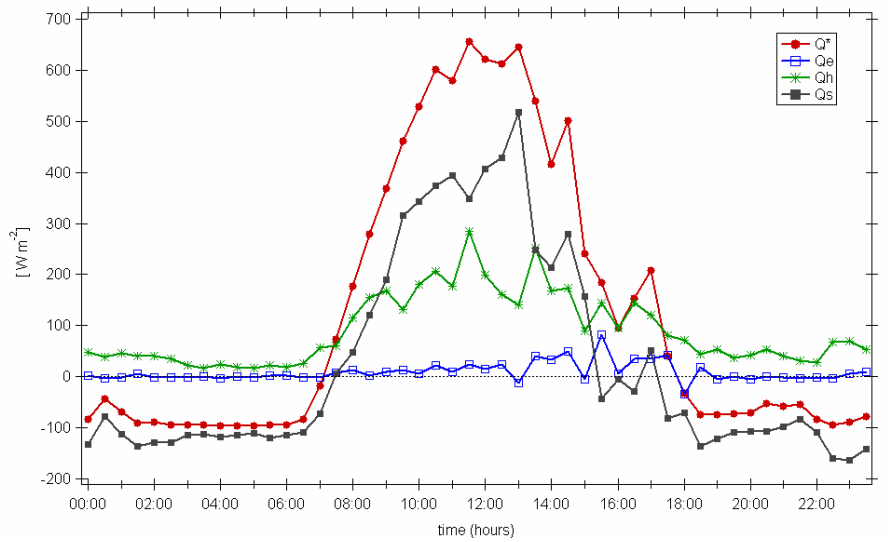

Fig. 3. Energy balance measured on 24 March 2006 in the urban core of Mexico City during the MILAGRO field campaign. The sensible (Q_h) and latent (Q_e) heats were measured by eddy covariance, Q^* by a net radiometer and ΔQ_s was obtained as the residual of the measured energy components ($\Delta Q_s = Q^* - (Q_h + Q_e)$) (Velasco et al., 2007[1]).

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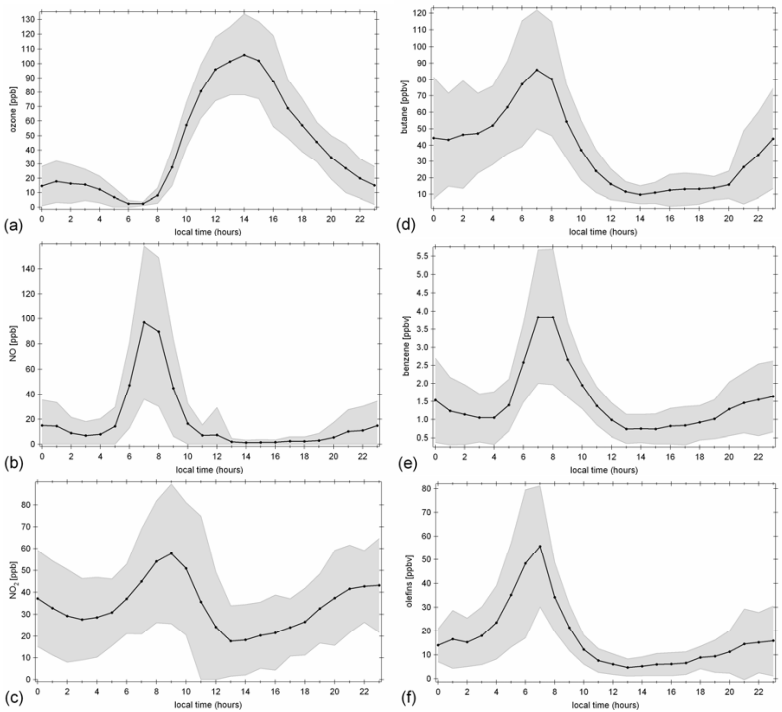

Fig. 4. Average diurnal patterns of different trace gases measured at ground level at the CENICA supersite during April 2003 (see Molina et al., 2007 and the references therein). **(a)** Ozone measured by UV Differential Optical Absorption Spectrometry (DOAS). **(b)** NO measured by a standard chemiluminescence monitor. **(c)** NO_2 measured by a standard chemiluminescence monitor. **(d)** Butane measured by Fourier Transform Infra Red Spectroscopy (FTIR). **(e)** Benzene measured by DOAS. **(f)** Olefinic mixing ratio (as propylene) measured by a Fast Olefin Sensor (FOS). The gray shadows represent the one standard deviation ranges, and give an indication of the day-to-day variability in each phase of the daily cycle.

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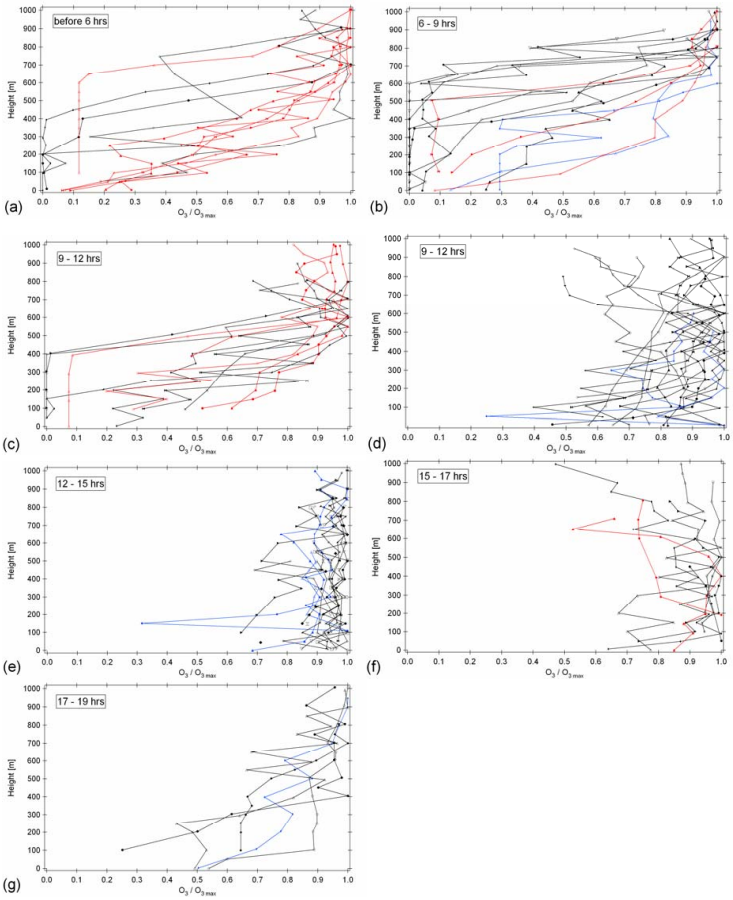

Fig. 5. Ozone vertical profiles normalized to their maximum concentrations for different periods of the day. Profiles in black correspond to the dry-cold season, in red to the dry-warm season, and in blue to the rainy season.

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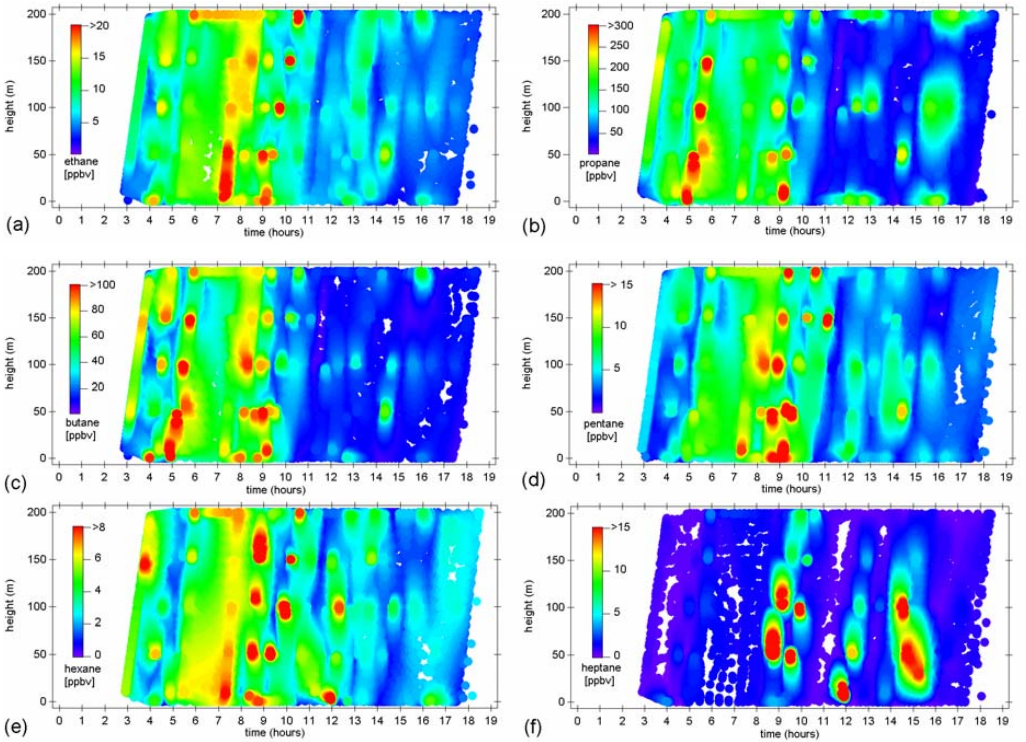

Fig. 6. Vertical distributions of the 13 VOCs monitored. **(a)** ethane, **(b)** propane, **(c)** butane, **(d)** pentane, **(e)** hexane, **(f)** heptane, **(g)** octane, **(h)** nonane, **(i)** propylene, **(j)** acetylene, **(k)** benzene, **(l)** toluene, **(m)** o-xylene.

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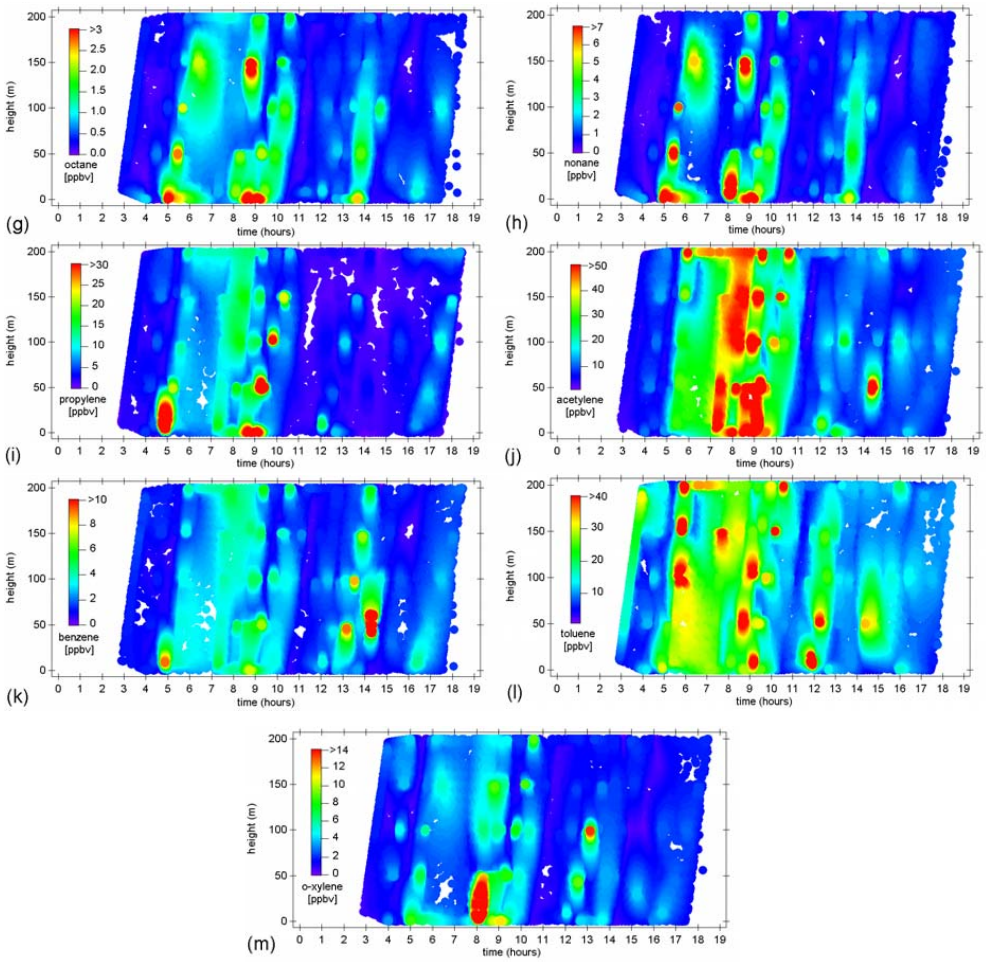

Fig. 6. Continued.

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