# **Accepted Manuscript**

Title: Tethered balloon-based soundings of ozone, aerosols, and solar radiation near Mexico City during MIRAGE-MEX

Authors: J.P. Greenberg, A.B. Guenther, A. Turnipseed

PII:\$1352-2310(09)00139-3DOI:10.1016/j.atmosenv.2009.02.019Reference:AEA 8886

To appear in: Atmospheric Environment

Received Date: 17 December 2008 Revised Date: 6 February 2009 Accepted Date: 8 February 2009

Please cite this article as: Greenberg, J.P., Guenther, A.B., Turnipseed, A. Tethered balloon-based soundings of ozone, aerosols, and solar radiation near Mexico City during MIRAGE-MEX, Atmospheric Environment (2009), doi: 10.1016/j.atmosenv.2009.02.019

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.



| 1<br>2 | Tethered balloon-based soundings of ozone, aerosols, and solar radiation near                    |
|--------|--|
| 3      | Mexico City during MIRAGE-MEX  |
| 4      | J.P. Greenberg <sup>*</sup> , A.B. Guenther, A. Turnipseed                                       |
| 5      | National Center for Atmospheric Research, Boulder, Colorado 80307, USA                           |
| 6      |  |
| 7      | Abstract   |
| 8      | A tethered balloon sampling system was used to measure vertical profiles                         |
| 9      | of ozone, particles, and solar radiation in the atmospheric boundary layer on the                |
| 10     | northern edge of Mexico City, in March 2006 as part of the Megacity Impact on                    |
| 11     | Regional and Global Environment-Mexico experiment. Several commercial                            |
| 12     | sensors, designed for surface applications, were deployed on a tethered balloon                  |
| 13     | platform.  |
| 14     | Profiles indicate that for these 3 scalars the boundary layer (surface up to                     |
| 15     | 700 m) was well mixed in the period 10:00-16:00 LST. Good agreement was                          |
| 16     | observed for median surface and balloon ozone and particle number                                |
| 17     | concentrations. For most profiles, the surface deposition of ozone was not                       |
| 18     | significant compared to median profile concentrations. Particle number                           |
| 19     | concentration (0.3, 0.5, 1.0 and 5.0 $\mu\text{m}$ ) also showed little variation with attitude. |
| 20     | Radiation profiles showed a monotonic increase in diffuse radiation from the                     |
| 21     | maximum altitude of profiles to the surface. Consequently, it was inferred that                  |
| 22     | surface measurements of these likely were representative of lower boundary                       |
| 23     | layer values during this time period.  |

- <sup>1</sup> \*corresponding author: <u>greenber@ucar.edu</u>; P.O. Box 3000, Boulder, Colorado,
- 2 80307, USA. Telephone: 303-497-1454, FAX: 303-497-1400
- 3
- 4 Keywords: tethered balloon, boundary layer, ozone, radiation, particles

A CERTING

# 1 **1. Introduction**

| 2  | The MIRAGE (Megacity Impact on Regional and Global Environment)-                   |
|----|--|
| 3  | MEX field campaign (March 2006) was designed to examine the chemical and           |
| 4  | physical transformations of gases and aerosols in the polluted outflow from        |
| 5  | Mexico City. The campaign included observations from ground stations, aircraft,    |
| 6  | and satellites. (An overview of the experiment is given in Molina et al., 2008.)   |
| 7  | Surface measurements were made at three primary sites: central Mexico City         |
| 8  | (T0, Instituto Mexicano de Petroleo), the Technical University of Tecamac (T1),    |
| 9  | approximately 35 km NW of T0, and Rancho de Bisnaga (T2), approximately 70         |
| 10 | km from T0. The sites were selected to characterize polluted MC air as it aged in  |
| 11 | transit from its source (arbitrarily set at T0).                                   |
| 12 | The balloon-platform profiles presented here are from the T1 site                  |
| 13 | (19N42.184, 98W59.917, 2270 m asl) from 13-28 March, 2006. The primary             |
| 14 | objective of the tethered balloon study was determine if surface measurements      |
| 15 | accurately reflected concentrations in the boundary layer, so that ground based    |
| 16 | data might be extended to characterize to the atmospheric boundary layer           |
| 17 | analysis. Vertical profiles of several variables (ozone, particles, and direct and |
| 18 | diffuse solar radiation) were made to illustrate mixing from the surface to the    |
| 19 | maximum balloon height (usually between 400 and 700m above ground level).          |
| 20 |  |

- 21 **2. Experiment Details**
- Instrumentation: Extensive details of tethered balloon profiling in the
  atmospheric boundary layer have been provided previously (Greenberg et al.,

1 1999; Greenberg and Guenther, 2000). Several commercial, light weight sensors 2 were deployed on the balloon platform. Ozone was measured by a UV absorption ozone analyzer (2B Technologies, Boulder, CO, 2.1 kg); a glass fiber 3 4 filter was placed on the inlet to prevent interference of dust in the optical cell. Ten 5 secondhowever average data is reported for each profile. The relative standard 6 deviation of one minute averaged data was determined experimentally to be 7 approximately 1.3% at approximately at 70 ppb. An optical particle counter 8 (Abacus, Particle Measurement Systems, Boulder, CO, 1 kg) was also deployed. 9 Particles numbers were counted for discrete 0.3, 0.5, 1 and 5 micron sizes; 45 10 second average number concentrations are reported. The reported collection 11 efficiency is approximately 20% for 0.3 micron particles. Total (global), direct 12 (total minus diffuse) and diffuse radiation were measured using Sunshine Sensor, model BF3 (Delta-T Devices, Ltd., Cambridge, UK, 0.5 kg). This 13 14 detector has a sensor array which requires no shadow band and need not be 15 pointed toward the north. The BF3 radiation sensor computes direct solar radiation as the difference between total and diffuse radiation. While the sensor 16 is normally deployed on level surface, significant errors from a tilted surface only 17 occur at low solar elevation (Wood et al., 2003); small changes in the angle of 18 19 incidence caused by balloon attitude had generally little effect on the measure of 20 direct or diffuse radiation. One second data are reported. The overall accuracy 21 for total and diffuse radiation is reported as 12% and 15%, respectively. 22 Measurements of wind speed and direction and pressure-altitude were 23 made using an NCAR-made instrument (inquiries on specifications may be

1 directed to the authors). Commercial tethered atmospheric sounding systems 2 (Model TS-5A-SP. Atmospheric Instrumentation Research, Boulder, CO, USA and DigiCORAS Tethersonde System, Vaisala, Inc., Helsinki, Finland) have been 3 4 used in previous studies but are no longer available from the manufacturers. A 12 m<sup>3</sup> Skydock balloon (Flotograph Technologies, LLC, Silver Springs, 5 MD, USA) and a 9 m<sup>3</sup> blimp (Fire Fly Balloons, Inc., Statesville, NC, USA) were 6 7 used to lift the tethered measurement systems. Instruments were mounted on a 8 horizontal platform approximately 3 m below the Skydock balloon (ozone, particle 9 and radiation instruments) or, when the blimp was employed, ozone or particle sensors were approximately 1 m below the balloon. The radiation sensor was 10 only deployed on the Skydock platform. The meteorological system was 11 12 deployed on each flight. Balloons were generally raised and lowered at a constant rate (0.5 m s<sup>-1</sup>), with approximately the same time (30 minutes) for 13 14 ascent and descent. Occasionally, circumstances (usually strong or gusty winds) 15 required differing ascent and descent rates.

Balloon-based measurements were compared with simultaneous
measurements made on the surface at the T1 site: ozone by UV absorption
(Model 49C, ThermoEnvirmonmental Co., USA) and particles by an optical
particle counter (Lasair model 1002, Particle Measurement Systems, Boulder,
Colorado, USA).

#### 1 2 **3. Results**

3 Ozone: Five minute average ozone concentrations measured by colocated balloon and surface ozone instruments were compared (March 12-14), 4 5 Figure 1). The 5 minute averaging period was arbitrarily for this 3 day 6 comparison (ozone profile measurements used 1 minute averaged data to 7 provide more time resolution). The relative standard deviation of balloon 8 instrument ozone concentrations for 5 minute averaged data was determined 9 experimentally to be approximately 0.7%. Good agreement was seen for a 14 day comparison (slope=0.97, intercept 6 ppb,  $R^2 = 0.97$ ). The balloon profiles 10 11 were collected during the earlier part of this period (Julian days 72 to 79, or 12 March 13 through March 20, respectively).

The balloon and surface particle sensors (Abacus and Lasair) were both 13 14 manufactured by Particle Measurement Systems (Boulder, CO); Lasair is the 15 newer model of the Abacus instrument. The balloon particle counter number 16 concentrations at the surface were compared with simultaneous surface counter 17 number density (Figure 2). For 0.3 and 0.5 micron particles measurements were highly correlated ( $R^2 = 0.87$ , and 0.86, respectively), with some differences in 18 19 slope and intercept of the regression of medians particle concentrations from the 20 simultaneous sampling periods (balloon[x]=0.76\*surface[x] + 541 and 21 balloon[x]=1.05\*surface[x] + 20, for 0.3 and 0.5  $\mu$ m particles, respectively). The balloon platform optical particle counter consistently detected more 1 and 5 22 micron particles than the surface instrument. 23

Most balloon profiles were made between 10:00 and 16:00 local time; strong winds and dust-devils prevented balloon profiles after approximately 16:00 local time. No nighttime profiles were attempted. Balloon launches were not permitted during research aircraft over-flight periods. Eleven profiles of ozone, seventeen of particles and nine radiation profiles were made during the experiment and several examples of each are presented in Figure 3, 4, and 5, respectively.

8 **4. Discussion** 

9 **Meteorology:** During the dry season (coinciding with the period of the 10 experiment), the boundary layer above the Mexico City area has been shown to 11 grow slowly after sunrise to a depth of approximately 1000 m by 11:00 LST, then 12 rapidly increase to approximately 2500 m by 13:30 LST, and to grow at a slower rate subsequently to reach about 3000 m by 16:00 LST (Whiteman et al., 2000). 13 14 A sudden cooling of the boundary layer to an altitude of 2250 m occurs between 15 16:30 and 19:30 LST, after the surface energy budget reverses (Velasco et al., 16 2008). Since most tethered balloon-based observations were made between 17 9:30 and 16:00 LST, when boundary layer growth was rapid, deep and uniform 18 mixing of air through this layer is expected.

Ozone: The UV absorption technique allows a direct and precise measurement of ozone concentrations. On the tethered balloon platform, it is also an economical alternative to electrochemical sondes (Komhyr, 1969). (The electrochemical ozone sonde measures the change in conductivity resulting from the reaction of potassium iodide in a solution through which ozone-containing air

1 is bubbled; this technique requires separate and repeated calibration of each 2 sonde, both for chemical reaction and sample flow rates and is subject to 3 chemical interferences ((Parrish and Fehsenfeld, 2000; Velasco et al., 2007)). 4 Generally, very little gradient of ozone with altitude is observed (Table 2, 5 Figure 3), even as concentrations increase through the afternoon. Ozone 6 produced during the daytime is apparently quickly and evenly distributed 7 throughout the boundary layer profiled. Surface deposition of ozone was at most 8 small. This is expected, resulting from the vigorous mixing of the boundary layer 9 and the low productivity of the arid landscape (which precluded deposition to 10 vegetation through stomatal conductance). The observations are also consistent 11 in pattern with those reported previously using the electrochemical sonde from 12 late morning through mid-afternoon (Wöhrnschimmel et al., 2006; Velasco et al., 2008). 13

14 **Particles:** Ninety-nine samples of 45 second averaging length were taken 15 in each profile, approximately an equal number of samples in ascent and 16 descent. Typical profiles are shown in Figure 4. Only small differences were seen 17 between particle counts in each size range for ascent and descent. Absolute 18 number densities varied among profiles at different times and days, but remained 19 within the ranges recorded by surface instruments (Figure 2). Additionally, only 20 small negative or positive gradients were observed; no distinct layers or 21 discontinuities were detected in any profiles (Table 1). The results suggest 22 uniform mixing of aerosols in the boundary layer, resulting from the strong mixing

during the daytime, and also indicate that surface observation may be directly
 applied in calculation of radiative transport in the lower boundary layer.

Vertical profiles of aerosol size distribution have also been made using an
optical particle counter (model 9722, Met One Instruments, Inc., Grants Pass,
OR) aboard an unmanned, remote-controlled aircraft (Corrigan et al., 2008). The
Met One optical particle is similar to the one used in balloon profiling here, but
the unmanned aircraft platform is considerably more expensive and complex.

8 Solar radiation: Diffuse radiation in all profiles varied monotonically and 9 slowly and was usually higher near the surface. In the morning hours, more 10 diffuse radiation was generally measured during descent than ascent, as total 11 radiation increased as the solar zenith angle approached zero. Simultaneous 12 measurement profiles of aerosols and radiation were not made because of balloon payload weight limitations; consequently, aerosol loading and diffuse 13 14 radiation in profiles could not be correlated. Several clear sky profiles are 15 presented in Figure 5. Typically, direct solar radiation decreased and indirect increased from the top of the profiles to the surface. Consistent with aerosol 16 17 profiles (although not measured simultaneously) during the period of rapid boundary layer growth, no evidence of a significant absorbing or scattering layer 18 19 for radiation was observed.

20

#### 21 **5. Conclusions**

A tethered balloon-based platform was deployed just north of Mexico City during the 2006 MIRAGE-MILAGRO experiment. The tethered balloon platform

- 1 used light weight, commercially available sensors and provided similar
- 2 information to that provided from aircraft platforms, with considerably fewer
- 3 logistical concerns and lower cost.

4 Continuous profile measurements of ozone, aerosols and solar diffuse and 5 direct radiation were measured in order to represent mixing in the boundary layer 6 and to determine whether surface measurements were useful for characterizing 7 the mixed layer. The balloon profiles indicate that the lower boundary layer was 8 well mixed, with no significant plumes of aerosol or ozone, and no indication of 9 aerosol layers from radiation profiles. A comparison with stationary ground 10 sensors indicated that the ground level measurements at the site were reflective 11 of lower boundary layer mixing ratios of ozone and particle numbers from 10:00 12 to 16:00 local time during the period of the experiment...

13

#### 14 Acknowledgements

15 Surface ozone was measured by G. Huey et al., Georgia Institute of Technology.

16 The National Center for Atmospheric Research is sponsored by the

17 National Science Foundation.

18

#### 19 **References**

- 20 Corrigan, C.E., G.C. Roberts, M.V. Ramana, D. Kim, and V. Ramanathan,
- 21 Capturing vertical profiles of aerosols and black carbon over the Indian Ocean
- using autonomous unmanned vehicles, Atmos. Chem. Phys., 8, 737-747, 2008.
- 23

| 1  | Greenberg, J. P. and A.B. Guenther, Tethered-balloon profiling for boundary    |  |  |
|----|--|--|--|
| 2  | layer atmospheric chemistry, in Environmental Monitoring Handbook, Eds.        |  |  |
| 3  | Burden, I McKelvie, U. Forstner and A. Guenther, McGraw-Hill Handbooks,        |  |  |
| 4  | McGraw Hill, New york, Chapter 20, pp. 20.1-20.14, 2002.                       |  |  |
| 5  |  |  |  |
| 6  | Greenberg, J.P., A. Guenther, P. Zimmerman, W. Baugh, C. Geron, K. Davis.      |  |  |
| 7  | Tethered Balloon measurements of biogenic VOCs in the atmospheric boundar      |  |  |
| 8  | layer. Atmos. Env., 33, 855-867, 1999.   |  |  |
| 9  |  |  |  |
| 10 | lida, K., M.R. Stolzenburg, P.H. McMurry, and J.N. Smith. Estimating nano-     |  |  |
| 11 | particle growth rates from size-dependent charged fractions: Analysis of new   |  |  |
| 12 | particle formation events in Mexico City. J. Geophys. Res., 113 (D05207), doi: |  |  |
| 13 | 10.1029/2007/JD009260, 2008.   |  |  |
| 14 |  |  |  |
| 15 | Komhyr, W.D., Electrical concentration cells for gas analysis. Annals of       |  |  |
| 16 | Geophysics, 25, 203-210, 1969.   |  |  |
| 17 |  |  |  |
| 18 | Molina, L.T. S. Madronich, J. Gaffney et al., An Overview of the MILAGRO       |  |  |
| 19 | Campaign: Mexico City Emissions and its Transport and Transformation, in       |  |  |
| 20 | prep., 2008  |  |  |
| 01 |  |  |  |

| 1  | Parrish, D.D., and F.C. Fehsenfeld, Methods for gas-phase measurements of       |
|----|---|
| 2  | ozone, ozone precursors and aerosol precursors, Atmos Environ, 34, 1921-1957,   |
| 3  | 2000.   |
| 4  |   |
| 5  | Velasco, E, C. M'arquez, E. Bueno, R. M. Bernab'e, A. S'anchez, O. Fentanes,    |
| 6  | H. W"ohrnschimmel, B. C´ardenas, A. Kamilla, S. Wakamatsu, and L. T. Molina.    |
| 7  | Vertical distribution of ozone and VOCs in the low boundary layer               |
| 8  | of Mexico City, Atmos. Chem and Phys., 8, 3061-3079, 2008.                      |
| 9  |   |
| 10 | Whiteman, c.D., S. Zhong, X. Bian, J.D. Fast and J.C. Doran, Boundary layer     |
| 11 | evolution and regional-scale diurnal circulations over the Mexico Basin and     |
| 12 | Mexican plateau, J. Geophys. Res., 105 (D8), 10,081-10,102, 2000.               |
| 13 |   |
| 14 | Wöhrnschimmel, H, C Márquez, V Mugica, W. A. Stahel, J Staehelin, B             |
| 15 | Cárdenas, S Blanco Vertical profiles and receptor modeling of volatile organic  |
| 16 | compounds over Southeastern Mexico City, Atmos. Environ., 40 (27), 5125-        |
| 17 | 5136, 2006.   |
| 18 |   |
| 19 | Wood, J., T Muneer, and J. Kubie, Evaluation of a new photodiode sensor for     |
| 20 | measuring global and diffuse Irradiance, and sunshine duration, J. Solar Energy |
| 21 | Engineering, 125, 43-46, 2003.  |
| 22 |   |
| 23 |   |

**Table 1**: Particle number concentrations (median and inter-quartile ranges) from balloon-borne optical particle counter. The variation in particle number concentrations (number/cm<sup>3</sup>) for each size over the profiles spanned a narrow range, indicating, in almost all profiles, only small changes with height.

| Date     | Time        | 0.3µm            | 0.5 μm        | 1 μm          | 5 µm       |
|----------|-------------|------------------|---------------|---------------|------------|
| 13-March | 13:20-14:05 | 1005 (573-1126)  | 54 (46-56)    | 23 (20-27)    | 2 (2-4)    |
| 15-March | 16:00-16:45 | 1205 (1129-1230) | 131 (119-160) | 60 (49-81)    | 4 (2-6)    |
| 16-March | 16:00-16:45 | 1095 (941-1177)  | 274 (199-330) | 208 (153-347) | 31 (16-74) |
| 17-March | 13:45-14:30 | 842 (797-919)    | 44 (42-46)    | 12 (11-13)    | 3 (3-3)    |
| 18-March | 10:40-11:25 | 1809 (1644-1977) | 135 (120-153) | 38 (35-41)    | 5 (5-6)    |
| 18-March | 12:20-13:05 | 1787 (1743-1849) | 149 (144-153) | 43 (41-47)    | 7 (7-9)    |
| 21-March | 12:00-12:45 | 1138 (1096-1195) | 67 (64-72)    | 23 (22-24)    | 2 (2-3)    |
| 21-March | 14:00-14:45 | 1442 (1395-1467) | 95 (90-99)    | 24 (22-26)    | 2 (2-3)    |
| 21-March | 16:00-16:45 | 1956 (1925-2042) | 144 (140-152) | 31 (29-32)    | 3 (2-4)    |
| 22-March | 9:25-10:10  | 2745 (2661-2813) | 532 (362-697) | 45 (41-73)    | 2 (2-2)    |
| 22-March | 13:00-13:45 | 2684 (2626-2726) | 391 (304-423) | 40 (34-44)    | 2 (2-3)    |
| 23-March | 10:00-10:45 | 1576 (1457-1808) | 98 (87-121)   | 21 (18-24)    | 1 (1-2)    |
| 23-March | 12:00-12:45 | 1489 (1444-1524) | 84 (81-88)    | 24 (22-26)    | 2 (2-3)    |
| 24-March | 12:30-13:15 | 2451 (2344-2548) | 249 (207-294) | 31 (27-35)    | 4 (3-4)    |
| 25-March | 9:30-10:15  | 2850 (2744-2930) | 235 (202-269) | 21 (18-22)    | 1 (1-1)    |
| 25-March | 11:30-12:15 | 2337 (2234-2408) | 140 (120-148) | 12 (11-14)    | 1 (0-1)    |
| 26-March | 10:30-11:15 | 2059 (1980-2231) | 63 (59-74)    | 4 (3-5)       | 1 (1-1)    |

**Table 2**: Median and inter-quartile range (IQR) ozone concentrations (ppb) along

 boundary layer profiles. At most, only small, smooth gradients were observed in the

 profiles, with increasing average concentrations during the day.

| Date   | Time (LST) r  | nedian | IQR       |
|--------|---------------|--------|-----------|
| 13-Mar | 9:33 - 10:18  | 47     | (42-49)   |
| 13-Mar | 15:44 - 16:28 | 47     | (41-50)   |
| 14-Mar | 11:27 - 12:30 | 53     | (51-54)   |
| 15-Mar | 8:52 - 9:41   | 41     | (37-44)   |
| 15-Mar | 12:53 - 13:50 | 76     | (65-78)   |
| 16-Mar | 15:08 - 16:06 | 106    | (104-108) |
| 17-Mar | 9:31 - 10:03  | 45     | (42-50)   |
| 17-Mar | 11:04 - 11:57 | 78     | (74-84)   |
| 17-Mar | 13:19 - 13:53 | 58     | (48-61)   |
| 18-Mar | 10:11 - 11:32 | 70     | (58-75)   |
| 18-Mar | 11:32 - 12:32 | 78     | (73-82)   |
| 20-Mar | 13:51 - 15:13 | 114    | (104-118) |

| 1 | Figure | captions |
|---|--------|----------|
|---|--------|----------|

- 2 **Figure 1**: Ground and balloon instrument inter-comparison of ozone
- 3 measurements: Both the balloon (2B Technologies, Inc., Boulder, CO, USA) and
- 4 surface instruments (Model 14, ThermoEnvironmental Corp, Franklin, MA, USA)
- 5 operated on the principal of UV absorption by ozone of light (254 nm) from a

6 mercury lamp.

- 7 Figure 2: Comparison of ground (LASAIR, Particle Measurement System,
- 8 Boulder, Colorado, USA, lida et al., 2008) and balloon (Abacus, Particle
- 9 Measurement System, Boulder, Colorado, USA) instruments during the
- 10 MILAGRO campaign. Very good agreement between 2 optical particle counters
- 11 was observed for 0.3 and 0.5  $\mu$ m particles.
- 12 **Figure 3**: Selected profiles of ozone from the surface up to approximately 700 m.
- 13 Ozone concentrations were relatively constant over the altitudes measure.
- 14 **Figure 4**: Selected profiles of particle number densities (0.3, 0.5, 1.0 and 5.0  $\mu$ m
- 15 particles) from the surface up to approximately 700 m. Particles, in general,
- 16 showed uniform number densities throughout profiles.

17 **Figure 5**: Typical clear sky radiation profiles. Profiles show, at most, small

- 18 increase/decrease or diffuse /direct radiation from the top of the profile to the
- 19 surface, illustrating the general scattering effect of uniform aerosol number
- 20 densities throughout the profile.





Figure 2







Figure 3



0

C

0

4

Ą

Ĩ

\*\*\*\*



Figure 4

200







Figure 5