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MEASUREMENTS OF CO₂ FLUXES IN THE MEXICO CITY MEGACITY

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1. INTRODUCTION

Urban areas are acknowledged to be major sources of anthropogenic CO₂ (IPCC, 2001), however, there are few direct measurements of CO₂ emissions in urban areas. This is particularly true for megacities, such as Mexico City, where there is a rapid growth with a wide range of direct and indirect sources, such as the high levels of traffic and land use changes involved with urbanization. Several authors have attempted to quantify the CO₂ levels in urban environments through emission inventories from estimates of fossil fuel consumption, evaluations of the amount of carbon sequestered in urban vegetation, and short term studies of CO₂ concentrations. Grimmond et al. (2002) provided a list of studies CO_2 concentrations measuring in urban environments. For Mexico City, results of only two studies have been reported; the first was a study during 1981 and 1982, in which CO₂ was sampled at different locations in the city and analyzed by gas chromatography (Baez et al., 1988). In the second study CO₂ concentrations were measured bv a Fourier Transform Infrared (FTIR) spectrometer at a fixed site in the southwest of the city in a residential area during fall 2001 (Grutter, 2003).

As part of a large air quality field campaign conducted in Mexico City (MCMA-2003), we deployed an eddy covariance flux system on a tall urban tower within a densely populated section of the city to obtain direct measurements of CO_2 emissions in a typical Mexican neighborhood. In this paper we demonstrate the applicability of the eddy covariance (EC) technique to a potentially inhomogeneous area, such as a city, where the spatial variability of surface cover and roughness is high. This paper also reports the magnitude of the CO_2 fluxes in relation to wind direction and vehicular activity. Although micrometeorological techniques have been widely applied to measure fluxes of CO₂, water vapor, volatile organic copounds (VOC) and other trace gases above vegetation (Baldocchi, *et al.*, 2001; Schmid *et al*, 2000; Westberg, *et al.*, 2001), direct flux measurements of pollutants in urban environments are relatively recent (Grimmond *et al.*, 2002; Nemitz, *et al.*, 2002; Dorsey *et al.*, 2002). Similar micrometeorological approaches have been applied to measure fluxes of momentum and heat in urban areas (Grimmond and Oke, 1995; Oke *et al.*, 1999).

2. FIELD EXPERIMENT

The flux measurements were performed in a suburb located in the southeast of Mexico City $(19^{\circ} 21' 29'' N, 99^{\circ} 04' 24'' W)$ for 23 days during the dry seas on in April 2003 (April 7 - 29). The study period includes the Holy Week (April 14 – 20), a time in which the vehicular traffic is typically reduced as many of the city residents leave for the holiday period. By taking measurements before, during and after this period, we expected to obtain a better understanding of the influence of the vehicular emissions upon CO2 fluxes.

The selected site was located in the Iztapalapa suburb, which is the suburb with the highest population in Mexico City (1,771,673 inhabitants) and the highest density (12,000 inhabitants km⁻²) (INEGI, 2000). In this area the number of CO₂ sources is large, and it is composed of a mix of commercial, industrial, residential and mobile sources. Mexico City is the second largest city in the world, and it is located at 2240 m above sea level in a subtropical region surrounded by mountains with mild weather, temperatures of over 20°C, and intense solar radiation all the year round.

3. INSTRUMENTATION

The eddy covariance system was mounted on a tower on the rooftop of a building, with a total height of 37 m, 3 times taller than the surrounding buildings, and of sufficient height to be in the constant flux layer. A 3-D sonic anemometer (Applied Technologies, Inc., model SATI-3K), an

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open-path infrared gas analyzer (IRGA) to monitor CO_2 and water vapor were mounted at the top of the tower at the end of a 3 m boom. Signal/power cables were run from the sensors to a shelter on the roof where the pc data acquisition system was operated through LabView software specifically designed for this experiment. In operation, the flux system collected data at 10 Hz, ensuring that all turbulence contributing to the flux is resolved. Data was used to calculate 30 min average fluxes using the direct EC mode.

The IRGA is an instrument specifically designed for fast response measurements of CO_2 and H_2O fluctuations, quantifying the attenuated radiation in an absorption band between an infrared source and the detector. A detailed description of it is given by Auble and Meyers (1992). This instrument is quite robust, and we found that the response is relatively constant. For CO_2 it was calibrated twice per week using two CO_2 standard gas mixtures (β 27 and 402 ppm). We compared the water vapor response to a humidity sensor (Vaisala, model HMP45A) on the tower as a basis for checking the instrument performance for water vapor.

4. EDDY COVARIANCE FLUX TECHNIQUE

The flux of a trace gas ($F_{?}$) is calculated according to the EC technique as the covariance between the instantaneous deviation of the vertical wind velocity (*w*) and the instantaneous deviation of the trace gas ($c_{?}$ ') from their 30 minute mean. The equation is given below, where the over bar denotes a time-averaged quantity. Fundamental aspects of EC have been widely discussed elsewhere (e.g. McMillen, 1988; Aubinet *et al.*, 2000).

$$F_{c} = \overline{w'c_{c}'} = \frac{1}{t_{2} - t_{1}} \int_{t_{1}}^{t_{2}} w'(t)c'(t)dt$$
(1)

The quality of flux measurements is difficult to assess, because there are various sources of errors, ranging from failure to satisfy any of a number of theoretical assumptions to failure of the technical setup. Conflicts with the assumptions of the eddy covariance technique to estimate fluxes arise under certain meteorological conditions and site properties. As these effects cannot be quantified solely from eddy covariance data, a classical error analysis and error propagation will remain incomplete. Instead, Aubinet *et al.* (2000) suggested an empirical approach to determine whether the fluxes meet certain plausibility criteria. We investigated three criteria: the statistical characteristics of the raw instantaneous measurements, the frequency resolution of the eddy covariance system through the spectra and cospectra of the measured variables, and the stationarity of the measuring process.

The quality control of raw instantaneous data is applied during the post-processing of the fluxes, where two types of spikes are identified and removed: hard spikes and soft spikes. Hard spikes can be caused by random electronic spikes or sonic transducer blockage (e.g. during precipitation). They are identified by absolute limits for each variable. Soft spikes are large short-lived departures from the period means. We followed the algorithm proposed by Schmid *et al.* (2000) to identify and remove them.

5. SPECTRAL AND CO-SPECTRAL ANALYSIS

An eddy covariance system attenuates the true turbulent signal at sufficiently high and low frequencies due to limitations imposed by the physical size of the instruments, their separation distances, their inherent time response, and any signal processing associated with detrending or mean removal (Massman and Lee, 2002). Spectral and co-spectral analyses demonstrated the expected frequency distributions in an unstable surface layer for sonic temperature (T), vertical wind speed (w), water vapor and CO₂. Thus, the highest frequency eddies contributing to the flux had a period of one second or more. indicating that little or no loss in flux would be expected for all parameters. Figure 1 shows the spectra and cospectra between w and CO₂ for 6 periods of 30 minutes at different hours, showing the expected -5/3 and -7/3 slopes in the inertial subrange.

6. STATIONARITY TEST

The applicability of an urban flux tower is confined to stationarity conditions, such that the tower height exceeds the blending height at which the small scale heterogeneity merge into a net exchange flux above the city. One criterion for stationarity is if the average flux from 6 continuous subperiods of 5 min is within 60% of the flux obtained from a 30 min average (Aubinet *et al.*, 2000). When the turbulent variables are not stationary, the fluxes could be suspicious, and therefore they should not be considered for subsequent analyses. In our study the stationarity condition was fulfilled in 74% of the half hour periods. Conditions of nonstationarity were related to conditions of strong atmospheric stability (see Fig. 2).



Figure. 1. Spectra for CO₂ mixing ratio (a) and cospectra for CO₂ mixing ratio and vertical wind speed (b) for 6 different periods of 30 minute . The -5/3 and -7/3 slopes indicate the theoretical slopes in the inertial subrange.

7. FOOTPRINT ANALYSIS

In a homogeneous surface the footprint is not an issue, because the fluxes from all parts of the surface are by definition equal. However, in an inhomogeneous surface such as a city, the measured signal depends on which part of the surface has the strongest influence on the sensor and therefore the location and size of the footprint.

To evaluate the footprint in our experiment we, used the model developed by Hsieh et al. (2000), considering a zero displacement plane of 8.4 m and a roughness height of 1 m. We applied this model to the complete set of periods measured during the campaign to determine the fraction of the flux measured (F/S_0) as a function of the upwind distance (x) and the atmospheric stability condition. F represents the flux and S_0 the source strength. Considering a fraction of the measured flux equal to 80%, we observe in Figure 3 that the largest footprints (4.9 km in average) correspond to stable conditions, which prevail at nighttime; while the smaller footprints (500 m) correspond to unstable conditions, characteristic of morning and early afternoon. The average footprint, considering all stability conditions, was 1.3 km, which represents а distance large enough to characterize the CO₂ fluxes of a typical neighborhood in Mexico City.

8. RESULTS

8.1. Concentrations

The CO₂ concentrations showed a clear diurnal pattern similar to other typical pollutants emitted by mobile sources, such as NO₂ and CO (INE, 2000). Figure 4 shows that the highest concentrations occurred between 6:30 and 8:00 h with a range from 398 to 444 ppm and an average of 421 ppm.. This morning peak is attributed to anthropogenic emissions (mainly vehicles), nocturnal respiration, and the shallow early morning mixed layer. The lowest concentrations were observed during the afternoon, with an average of 375 ppm. This diurnal profile is consistent with observations at other urban sites, such as Chicago (Grimmond et al., 2002). The diurnal pattern was relatively constant during the entire study. However, an average difference of 20 ppm was observed during the morning rush hour between the holy week (week 2) and the first week of the campaign. This difference represents the vehicular traffic reduction due to the national holiday period during week 2. The difference between week 1 and week 3, in which almost all schools were still on holiday was 6 ppm.

The mean CO_2 concentration measured during our study was 388 ppm with a standard deviation of 14 ppm. This concentration is elevated compared to the global background concentration of 360 ppm (IPCC, 2001), but it is similar to concentrations observed in other cities (Grimmond



Figure 2. Stationarity test for CO₂ flux. 56% of the periods showed a difference lower than 30%, and they are considered of high quality. 18% presented a difference between 30 and 60%, which means that they have an acceptable quality.



Figure 3. Fraction of the flux measured (F/S_0) versus the upwind distance or effective fetch (x).

et al., 2002; Nemitz, et al., 2002; Idso et al., 2002; Reid and Steyn, 1997; Aikawa et al., 1995). From Baez et al. (1988), we observe that CO₂ concentrations in Mexico City have increased 11% in 21 years. As an indicator, our average concentration equal to the maximum is concentration measured in 1982. In 2001, Grutter (2003) measured an average concentration of 374 ppm for a residential section of Mexico City. The two measurements are similar, and within the range of uncertainties considering that our measurements were made during the dry season compared to Grutter's measurements during the rainy season. However, diurnal patterns are Grutter (2003) identified a later and different. longer morning rush hour peak in CO₂ concentrations and a second peak at night that we did not observe. These differences are possibly due to the different distribution of CO₂ sources, vehicular fleet composition, patterns of urban vegetation and irrigation, and different human activities at each site. These differences demonstrate that measurements at a single site are not enough to represent an entire city.

8.2. Fluxes

The CO₂ flux measurements showed a clear diurnal pattern, with the highest emissions during the morning, and lower emissions during nighttime (see Figure 5). Fluxes ranged from -0.22 to 1.60 mg m² s⁻¹, with an average of 0.41 mg m² s⁻¹. Although negative fluxes were registered for specific hours, on average fluxes always remained positive during our study, indicating that the urban surface is always a net source of CO₂, and that the urban vegetation effect during the day is not strong enough significantly to decrease the anthropogenic sources.

Diurnal patterns of concentrations and fluxes are different. Concentrations not only reflect the variability in the emissions, but also the evolution of the atmospheric boundary layer. During the early morning, concentrations increase until 7:00 h, while fluxes remain constant until 6:00 h, when they start to increase, reaching their maximum at 9:00 h. At this hour concentrations have already started to decline, continuing until noon, while fluxes remain high during the entire morning. This shows the dilution of CO₂ from the actual emissions and from the pool stored in the residual layer, as a function of the atmospheric boundary layer growth. Both concentrations and fluxes remain constant during the afternoon. After 19:00 h, fluxes start to decrease, but concentrations

increase again, indicating that a new nocturnal boundary layer has started to form.

Fluxes showed constant diurnal patterns during the three studied weeks, as did concentration patterns. The highest fluxes were observed in the first week, and the lowest during the second week. Only a small difference was observed during holy week (week 2) from 19:00 h to midnight, when fluxes were slightly greater than the other two weeks. This nocturnal increment during holiday could occur because people extend their social activities until late hours of the day. Figure 5 shows the average diurnal patterns for weekdays and weekends. Weekends presented lower fluxes between 5:00 and 9:00 h than weekdays. This effect is directly related to vehicular traffic, since on weekends the traffic is usually lower during morning hours. During the remainder of the day, fluxes are similar between weekends and weekdays.

In an urban area, where the emission sources are not homogeneous, it is necessary to determine the magnitude of the fluxes as a function of the upwind direction to identify the strongest sources. Figure 6 shows the CO_2 flux distribution as a function of the wind direction superimposed on a map of the studied suburb for a footprint with a fraction of the measured flux equal to 80%. Fluxes were lower from areas with fewer streets and residences, for example from the north and northwest directions. The largest emissions came from the east and southeast directions, where the avenue (Anillo Periferico) with the highest vehicular traffic near the measurement site is located.

During the MCMA field campaign, traffic counts were performed at two intersections, one between the avenues labeled 1 and 2 (I_{1-2}) in Figure 6, and the other between avenues 2 and 3 (I₂₋₃). Figure 7 presents the diurnal flux pattern along with the vehicular count distributions, where the vehicular fleet was classified into four different groups: passenger cars, taxi cabs, light trucks/buses, and heavy trucks/buses. Although both intersections share avenue 2, I₂₋₃ has a higher traffic density than I₁₋₂, since avenue 3 encircles the entire city, making it one of the busiest avenues, and one of the largest emission sources (see Figure 6). Several routes of "colectivos" (small buses with a capacity for 20 passengers) start from l_{-2} , which can be observed in the higher number of light buses and trucks compared to I₂₋₃. The high CO₂ fluxes emitted from the southwest shown in Figure



Figure 4. Average diurnal pattern of CO_2 concentrations for the entire study and for separated weeks. The green area represents ± 1 standard deviation from the total average.



Figure. 5. Average diurnal pattern of CO_2 fluxes for the entire study and for weekdays and weekends. The green area represents ±1 standard deviation from the total average.



Figure 6. CO₂ flux distribution as a function of the upwind direction during the entire study. The orange contour indicates the fraction of the flux measured equal to 80%. The black spot indicates the position of the flux tower; the green area represents part of the National park "Cerro de la Estrella", the blue lines are streets and the red lines are primary roadways. The four primary roads surrounding the measurement site are: (1) Av. Rojo Gomez, (2) Av. Ermita Iztapalapa, (3) Anillo Periferico, (4) Av. Jalisco, and (5) Calz. San Lorenzo.

6 may be due to these colectivos, which remain stopped and idling at a short distance from this intersection, while waiting for passengers.

The typical morning and afternoon traffic peaks are not identified at either intersection, instead a single peak is observed during the entire day. This peak begins at 6:00 h, and extends until late afternoon for I_{1-2} , and into the night for I_{2-3} . Assuming that the small peaks during the morning are due to the atmospheric boundary layer growth, we conclude that CO_2 fluxes follow the vehicular traffic diurnal profile. Both remain constant during most of the daytime and then decline at night. . Figure 8 confirms the high correlation between vehicular traffic and CO_2 emissions, where the correlation coefficients from linear regressions are 0.80 and 0.65 for I_{1-2} and \underline{b}_{-3} , respectively. The statistical offset indicates the presence of other sources different than traffic sources, such as food cooking, water heating, and combustion processes from factories and stores, among others.

Using the Mexican vehicular fleet distribution (SMA-GDF, 2002) and the emission factors developed by Zavala (personal communication) through the stoichiometric combustion equation and the characteristics of Mexican fuels, we can roughly determine the CO_2 fraction emitted for each group of vehicles considered in the traffic counts in the two intersections discussed above. Figure 9 shows that the emission contributions are similar for both intersections, where the group of passenger cars is the largest vehicular source with a 60% contribution. Colectivos and taxis contribute 17% each, while heavy trucks and buses represent 6% of the mobile CO_2 emissions.



Figure 7. Diurnal profile of CO₂ fluxes superimposed over plots of traffic counts for two intersections in the footprint studied: intersection between Av. Ermita Iztapalapa and Av. Rojo Gomez (I₁₋₂), and the intersection between Av. Ermita Iztapalapa and Anillo Periferico (I₂₋₃).



Figure 8. Correlation between CO₂ fluxes and vehicular traffic for the two discussed intersections: $I_{1-2,}$ red spots, and $I_{2-3,}$ blue open squares.



Figure 9. CO_2 emission fraction per type of vehicle as a function of the hour of the day for the two intersections discussed in the text: intersection between Av. Ermita Iztapalapa and Av. Rojo Gomez (I₁₋₂), and intersection between Av. Ermita Iztapalapa and Anillo Periferico (I₂₋₃). For heavy trucks and buses we used an emission factor of 322 g km⁻¹, for light trucks and buses 525 g km⁻¹, for taxi cabs 216 g km⁻¹, and for passenger cars 246 g km⁻¹.

9. CONCLUSIONS

Results of this study have demonstrated the capacity of the eddy covariance technique to measure CO₂ fluxes in an urban area, where the inhomogeneous surface, the high roughness and wide distribution of emission sources complicate the measurements. The measured fluxes from the local landscape may be representative of similar neighborhoods of Mexico City, but these fluxes cannot represent the entire city, as demonstrated by the difference between previous CO₂ measurements in a residential area and our measurements. Multiple measurement locations will be needed to characterize the diurnal profiles of an entire city, where significant variability can be expected between various sites due to the distribution of anthropogenic sources.

Our CO_2 measurements show clear diurnal profiles for both concentrations and fluxes, which are strongly correlated to vehicular traffic during the day The effects of urban vegetation absorbing CO_2 during daytime does not appear to be significant for this site.

If we assume that fluxes measured during the studied period are representative of the entire year, we can infer from the average flux an annual emission of ~3.5 kT of C km⁻² yr⁻¹. This annual emission is 2.4 times lower than emissions obtained for Edinburgh, Scotland using similar flux techniques (Nemitz et al., 2002). While this difference can be attributed to the different urban footprints and seasonal conditions, it may also indicate the emission differences between developed and developing cities. Mexico City has a higher population density, less vegetated areas and an older vehicular fleet than Edinburgh; these factors would suggest higher CO2 fluxes in Mexico City. However social activities and energy consumption is very different and may result in less production of CO₂ emissions in Mexico City.

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