

Mobile mini-DOAS measurement of the outflow of NO₂ and HCHO from Mexico City

M. Johansson¹, C. Rivera¹, B. de Foy², W. Lei^{3,4}, J. Song^{3,4}, Y. Zhang¹, B. Galle¹, and L. Molina^{3,4}

¹Chalmers University of Technology, Göteborg, Sweden

²Saint Louis University, St Louis, Mo., USA

³Molina Center for Energy and the Environment, La Jolla, Ca, USA

⁴Massachusetts Institute of Technology, Cambridge, Ma, USA

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Abstract. We here present the results from mobile measurements using two ground-based zenith viewing Differential Optical Absorption Spectroscopy (DOAS) instruments. The measurement was performed in a cross-section of the plume from the Mexico City Metropolitan Area (MCMA) on 10 March 2006 as part of the MILAGRO field campaign. The two instruments operated in the UV and the visible wavelength region respectively and have been used to derive the differential vertical columns of HCHO and NO₂ above the measurement route. This is the first time the mobile mini-DOAS instrument has been able to measure HCHO, one of the chemically most important and interesting gases in the polluted urban atmosphere.

Using a mass-averaged wind speed and wind direction from the WRF model the instantaneous flux of HCHO and NO₂ has been calculated from the measurements and the results are compared to the CAMx chemical model. The calculated flux through the measured cross-section was 1.9 (1.5–2.2) kg/s of HCHO and 4.4 (4.0–5.0) kg/s of NO₂ using the UV instrument and 3.66 (3.63–3.73) kg/s of NO₂ using the visible light instrument. The modeled values from CAMx for the outflow of both NO₂ and HCHO, 1.1 and 3.6 kg/s, respectively, show a reasonable agreement with the measurement derived fluxes.

1 Introduction

Formaldehyde (HCHO) is the most abundant carbonyl in ambient air and can reach concentrations of up to 60 ppb in polluted air (Finlayson-Pitts and Pitts, 1999). Being both car-

cinogenic (Vaughan et al., 1986; Hauptmann et al., 2003) and soluble in water, it is easily absorbed by the human respiratory system and has a major impact on residents in polluted areas. HCHO is emitted both directly (primary HCHO) as a result of incomplete combustion and generated in the atmosphere (secondary HCHO) in the oxidation of the most common VOCs (Finlayson-Pitts and Pitts, 1999; Garcia et al., 2006). Mainly due to photolysis by UV-light below 360 nm and reaction with OH, HCHO has a lifetime in ambient air of a few hours. Its oxidation chain leads to the formation of OH and HO₂, for which it can be one of the major producers in polluted air (Atkinson, 2000; Volkamer et al., 2005).

Mexico City is located at 19.4 latitude and elevation of 2200 m approximately, within a basin on the central Mexican plateau (Fast et al., 2007). Mexico City presents severe air pollution problems and is one of the most polluted cities in the world (Molina and Molina, 2002; Molina et al., 2007). Formaldehyde levels in Mexico City, both indoor and outdoor have been extensively studied, revealing higher mean concentrations in indoor air (Baez et al., 2003, 2006) and formaldehyde as the most abundant aldehyde both in indoor and outdoor air (Baez et al., 2006). Studies reveal a decrease in formaldehyde levels in Mexico City since the beginning of the 1990s (Baez et al., 1995, 2003, 2006), however they are still among the highest reported in the literature (Baez et al., 1995). Typical observed formaldehyde concentrations in downtown Mexico City are between 12.7–23.9 ppb (Madronich, 2006; Grutter et al., 2005); however mean values above 40 ppb and peak values of 110 ppb have also been reported, finding the maximum concentrations between 10:00–12:00 h, indicating the combined sources of HCHO-primary emissions probably from motor vehicles during rush hours and the secondary photochemical production (Lei et al., 2009). Studies of in-vehicle formaldehyde exposure in



Correspondence to: M. Johansson
(mattias.johansson@chalmers.se)

Mexico City using different transportation modes indicate higher level of exposure in a microbus than in a car, bus and metro (Shiohara et al., 2005).

The MILAGRO (Megacity Initiative: Local and Global Research Observations) field campaign held in the Mexico City Metropolitan Area (MCMA) during March 2006 was aimed at characterizing the chemical processes leading to the formation of photochemical smog in the MCMA and the outflow of pollutants to the surrounding regions (Molina et al., 2009).

The 10 March 2006 was characterized by mostly sunny and dry conditions, no deep convection, clear mountains in the vicinity of Mexico City and periods of cirrus clouds (Fast et al., 2007). In addition, the 10 March was a period with the most direct transport towards the northeast (de Foy et al., 2008; Fast et al., 2007; Doran et al., 2007). This paper presents the results of one mobile mini-DOAS measurement that successfully traversed the entire extent of the plume from the MCMA, enabling the first direct measurement of the outflow of NO₂ and HCHO from the MCMA using a mobile mini-DOAS instrument.

The Differential Optical Absorption Spectroscopy (DOAS) technique has for a long time been used to measure HCHO levels in ambient air, both using active (Platt et al., 1979; Hak et al., 2005) and passive instruments (Heckel et al., 2005). However, this is the first detection of HCHO using a mobile mini-DOAS instrument.

2 Experimental

The mobile mini-DOAS instrument (described by Galle et al., 2002) uses a telescope to collect zenith scattered light in the UV or visible region. This light is led through an optical quartz fibre into a miniaturized spectrometer (Fig. 1). The spectrometer is connected to a laptop which stores the spectra and simultaneously stores the position using an attached GPS-receiver.

Each measured spectrum is ratioed to a Fraunhofer reference spectrum, selected as the first collected spectrum in the measurement. The result of the DOAS evaluation is the differential vertical column of the spectrum, i.e. the difference in the vertically integrated concentration between the time and location where the spectrum was collected and the time and location where the Fraunhofer reference spectrum was collected. If the measurement has passed underneath a gas plume, then the flux of the plume can be calculated by integrating the total number of molecules in the cross section of the plume, multiplying with the wind speed and correcting for the angle between the wind direction and the traverse direction.

During the MILAGRO field campaign, a car equipped with two mobile mini-DOAS instruments, one measuring mostly in the UV (280 to 425 nm) and one mostly in the visible (340 to 480 nm), performed measurements in the MCMA

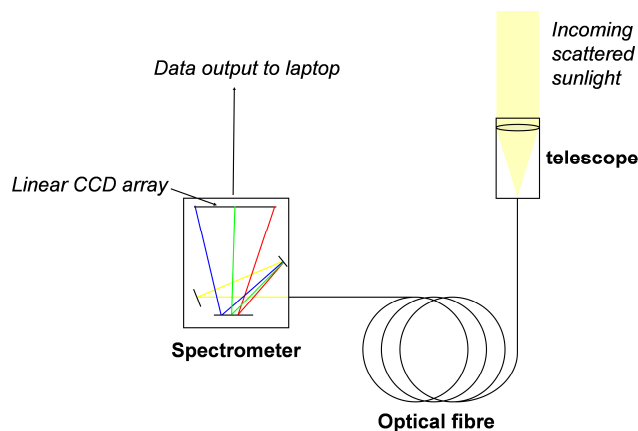


Fig. 1. The mobile Mini-DOAS instrument collects zenith scattered light.

to capture the distribution and possible outflow of air pollutants. On 10 March 2006, a measurement was made on the entire width of the plume flowing out of the Mexico City basin.

The spectra collected with the UV-spectrometer have been evaluated for NO₂ (using the NO₂ cross section by Vandaele et al., 1998) and HCHO (using the HCHO cross section by Meller and Moortgat, 2000) in the wavelength range 311 to 347 nm using the DOAS technique and the WinDOAS software package (Van Roozendael and Fayt, 2001). To increase signal to noise ratio, the collected spectra have been co-added giving 900 single exposures in each evaluated spectrum and a time-resolution of the measurement of slightly less than two minutes. Included into the fit were also the cross sections of SO₂ (Bogumil et al., 2003), O₃(223 K) (Burrows et al., 1999), O₃(293 K) (Burrows et al., 1999), O₄ (Hermans et al., 1999) and a synthetic Ring spectrum generated from the measured Fraunhofer reference spectrum using the DOASIS software (DOASIS – Kraus). An example of a DOAS-fit in the wavelength range 311 to 347 nm can be seen in Fig. 2.

The spectra collected with the visible light spectrometer have been evaluated for NO₂ in the wavelength range 410 to 460 nm using the DOAS technique and the WinDOAS software (Van Roozendael and Fayt, 2001). Also these spectra have been co-added to increase the signal to noise ratio, giving 2240 single exposures in each evaluated spectrum and a time-resolution of slightly less than two minutes. Included into the fit were also the cross section of O₄ (Hermans et al., 1999) and a synthetic Ring spectrum calculated using the DOASIS software (DOASIS – Kraus).

The largest error in estimation of the pollutant fluxes is the uncertainty in the wind speed and wind direction at the time of the measurement. For this purpose, the WRF mesoscale meteorological model was used to simulate the local meteorological conditions in the Mexico City basin. Three nested grids were used with resolutions of 36 km covering the

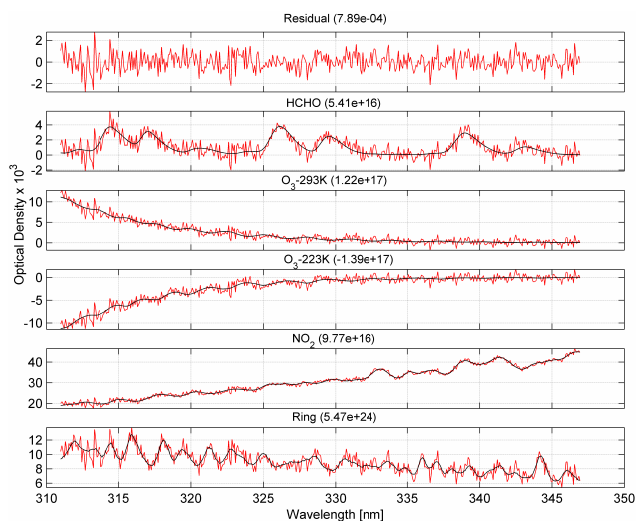


Fig. 2. The result of the DOAS fit in the 311 to 347 nm region. Top graph shows the residual of the fit, below are the fitted cross sections (from top to bottom); HCHO, O₃(293 K), O₃(223 K), NO₂ and a synthetic ring spectrum.

whole of Mexico (D1), 12 km covering the region around the MCMA (including the Gulf and the Pacific Ocean) (D2) and 3 km covering the MCMA basin and immediate surroundings (D3). In the vertical, 51 levels were used with the model top at ~ 7 km a.g.l. The land surface provides an important forcing term for the local winds in the basin. In order to capture these, high resolution data from MODIS was used to initialize the land use, vegetation fraction, surface albedo and soil temperature (de Foy et al., 2006). The WRF model contains certain hard-coded modifications to handle urban surfaces. These however were not found to be representative of Mexico City and were removed. The NOAA land surface model was used together with the YSU boundary layer scheme and Kain-Fritsch convection. The z -diffusion scheme was used for the fine grid only. This model configuration was evaluated in de Foy et al. (2009; “WRFa” case) and the simulated wind transport was found to be representative of the actual transport in the basin.

Horizontal wind flux was calculated based on mass-averaged fluxes in the meridional and zonal directions. This was performed for the column below the simulated boundary layer height at the grid column closest to the measured column. This horizontal wind flux was then used to estimate the flux of NO₂ and HCHO through the measured cross-section.

The measured columns have been compared to the simulation results for the Comprehensive Air Quality Model with Extensions (CAMx; Environ International Corporation, 2008) chemical model which was setup for the region surrounding the MCMA during the MILAGRO campaign. CAMx was driven by hourly prognostic meteorological fields from WRF. The CAMx domain configuration was the same as the WRF inner-most domain (D3) except for a smaller

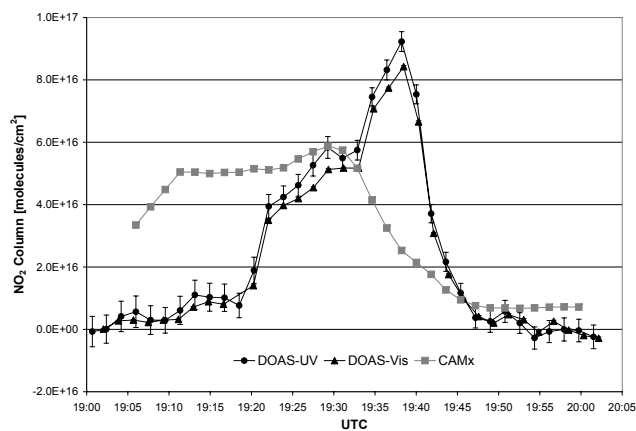


Fig. 3. Derived differential columns of NO₂ from the DOAS instrument working in the UV-region (black circles), the DOAS instrument working in the visible region (black triangles) and extracted columns of NO₂ from the CAMx model (grey squares). Notice that the modeled columns are not differential.

domain of 70×70 grids, and emission estimates were constructed from the official emission inventory for the year 2006 for MCMA, and were adjusted based on the NO_x and CO measurements from a local monitoring network and the extensive VOC measurements at CENICA and T0 during the MILAGRO-2006 campaign following the adjustment procedure of Lei et al. (2007, 2008). The emissions were adjusted such that the measured and modeled morning rush hour surface concentrations of CO, NO_y and various speciated VOCs reached a good agreement during the one-month long MILAGRO campaign. The simulated columns of NO₂ and HCHO have been bi-linearly interpolated in space and linearly interpolated in time along the measurement route from the 1-h average concentration fields of the model output to be able to compare the distribution of NO₂ or HCHO along the measurement route.

3 Results and discussion

The evaluated measurement was performed on 10 March 2006 starting at 12:58 local time (18:58 UTC) and resulted in a series of differential columns of NO₂ and HCHO along the measurement route.

Figure 3 shows the evaluated differential columns of NO₂ from both the UV and the visible light spectrometer together with the extracted columns of NO₂ from the CAMx model. The derived differential NO₂ columns from the UV spectrometer are somewhat higher than from the visible light spectrometer. This is most likely due to somewhat longer path lengths in the UV than in the visible due to the higher cross section for Rayleigh and Mie scattering. However the difference between the two measurements is less than 2σ of the spectral fit from the UV measurement.

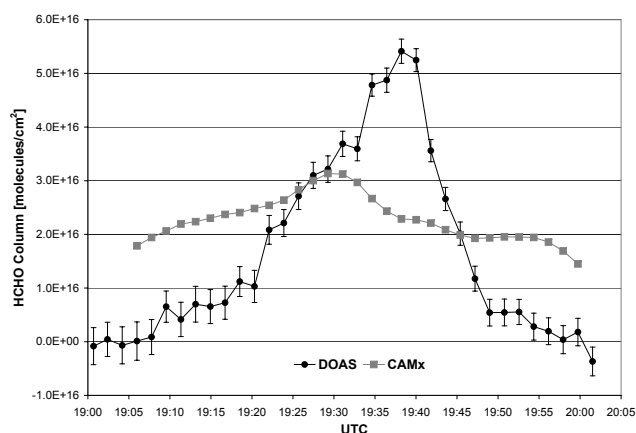


Fig. 4. Evaluated differential column of HCHO from the DOAS instrument working in the UV-region (black circles) and extracted columns of HCHO from CAMx (gray squares). Notice that the modeled columns are not differential.

Table 1. Estimated NO₂ fluxes from the two instruments and CAMx using the mass-averaged wind-speed and wind-direction from the WRF model.

Instrument	Flux [kg/s]
UV-spectrometer	4.4 (4.0–5.0)
Vis-spectrometer	3.66 (3.63–3.73)
CAMx	3.6

By using the mass-averaged wind speed and wind direction from the WRF-model, the flux of NO₂ through the measured cross-section of the plume can be estimated from both DOAS-instruments, see Table 1. The same estimation can be done for the modeled columns. However since the measured columns are differential with respect to the column in the Fraunhofer reference spectrum, the modeled columns must be transformed into differential columns for the results to be comparable. This has been done by subtracting the lowest modeled column value from all other modeled values, the resulting flux can be seen in Table 1. The CAMx model estimates a flux that is in good agreement with the measurements; however with a difference in the distribution of NO₂ along the measurement route. The model shows a broader and lower plume than does the measurements and with a peak located approximately 10 km from the location of the measured peak.

Figure 4 shows the evaluated differential columns of HCHO from the UV spectrometer and the extracted columns of HCHO from the CAMx model, the route of the measurement is seen in Fig. 5. By using the mass-averaged wind-speed and wind-direction from the WRF-model, the flux of HCHO through the measured cross-section of the city-plume can be calculated from the DOAS-measurement and the dif-

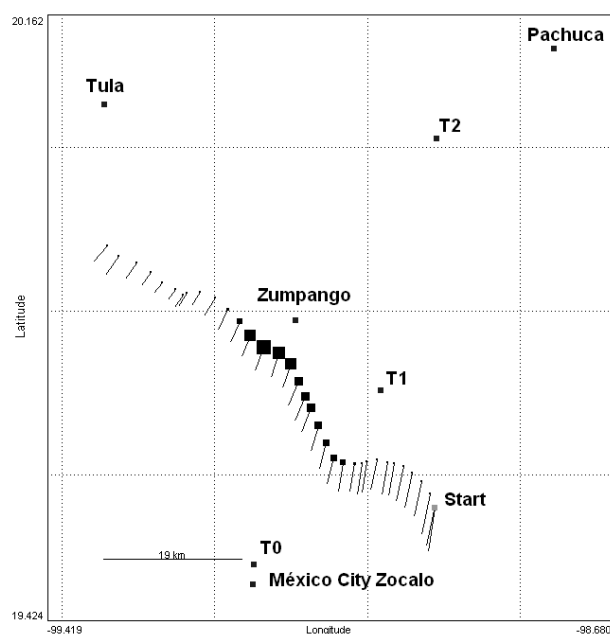


Fig. 5. The route for the HCHO measurement shown in Fig. 4. Larger differential HCHO columns are shown as larger squares, smaller columns as smaller squares. The direction from which the wind comes is marked as lines starting at each measurement point.

Table 2. Estimated HCHO fluxes from the DOAS instrument and the CAMx chemical model using the mass-averaged wind-speed and wind-direction from the WRF model.

Instrument	Flux [kg/s]
UV-spectrometer	1.9 (1.5–2.2)
CAMx	1.1

ferentiated columns from the CAMx model see Table 2. The range for the flux calculated from the DOAS-instrument has been calculated by error propagation of the error from the spectral fit.

The CAMx model shows a much more smooth distribution of HCHO throughout the city compared to the measurement. To be able to compare the model and measurement, we must transform the modeled columns into differential columns. In the measurement are the columns differential relative to the vertical column at the location and time of the Fraunhofer spectrum, which here was chosen as the first spectrum in the measurement series. However, since the model spreads out the HCHO concentration too much, as judged from the distribution seen in the measurement, subtracting the modeled column at the time and location where the Fraunhofer spectrum was collected would give artificially low differential columns for the model. We have instead subtracted the HCHO column upwind Mexico City, 8×10^{15} molecules/cm², which was estimated as the background column from the modeled column

in the MCMA. This gives an estimated flux from the model of 1.1 kg/s, which is in reasonably good agreement with the measured flux.

The main difference between the simulated and measured columns is that the urban plume is more spread out in the numerical simulations even though the total fluxes are in reasonable agreement. This suggests that the numerical plume is representative of the real one, but that there is too much horizontal dispersion in the model. Cluster analysis of the radar wind profiler data showed that there were complex channeling flows around the Sierra de Guadalupe, the hill between T0 and T1 that rises to 3000 m MSL (de Foy et al., 2008). The column measurements suggest that the plume was constrained to the western side of the hill as it moved northwards, turning to the east afterwards. The hill is only represented by 9 cells in WRF with a lower maximum height of 2640 m MSL. Rather than being channeled, the numerical plume was able to spread out leading to a much broader signature in the numerical columns. Past simulations of the industrial plume from the Tula refinery during MCMA-2003 likewise found excess dispersion at the Sierra de Guadalupe hill (de Foy et al., 2007). In addition, the relative coarse output time frequency (1 h) and the grid resolution (3 km) might help the spread out of the plume. This dataset provides a test case that could be used to evaluate the impact of increased horizontal and vertical resolution or the impact of modified model configurations on numerical dispersion in complex terrain using WRF and CAMx.

There is also a noticeable difference in the spatial and temporal distribution of the simulated HCHO and NO₂ columns, which probably reflects the difference in the sources of HCHO and NO₂. The NO₂ column is originated from the emissions undergoing the NO_y interconversion, but HCHO is attributed to both emissions and photochemical production. The dispersion and transport can smooth and spread out the secondary HCHO plume to a larger extent when the plume moves over a complex terrain, such as the Sierra de Guadalupe hill in this case.

The collected spectra have also been evaluated for O₄ both in the UV and the visible wavelength range and neither of the ranges shows differential O₄ columns above the detection limit and thus no obvious elongation of the optical path length due to radiative transport (Johansson et al., 2008; Wagner et al., 2004).

4 Conclusions

We have in this paper presented the method and the results of the first detection of formaldehyde using a mobile mini-DOAS instrument. The mobile-DOAS technique allows for efficient large scale monitoring of the distribution of air pollutants, its inherent ability to vertically integrate concentrations makes it an efficient tool for measuring fluxes. The pre-

sent measurement was made on 10 March 2006 in Mexico City, during the MILAGRO field campaign.

The measurement resulted in an estimation of the instantaneous outflow of NO₂ and HCHO from the entire MCMA. These fluxes have been compared to modeled columns using the CAMx model. The total outflow fluxes of NO₂ and HCHO show a reasonable agreement between the measurement and simulation, but the simulated plume is more spread out, and the location traversed by the instrument is shifted due to excessive numerical dispersion in a complex terrain, insufficient temporal and spatial resolution used in the model. This study provides a test case for evaluating the impact of increased horizontal and vertical resolution or the impact of modified model configurations on numerical dispersion in complex terrain.

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References

- Atkinson, R.: Atmospheric chemistry of VOCs and NO_x, *Atmos. Environ.*, 34, 2063–2101, 2000.
- Baez, A., Padilla, H., Garcia, R., Torres, M., Rosas, I., and Belmont, R.: Carbonyl levels in indoor and outdoor air in Mexico City and Xalapa, Mexico., *Sci. Total Environ.*, 302, 211–226, 2003.
- Baez, A. P., Belmont, R., and Padilla, H.: Measurements of formaldehyde and acetaldehyde in the atmosphere of Mexico City., *Environ. Pollut.*, 89, 163–167, 1995.
- Baez, A. P., Padilla, H., Garcia, R., Belmont, R., and Torres, M.: Measurement of indoor-outdoor carbonyls at four residential homes in Mexico City Metropolitan Area, *Int. J. Environ. Pollut.*, 26, 90–105, 2006.
- Bogumil, K., Orphal, J., Homann, T., Voigt, S., Spietz, P., Fleischmann, O. P., Vogel, A., Hartmann, M., Bovensmann, H., Frerik, J., and Burrows, J. P.: Measurements of Molecular Absorption Spectra with the SCIAMACHY PreFlight Model: Instrument Characterization and Reference Data for Atmospheric Remote-Sensing in the 230–2380 nm Region, *J. Photoch. Photobio. A*, 157, 167–184, 2003.
- Burrows, J. P., Richter, A., Dehn, A., Deters, B., Himmelmann, S., Voigt, S., and Orphal, J.: Atmospheric remote sensing reference data from GOME: 2. Temperature dependent absorption cross sections of O₃ in the 231–794 nm range, *J. Quant. Spectrosc. Ra.*, 61, 509–517, 1999.
- de Foy, B., Molina, L. T., and Molina, M. J.: Satellite-derived land surface parameters for mesoscale modelling of the Mexico City basin, *Atmos. Chem. Phys.*, 6, 1315–1330, 2006, <http://www.atmos-chem-phys.net/6/1315/2006/>.
- de Foy, B., Lei, W., Zavala, M., Volkamer, R., Samuelsson, J., Melqvist, J., Galle, B., Martínez, A.-P., Grutter, M., Retama, A., and Molina, L. T.: Modelling constraints on the emission inventory

- and on vertical dispersion for CO and SO₂ in the Mexico City Metropolitan Area using Solar FTIR and zenith sky UV spectroscopy, *Atmos. Chem. Phys.*, 7, 781–801, 2007, <http://www.atmos-chem-phys.net/7/781/2007/>.
- de Foy, B., Fast, J. D., Paech, S. J., Phillips, D., Walters, J. T., Coulter, R. L., Martin, T. J., Pekour, M. S., Shaw, W. J., Kasten-deuch, P. P., Marley, N. A., Retama, A., and Molina, L. T.: Basin-scale wind transport during the MILAGRO field campaign and comparison to climatology using cluster analysis, *Atmos. Chem. Phys.*, 8, 1209–1224, 2008, <http://www.atmos-chem-phys.net/8/1209/2008/>.
- de Foy, B., Zavala, M., Bei, N., and Molina, L. T.: Evaluation of WRF mesoscale simulations and particle trajectory analysis for the MILAGRO field campaign, *Atmos. Chem. Phys.*, 9, 4419–4438, 2009, <http://www.atmos-chem-phys.net/9/4419/2009/>.
- DOASIS ver 3.2.2734.: Programmed by Kraus, S., available at: <http://www.iup.uni-heidelberg.de/bugtracker/projects/doasis/>, 2005.
- Doran, J. C., Barnard, J. C., Arnott, W. P., Cary, R., Coulter, R., Fast, J. D., Kassianov, E. I., Kleinman, L., Laulainen, N. S., Martin, T., Paredes-Miranda, G., Pekour, M. S., Shaw, W. J., Smith, D. F., Springston, S. R., and Yu, X.-Y.: The T1-T2 study: evolution of aerosol properties downwind of Mexico City, *Atmos. Chem. Phys.*, 7, 1585–1598, 2007, <http://www.atmos-chem-phys.net/7/1585/2007/>.
- Comprehensive Air Quality Model with Extensions (CAMx) ver 4.5.: Programmed by Environ International Corporation, www.camx.com, 2008.
- Fast, J. D., de Foy, B., Acevedo Rosas, F., Caetano, E., Carmichael, G., Emmons, L., McKenna, D., Mena, M., Skamarock, W., Tie, X., Coulter, R. L., Barnard, J. C., Wiedinmyer, C., and Madronich, S.: A meteorological overview of the MILAGRO field campaigns, *Atmos. Chem. Phys.*, 7, 2233–2257, 2007, <http://www.atmos-chem-phys.net/7/2233/2007/>.
- Finlayson-Pitts, B. J. and Pitts, J. N.: *Chemistry of the Upper and Lower Atmosphere: Theory, Experiments, and Applications*, 1999.
- Galle, B., Oppenheimer, C., Geyer, A., McGonigle, A. J. S., Edmonds, M., and Horrocks, L.: A miniaturised ultraviolet spectrometer for remote sensing of SO₂ fluxes: A new tool for volcano surveillance, *J. Volcanol. Geoth. Res.*, 119, 241–254, 2002.
- García, A. R., Volkamer, R., Molina, L. T., Molina, M. J., Samuelson, J., Mellqvist, J., Galle, B., Herndon, S. C., and Kolb, C. E.: Separation of emitted and photochemical formaldehyde in Mexico City using a statistical analysis and a new pair of gas-phase tracers, *Atmos. Chem. Phys.*, 6, 4545–4557, 2006, <http://www.atmos-chem-phys.net/6/4545/2006/>.
- Grutter, M., Flores, E., Andraca-Ayala, G., and Baez, A.: Formaldehyde levels in downtown Mexico City during 2003, *Atmos. Environ.*, 39, 1027–1034, 2005.
- Hak, C., Pundt, I., Trick, S., Kern, C., Platt, U., Dommen, J., Ordóñez, C., Prévôt, A. S. H., Junkermann, W., Astorga-Lloréns, C., Larsen, B. R., Mellqvist, J., Strandberg, A., Yu, Y., Galle, B., Kleffmann, J., Lörzer, J. C., Braathen, G. O., and Volkamer, R.: Intercomparison of four different in-situ techniques for ambient formaldehyde measurements in urban air, *Atmos. Chem. Phys.*, 5, 2881–2900, 2005, <http://www.atmos-chem-phys.net/5/2881/2005/>.
- Hauptmann, M., Lubin, J. H., Stewart, P. A., Hayes, R. B., and Blair, A.: Mortality from lymphohematopoietic malignancies among workers in formaldehyde industries, *J. Natl. Cancer I.*, 95, 1615–1623, 2003.
- Heckel, A., Richter, A., Tarsu, T., Wittrock, F., Hak, C., Pundt, I., Junkermann, W., and Burrows, J. P.: MAX-DOAS measurements of formaldehyde in the Po-Valley, *Atmos. Chem. Phys.*, 5, 909–918, 2005, <http://www.atmos-chem-phys.net/5/909/2005/>.
- Hermans, C., Vandaele, A. C., Carleer, M., Fally, S., Colin, R., Jenouvrier, A., Coquart, B., and Mérienne, M.-F.: Absorption cross-sections of atmospheric constituents: NO₂, O₂, and H₂O, *Environ. Sci. Pollut. R.*, 6, 151–158, 1999.
- Johansson, M., Galle, B., Yu, T., Tang, L., Chen, D., Li, H., Li, J. X., and Zhang, Y.: Quantification of total emission of air pollutants from Beijing using mobile mini-DOAS, *Atmos. Environ.*, 42, 6926–6933, 2008.
- Lei, W., de Foy, B., Zavala, M., Volkamer, R., and Molina, L. T.: Characterizing ozone production in the Mexico City Metropolitan Area: a case study using a chemical transport model, *Atmos. Chem. Phys.*, 7, 1347–1366, 2007, <http://www.atmos-chem-phys.net/7/1347/2007/>.
- Lei, W., Zavala, M., de Foy, B., Volkamer, R., and Molina, L. T.: Characterizing ozone production and response under different meteorological conditions in Mexico City, *Atmos. Chem. Phys.*, 8, 7571–7581, 2008, <http://www.atmos-chem-phys.net/8/7571/2008/>.
- Lei, W., Zavala, M., de Foy, B., Volkamer, R., Molina, M. J., and Molina, L. T.: Impact of primary formaldehyde on air pollution in the Mexico City Metropolitan Area, *Atmos. Chem. Phys.*, 9, 2607–2618, 2009, <http://www.atmos-chem-phys.net/9/2607/2009/>.
- Madronich, S.: Chemical evolution of gaseous air pollutants downwind of tropical megacities: Mexico City case study, *Atmos. Environ.*, 40, 6012–6018, 2006.
- Meller, R. and Moortgat, G. K.: Temperature dependence of the absorption cross sections of formaldehyde between 223 and 323 K in the wavelength range 225–375 nm, *J. Geophys. Res.*, 105, 7089–7101, 2000.
- Molina, L. T. and Molina, M. J.: *Air Quality in the Mexico Megacity*, Kluwer Academic Publishers, Dordrecht, The Netherlands, 384 pp., 2002.
- Molina, L. T., Madronich, S., Gaffney, J., et al.: Overview of the 2006 MILAGRO Campaign in Mexico City: Transport and Transformation of Emissions from a Megacity, *Atmos. Chem. Phys. Discuss.*, in preparation, 2009.
- Molina, L. T., Kolb, C. E., de Foy, B., Lamb, B. K., Brune, W. H., Jimenez, J. L., Ramos-Villegas, R., Sarmiento, J., Paramo-Figueroa, V. H., Cardenas, B., Gutierrez-Avedoy, V., and Molina, M. J.: Air quality in North America's most populous city – overview of the MCMA-2003 campaign, *Atmos. Chem. Phys.*, 7, 2447–2473, 2007, <http://www.atmos-chem-phys.net/7/2447/2007/>.
- Platt, U., Perner, D., and Pätz, H. W.: Simultaneous Measurement of Atmospheric CH₂O, O₃ and NO₂ by Differential Optical Absorption, *J. Geophys. Res.*, 84, 6329–6335, 1979.
- Shiohara, N., Fernandez-Bremauntz, A. A., Blanco-Jimenez, S., and Yanagisawa, Y.: The commuters' exposure to volatile chemicals and carcinogenic risk in Mexico City, *Atmos. Environ.*, 39, 3481–3489, 2005.

- Song, J., Lei, W., Molina, L. T., et al.: Ozone response to emissions changes: A case study from the MILAGRO campaign, *Atmos. Chem. Phys. Discuss.*, in preparation, 2009.
- Wagner, T., Dix, B., Friedeburg, C. V., Frieß, U., Sanghavi, S., Sinreich, R., and Platt, U.: MAX-DOAS O₄ measurements: A new technique to derive information on atmospheric aerosols – Principles and information content, *J. Geophys. Res.-Atmos.*, 109, 1–19, 2004.
- Van Roozendaal, M. and Fayt, C.: WinDOAS 2.1 Software User Manual, BIRA-IASB, 2001.
- Vandaele, A. C., Hermans, C., Simon, P. C., Carleer, M., Colin, R., Fally, S., Merienne, M. F., Jenouvrier, A., and Coquart, B.: Measurements of the NO₂ absorption cross-section from 42 000 cm⁻¹ to 10 000 cm⁻¹ (238–1000 nm) at 220 K and 294 K, *Atmos. Spec. Appl., J. Quant. Spectrosc. Ra.*, 96, 59, 171–184, 1998.
- Vaughan, T. L., Strader, C., Davis, S., and Daling, J. R.: Formaldehyde and Cancers of the Pharynx, Sinus and Nasal Cavity. 1. Occupational Exposures, *Int. J. Cancer*, 38, 677–683, 1986.
- Vaughan, T. L., Strader, C., Davis, S., and Daling, J. R.: Formaldehyde and Cancers of the Pharynx, Sinus and Nasal Cavity. 2. Residential Exposures, *Int. J. Cancer*, 38, 685–688, 1986.
- Volkamer, R., Molina, L. T., Molina, M. J., Shirley, T., and Brune, W. H.: DOAS measurement of glyoxal as an indicator for fast VOC chemistry in urban air, *Geophys. Res. Lett.*, 32, L08806, doi:10.1029/2005GL022616, 2005.