Cal-Mex 2010 Field Campaign:
US-Mexico Collaborative Project in the
California-Mexico Border Region

Synthesis Report and Policy Implications

Prepared by the

Molina Center for Energy and the Environment

and the

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PREFACE

Cal-Mex 2010 Field Study is a US-Mexico collaborative project to characterize the sources of primary and secondary particulate matter and precursor gases in the California-Mexico border region, their transport and transformation, and the impact of these pollutants on regional air quality and climate.

This synthesis report is prepared by the Molina Center for Energy and the Environment with the collaboration of the University of California San Diego/Scripps Institution of Oceanography, Texas A&M University, Virginia Tech, San Diego State University, Centro de Ciencias de la Atmosféra from Universidad Nacional Autónoma de México, Instituto Nacional de Ecología y Cambio Climatíco, Centro de Investigaciones Químicas from Universidad Autónoma del Estado de Morelos, Universidad Autónoma de Baja California, and Universidad Tecnológica de Tijuana.

The measurement campaign was sponsored by the National Science Foundation, US Environmental Protection Agency, California Air Resources Board, Molina Center for Energy and the Environment, the Mexican Ministry of the Environment and the National Institute of Ecology and Climate Change, with support from the Government of the State of Baja California and the City of Tijuana, as well as local institutions hosting various monitoring sites, including: Sistema de Parques Temáticos de Tijuana, Colegio de Estudios Científicos y Tecnológicos, from the Universidad Tecnológica de Tijuana, Hunter Industry and Formosa Prosonic. We would also like to thank Jesús Lima from Tijuana Customs Office.

Additional information related to the measurements plan, logistics, descriptions of measurement sites, presentations of scientific meetings, and education and outreach programs is available on the website of the Molina Center: http://www.mce2.org.

1. INTRODUCCION

Cal-Mex 2010 Field Study is a US-Mexico collaborative project to characterize the sources of primary and secondary particulate matter and precursor gases in the California-Mexico border region, their transport and transformation, and the impact of these pollutants on regional air quality and climate. This objective has been pursued by performing several tasks, which include defining science questions and setting measurement strategies for the campaign, executing measurement plans, analyzing measurements obtained, developing emissions and meteorological input data needed for modeling studies, and evaluating the data using meteorological and photochemical models.

Trans-boundary air pollution across US and Mexico has become a growing concern due to increased commercial and industrial activities in the border region [Border 2012; US EPA 2011]. California and Baja California share two common air basins along the ~200 km border separated by the Sierra de Baja California (Figure 1). The economic activities in this region are heavily influenced by the US-Mexico binational trade and commerce that occurs mainly through the borders of San Diego–Tijuana and Calexico–Mexicali, two of the sister city pairs [Border 2012]. The industrial sector is largely concentrated in the Mexican side and has a strong share of medium to high production levels of multi-national plants (*maquiladoras*). A large number of light-duty and heavy-duty vehicles cross daily back-and-forth between the border cities, emitting pollutants into a shared air basin. While gasoline-powered vehicles are large emitters of VOCs, the high fraction of diesel-powered vehicles in this region can substantially contribute to emissions of NO_x and soot. Burning of waste also contributes to emissions in the area. In addition, agriculture is a major economic activity in the border areas (particularly in California). The border area is also prone to significant soil erosion due to its geological soil composition and predominant meteorological conditions that are favorable for dust resuspension.

Figure 1. Geographical location of the two pairs of sisters cities of San Diego-Tijuana and Calexico- Mexicali.

The intensive Cal-Mex 2010 field measurements took place during May 15-June 30, 2010 along the San Diego-Tijuana border region and involved the participation of about 100 investigators, technicians and students representing about 20 institutions from Mexico and the US. These include the Molina Center for Energy and the Environment (MCE2), University of California San Diego/Scripps Institution of Oceanography (UCSD/SIO), Texas A&M University (TAMU), Virginia Tech (VT), Centro de Ciencias de la Atmosféra from Universidad Nacional Autónoma de México (CCA-UNAM), Instituto Nacional de Ecología y Cambio Climatíco (INECC), Centro de Investigaciones Químicas from Universidad Autónoma del Estado de Morelos (CIQ-UAEM), Universidad Autónoma de Baja California (UABC), Universidad Tecnológica de Tijuana (UTT), and San Diego State University (SDSU). The measurement campaign was sponsored by the National Science Foundation (NSF), US Environmental Protection Agency (EPA), California Air Resources Board (CARB), Molina Center for Energy and the Environment (MCE2), the Mexican Ministry of the Environment (SEMARNAT) and the National Institute of Ecology (INE), with support from the Government of the State of Baja California and the City of Tijuana, as well as local institutions hosting various monitoring sites.

The Cal-Mex 2010 measurements phase has generated extensive data sets for trace gases and fine particles in the San Diego-Tijuana region, as well as meteorological parameters. Furthermore, the field study was planned to coincide with the much larger CalNex 2010 field study sponsored by the California Air Resources Board, the National Oceanic and Atmospheric Administration and the California Energy Commission to study the atmospheric processes over California and the eastern Pacific coastal region http://www.arb.ca.gov/research/calnex2010/calnex2010.htm. Thus, in addition to the data obtained from the measurements taken along the California-Mexico border, there are complementary datasets from the larger CalNex study [Ryerson et al., 2013].

This report describes the measurements and the results obtained to date during the Cal-Mex 2010 field study. A summary of the key findings and policy implications, as well as suggestion for future research are presented. Several results from this collaborative project have already been instrumental for the formulation of the new air quality management program (PROAIRE in Spanish) recently published for the border city of Tijuana [GobBC, 2013]. Additional detailed information on the measurement techniques, instrumentations, and methodologies employed during the field campaign and subsequent analyses can be found at the Molina Center website: http://mce2.org/en/activities/cal-mex-2010.

2. PROJECT SCOPE

The major goal of the project is to assess the sources and processing of air pollutants in the California-Mexico border region and their effects on regional air quality and climate in order to

provide scientific information to decision makers of both nations when addressing these two inter-related issues.

Specific objectives were:

- To characterize the emissions from major sources in the California-Mexico border regions;
- To determine the spatial and temporal variability in anthropogenic emissions ;
- To elucidate the transport and transformation of these emissions and assess their impacts on local and regional air quality and climate.

Our collaborative team has pursued these objectives through four main tasks:

1) Define science questions and set measurement strategies for Cal-Mex 2010 campaign;
2) Execute measurement plan; collect and archive measurement data;
3) Quality-assure data sets and perform preliminary analysis;
4) Evaluate data using meteorological and photochemical models.

Planning for the Cal-Mex 2010 field study

The initial phase of the campaign was to conduct measurements of air pollutants, comprising a central fixed site that housed state-of-the art instruments contributed by US and Mexican participants to quantify a wide range of gaseous and fine aerosol chemical species, as well as meteorological parameters; several downwind sites to measure criteria pollutants and meteorological parameters; and mobile vans circulating in various locations.

The Molina Center, with support from Administración Ambiental Integral (AAI), coordinated various meetings and site visits prior to the campaign and provided local logistical support in terms of space, infrastructure and electrical installations necessary for the appropriate and optimal operation of equipment on site requested by the investigators as well as administrative support. Collaboration with officials and researchers from the Mexican government agencies and local institutions was instrumental in the success of the field campaign. These officials and agencies provided logistical support, including access to the monitoring sites and preparing the required documents to ship the equipment to and from Mexico.

Site selection

In preparation for the field measurements campaign, an extensive analysis of long-term meteorological and criteria pollutants data in the Cal-Mex border region was performed by the Molina Center modeling team to determine the predominant wind and pollutant hourly patterns during May-June in the border region. The results of the analysis supported the selection of measurement sites on the basis of source-receptor criteria. Security and accessibility to infrastructure and services were also considered. The selected central site (Parque Morelos)

housed state-of-the art instruments contributed by US and Mexican participants to quantify a wide range of gaseous and fine aerosol properties and chemical species, as well as meteorological parameters. Six additional sites (Metales y Derivados, CECYTE, UTT, UABC-VP, Hunter, and Formosa Prosonic) were selected to deploy instruments for measuring criteria pollutants and meteorological parameters (Figure 2). Additional measurement platforms included a mobile laboratory for atmospheric measurement of emissions deployed at various sites, and mobile mini-DOAS instruments mounted on a private vehicle for measuring vertical columns of key species.

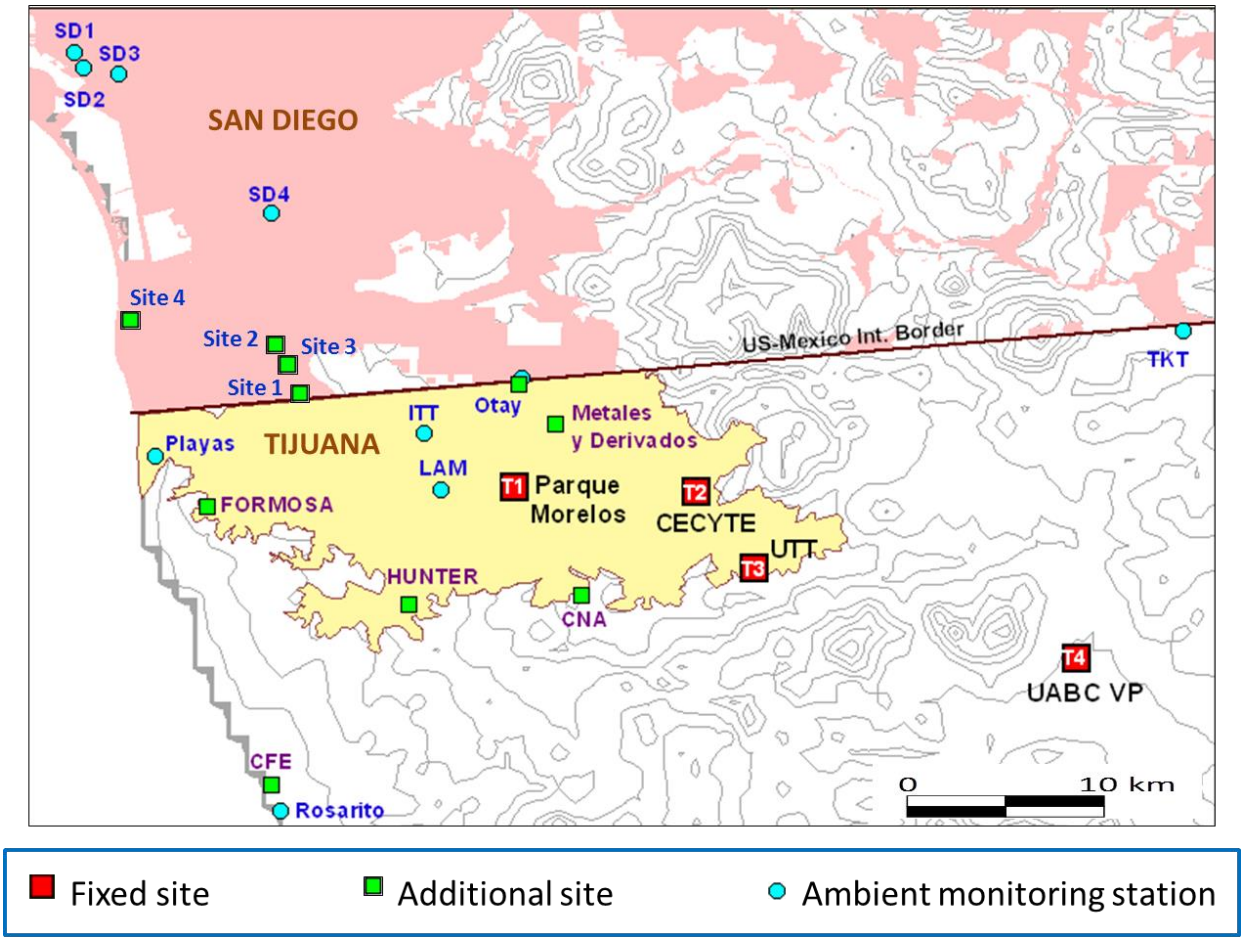


Figure 2. Monitoring sites during Cal-Mex 2010 Field Campaign. Fixed sites T1-T4 refer to locations with permanent instrumentation during the campaign whereas additional sites correspond to locations in which measurements were obtained for shorter specific periods during the campaign. Sites 1-4 in California correspond to black carbon and PM2.5 monitoring sites as described in Quintana et al., 2013. Ambient monitoring stations refer to government-maintained local monitoring networks in California and Baja California.

Instrumentation

During the campaign a suite of trace gases, particles, and meteorological parameters were measured at various sites using complementary techniques (see Tables 1 and 2). An extensive data set in the San Diego-Tijuana region was obtained, including the characterization of emission fluxes of trace gases and fine particles, highly time-resolved ambient fine particle (primary and secondary) chemical composition, size distributions, mass loadings, and ambient concentrations of secondary aerosol precursor gases. Meteorological vertical profile measurements were obtained during the field study using radiosondes and a tethered balloon launched 2-3 times daily, a ceilometer (for estimation of planetary boundary layer heights, PBL) at Parque Morelos and meteorological stations located at various sites measuring winds, pressure, temperature, and humidity. Additional meteorological data during the field study was obtained from the monitoring stations from the local ambient monitoring networks.

Emissions inventory and additional data

Additional data considered in the analysis include the official 2005 emissions inventories for Tijuana, Mexicali, and California [LT consulting, 2010; ERG, 2009; CARB 2012], previous measurements of black carbon obtained at various sites in Tijuana and San Ysidro by SDSU and UABC, as well as available historical records of O_3, NO_x, PM10, CO, SO_2 and meteorological data from the local monitoring stations in Tijuana, Tecate, Rosarito, Mexicali, and California from the Secretaria de Protección al Ambiente (SPA) and EPA-Air Quality System (EPA-AQS).

The conversion of the Mexican emissions inventories into model-ready datasets involved the development of a Geographical Information System platform for the creation of the spatial distributions, the temporal emissions distributions, as well as the chemical speciation of VOCs and PM for individual sources. The resulting emissions inventory has a 2-km spatial resolution for gaseous and PM pollutants and is compatible with the SAPRC99 chemical mechanism. The development of a model-ready emissions inventory and its implementation in air quality models allow further evaluating and improving the official emissions estimates in the California-Baja California border region.

Data evaluation

Analyses of the data obtained during the Cal-Mex 2010 field study have included an assessment of the diurnal and nocturnal pollutant profiles, the characterization of high pollution events, and the description and modeling of particular pollution transport events. These analyses help in characterizing the local and regional emission sources of photochemical precursors. Four science team meetings were organized to evaluate and inter-compare several pollutants measured simultaneously at different monitoring locations, to present and discuss preliminary results obtained by the US and Mexican participants during the field measurements and to prepare manuscripts for publication. Several manuscripts have been published in the special issue on US-

Mexico Border Studies in Atmospheric Environment (Volume 70, May 2013); additional manuscripts have been submitted to the special issue or are under preparation.

Measurements obtained from the intensive field campaign are used in the evaluation of air quality models in the region. State-of-the-art meteorological and photochemical models have been applied to better understand the impacts of atmospheric pollutants in the US-Mexico border region. These activities are based on the development of a model-ready version of the official emissions inventories for Tijuana and Mexicali.

In the following sections, we present a summary of the results obtained by the various research groups participating in Cal-Mex 2010, suggestions for future research and policy implications.

3. RESULTS

3.1. Meteorology and dynamics

During the field study, extensive meteorological measurements at the Parque Morelos were performed by the UNAM and MCE2 teams with the help of local students. An ozonesonde, attached to a tethered balloon, was launched three times a day from May 23 to June 30 (at 08:00, 12:00 and 17:00) to obtain vertical profiles of ozone. Radiosondes were launched two to three times daily to measure the vertical profiles of pressure, temperature, humidity, wind speed and wind direction. A ceilometer was co-located at the park.

The surface and vertical meteorological measurements obtained during the field study have been used to examine the synoptic situations and prevailing winds in the California-Mexico border region, to evaluate the model forecasts during the campaign, and to study the transport dynamics at the regional scale [Bei et al., 2013a].

Daily meteorological forecasts were performed by the MCE2 modeling team to support the Cal-Mex 2010 field campaign during the period from May 15 to June 30 using the Advanced Research WRF (ARW) model and were posted on the MCE2/Cal-Mex website. Hourly forecasts were produced daily, including upper levels and surface wind, temperature, and 1-h precipitation forecasts at regional scales. The WRF model forecasts obtained during Cal-Mex 2010 agree well with NCEP GFS reanalysis data at both surface and upper-level. The simulated soundings were also consistent with the radiosonde data at Tijuana in general, allowing the use of the meteorological data for plume transport analyses. The major findings are summarized below:

1) The complex topography in Southern California and Baja California and varied land use types together with the location and intensity of the North Pacific High Pressure Center determine the dry (April-September) and wet (October-March) seasons. During the dry

season, winds blow steadily along shore from the northwest, and the large-scale sinking motion almost completely suppresses precipitation. During the wet season, "common northwesterly", "onshore", and "Santa Ana" regimes are predominant. Land-sea breeze flows can be vigorous, especially during the spring and summer seasons.

2) Daily meteorological forecasts of upper levels and surface wind, temperature, and 1-h precipitation forecasts at regional scales were performed to support the Cal-Mex 2010 activities from May 15 to June 30 using the Advanced Research WRF (ARW) model. Both synoptic-scale and urban-scale forecasts (including wind, temperature, and humidity) agree reasonably well with the National Centers for Environmental Prediction (NCEP) and Global Forecast System (GFS) reanalysis data and the measurements; however, the WRF model frequently underestimates surface temperature and planetary boundary layer (PBL) height during nighttime compared to measurements.

3) The border area is mostly located in the low-pressure area at the surface and in the front of a trough in the upper level. The prevailing wind directions along the coastal area are mainly southwest to northwest during the daytime (9 to 17 PDT). The dominant wind varies at nighttime and early morning (21 PDT to 5 PDT the following day).

4) Radiosonde data obtained in Tijuana have been compared with measurements in San Diego obtained by the US National Weather Service during the field study. Although there is 2-hour difference in the launching time, both temperature and wind profiles from Tijuana and San Diego agree reasonably well. The simulated soundings were also consistent with the observed radiosonde data especially at the low-level wind fields, which are important for the transport of pollutants, allowing the use of the meteorological data for plume transport analyses.

5) Good agreement was observed for mixing layer heights (typical daily averages 500-750 m) obtained with soundings and from backscattering measurements from the ceilometer at Parque Morelos. The maximum PBL height mostly occurred from 12 to 3PM, varying from 300 to 1500 meters.

6) The tethered balloon data at Parque Morelos shows that the wind, temperature, and moisture characteristics below 800 m depend on the plume transport category, i.e., cool and dry, warm and dry, and warm and wet air correspond to the plume-southeast, plume-southwest, and plume-east categories, respectively, which are consistent with their synoptic conditions.

7) Based on the WRF-FLEXPART simulations with particles released in Tijuana in the morning, four representative plume transport patterns (Figure 3) were identified as "plume-southeast", "plume-southwest", "plume-east" and "plume-north", indicating the downwind

direction of the plume; this is useful for linking meteorological conditions with observed changes in trace gases and particular matter.

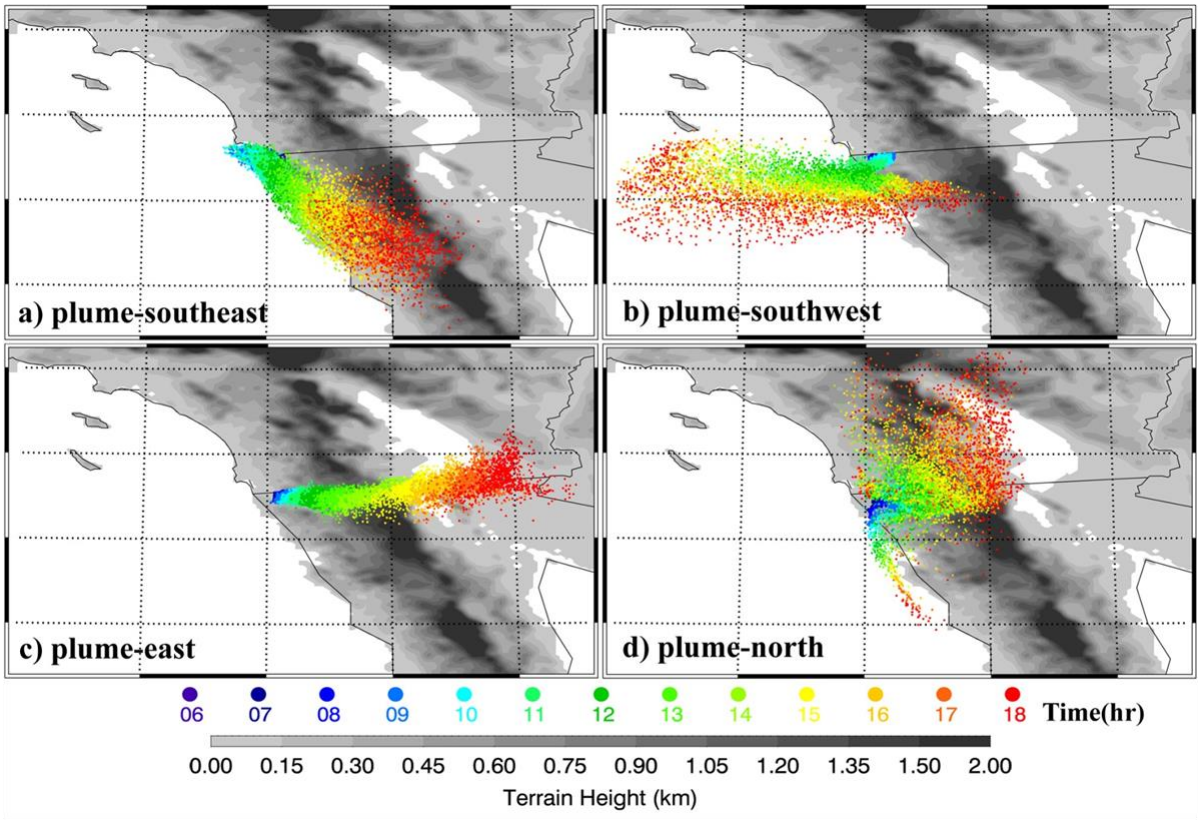


Figure 3. Four plume transport patterns (plume-southeast, plume-southwest, plume-east, and plume-north) identified during the Cal-Mex 2010 campaign [Source: Bei et al., 2013a]

8) Most of the days are classified as "plume-east" and "plume-southeast" during the campaign period, indicating that the plumes originated in Tijuana were mostly carried to the southeast and east of Tijuana during the daytime.

9) The plume transport direction was mostly determined by the low level (700 to 900 hPa) wind directions except for a few days, in which the plume transport directions are consistent with the surface wind in the border area because the weather system at the surface is much stronger. During the nighttime, the plumes start to move toward the coastline instead of inland due to the increasing land breeze.

10) Meteorological uncertainties have significant influences on O_3 and aerosol simulations, especially for nitrate and ammonia (Bei et al., 2013b). Data assimilation techniques can improve the air quality simulations.

3.2. Criteria Gases

1) Criteria pollutant average concentrations were relatively low during most of the field study, although short-term spikes in the concentrations of primary pollutants were common. Daily average NO_x concentrations ranged from 17.6 to 27.2 ppb among the various sites, whereas daily CO concentrations ranged from 0.25 to1.5 ppm. Both pollutants showed marked diurnal profiles consistent with daily anthropogenic activities and PBL development.

2) Analyses from time series trends show that carbon monoxide dropped substantially in the past few years in both San Diego and Tijuana, whereas O_3, SO_2, and NO_2 show much smaller reduction rates (see Figures 4 and 5). SO_2 has decreased significantly in Tijuana starting in 2003 after the introduction of natural gas in the power plant in Rosarito.

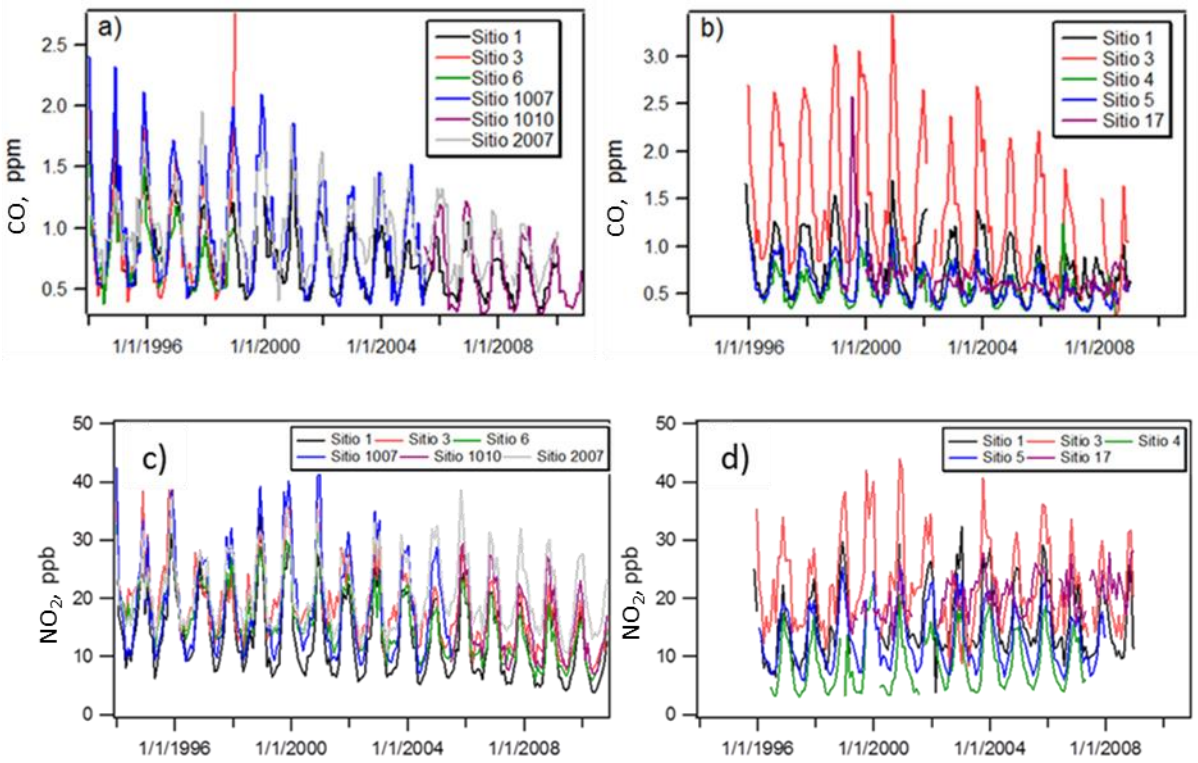


Figure 4. Monthly average concentrations of CO and NO_2 from monitoring stations in San Diego (plots a and c, respectively) and Tijuana (plots b and d, respectively). Sites IDs correspond to the site identification numbers used in the EPA-AQS.

3) Surface-atmosphere exchange fluxes of NO_x and CO_2were measured via eddy covariance at three locations in Tijuana and San Diego [Klapmeyer et al., 2013]. This effort produced a novel data set of NO_x fluxes, which have not previously been measured extensively in an

urban area. Weekday (8:30-18:30) NO_x fluxes averaged 1.8 μg m^{-2} s^{-1} across three sites. Fluxes did not exhibit regular diurnal patterns. Observed fluxes of NO_x were 1.4-17 times higher than those in the emission inventory, and observed fluxes of CO_2 were similar to those in a greenhouse gas emission inventory for the state of Baja California. NO_x fluxes estimated using column measurements from the mini-DOAS were also much higher than those derived from emissions inventories, suggesting the need for further investigation into their uncertainties [Rivera et al., 2013].

4) The observed ambient CO/NO_x ratio shows relatively good agreement with the emissions inventory [Klapmeyer et al., 2013]. In addition, comparison between simulated and observed concentrations of CO and NO_x for the limited number of days show good agreement.

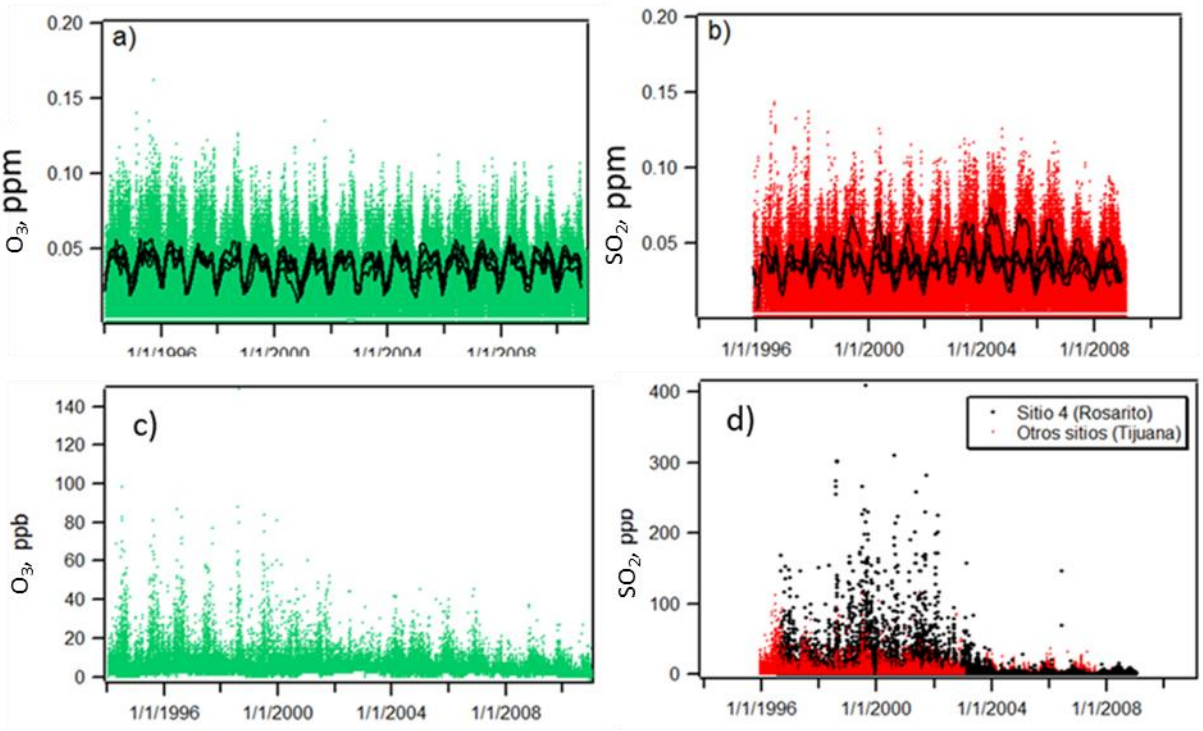


Figure 5. Hourly concentrations of O_3 and SO_2 from monitoring stations in San Diego (plots a and c, respectively) and Tijuana (plots b and d, respectively). Black lines in the ozone panels show the monthly average concentrations from diurnal periods (6-18 h LT).

5) SO_2 levels observed from the local monitoring stations and Parque Morelos were low in general during the campaign, in agreement with the vertical column SO_2 measurements obtained with the mini-DOAS. SO_2 levels at Rosarito were higher than at La Mesa, especially during nighttime, suggesting the need to investigate nighttime combustion emissions.

Ozone

During the Cal-Mex 2010 field campaign, ozone was measured at Parque Morelos, UTT and UABC-Tijuana.

1) Daily average ozone concentrations ranged from 23 to 41 ppb during the field study at various sites in Tijuana and were consistent with the levels measured at the local air quality monitoring stations. Comparison of the spatial variability of ozone concentrations, O_3/NO_y ratio, and wind data shows the effect of wind transport towards the east-southeast direction in the basin, impacting the spatial location and timing of the ozone peak.

2) Comparison of the ozone levels among the monitoring stations in the San Diego-Tijuana Air Basin shows that ozone concentrations are higher in stations at high altitude. For sites above 500 m, the peak ozone concentrations are frequently over 60 ppb.

3) The vertical profiles of ozone obtained at Parque Morelos generally showed the presence of an accumulation layer at about 400 m, indicating the presence of a stable inversion during morning. In addition, the profiles also indicated a strong influence of the wind's vertical structure on ozone concentrations. The WRF-CHEM model reproduces the observed ozone profile at Parque Morelos with a high ozone level aloft trapped within a static upper inversion layer between 500 and 1000 m. The ozone and its precursors trapped in the inversion layer have potential to facilitate the ozone formation at the inland foothills San Diego-Tijuana Air Basin within the inversion layer. The model results also show that the high ozone concentrations over mountain regions over 500 m are principally formed locally from the transported precursors emitted in the coastal regions and biogenic emissions, perhaps together with the pollutants fumigated from the inversion layer.

4) The WRF-CHEM model performs generally well in simulating ozone spatial distributions and temporal variations when comparing to monitoring stations in the San Diego-Tijuana Air Basin (Li et al., 2013). Sensitivity studies show that the biogenic emissions contribute to high ozone levels in the mountain area when anthropogenic precursors emitted along the coastal region are transported to and mixed with local biogenic emissions in the mountain area.

5) A factor separation analysis used to evaluate the contribution of trans-boundary emission transport to O_3 in the border region shows that in general the anthropogenic emissions from California contribute more to levels of O_3 than those from the Baja California in the border region, and the interaction of the trans-boundary transport of emissions between California and Baja California reduces the afternoon surface O_3 by 2-4 ppb in the border region on average. The impacts of the interactions of emissions from both parts on the O_3 formation in the border region are dependent on the meteorological conditions.

6) Figure 6 shows the pattern comparison of simulated vs. observed near-surface O_3 at 1400 LT during the four selected episodes, including 1) May 16-17 (plume north), 2) May 29-30 (plume southwest), 3) June 4-5 (plume east), and 4) June 13-14 (plume southeast). Generally, the predicted O_3 spatial patterns are consistent well with the observations at the ambient monitoring sites in the San Diego-Tijuana region during the four episodes. The model successfully reproduces the observed increasing O_3 concentrations from the coast to the mountain area, but the model tends to overestimate the observation in the coastal region sometimes. The high O_3 levels are primarily formed over the mountain area where the on-shore westerly winds encounter the inland easterly winds. The most polluted event occurs on June 4 and 5 (plume east), with the maximal O_3 concentration exceeding 100 ppb over the mountain area. In the Calexico-Mexicali region, the WRF-CHEM model only performs well in simulating the O_3 distribution during the plume north and east episodes. During the plume southwest and southeast episodes, the model substantially underestimates the observed O_3 concentrations, which is primarily caused by the simulated strong divergence in the morning in the region.

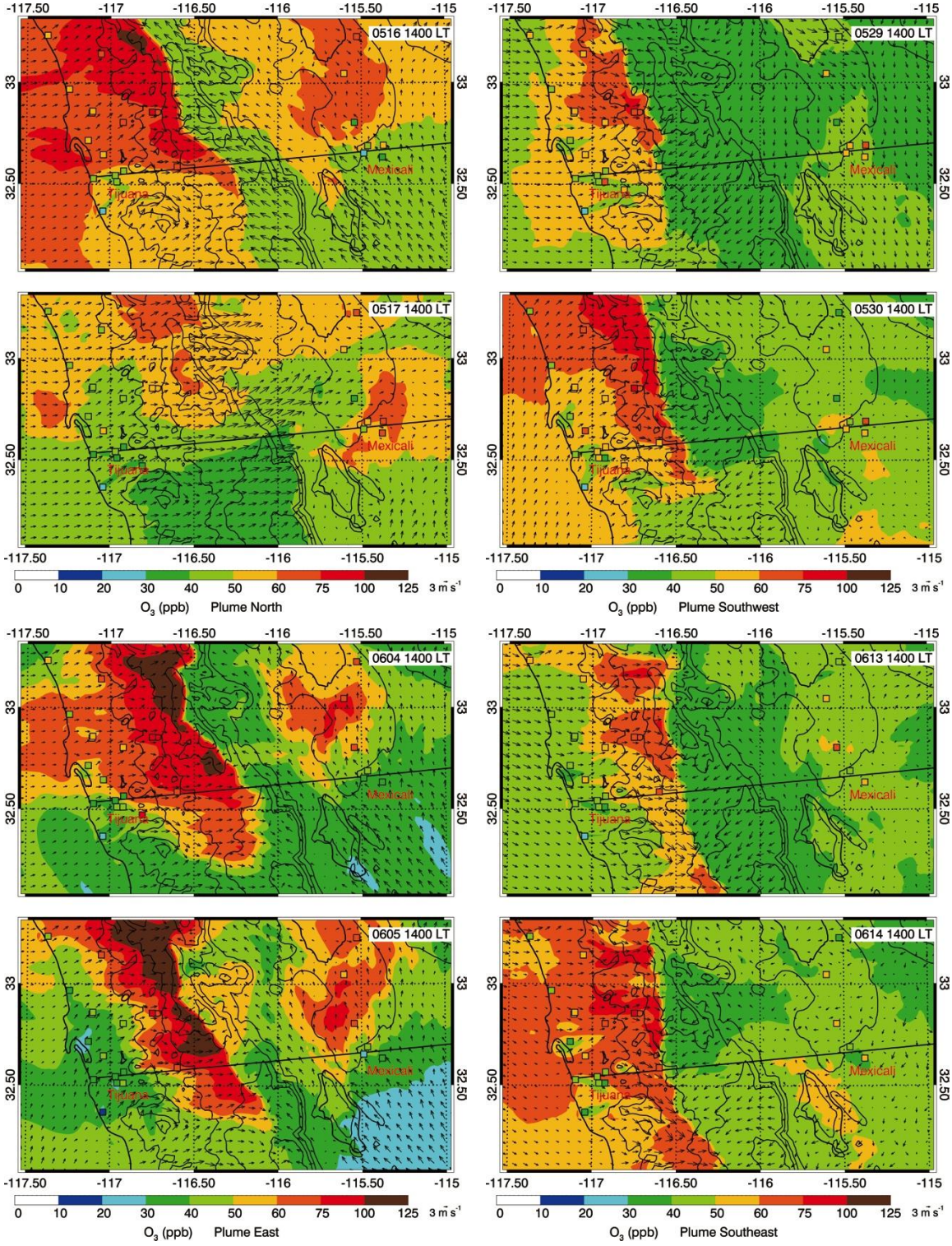


Figure 6. Pattern comparison of simulated vs. observed near-surface O_3 at 1400 LT during the four selected episodes, including 1) May 16-17 (plume north), 2) May 29-30 (plume southwest), 3) June 4-5 (plume east), and 4) June 13-14 (plume southeast).

3.3. Volatile organic compounds (VOCs)

During Cal-Mex, extensive real time concentrations of VOCs at Parque Morelos were obtained by TAMU using a Proton-Transfer Reaction Mass Spectrometry (PTR-MS), which sampled ~ 40 individual masses continuously from May 30 to June 6 [Zheng et al., 2013a].

Canister samples were collected by INECC team in Parque Morelos and Metales y Derivados. The INECC team also measured BTEX using Gas chromatography/photoionization detector (GC/PID) with 15-min resolution at Metales y Derivados (MyD) during May 15 – June 30.

1) The major VOCs identified from the PTR-MS included oxygenated VOCs (e.g., methanol, acetaldehyde, acetone, and methyl ethyl ketone) and aromatics (e.g., benzene, toluene, C_8- and C_9-aromatics) [Zheng et al., 2013a].

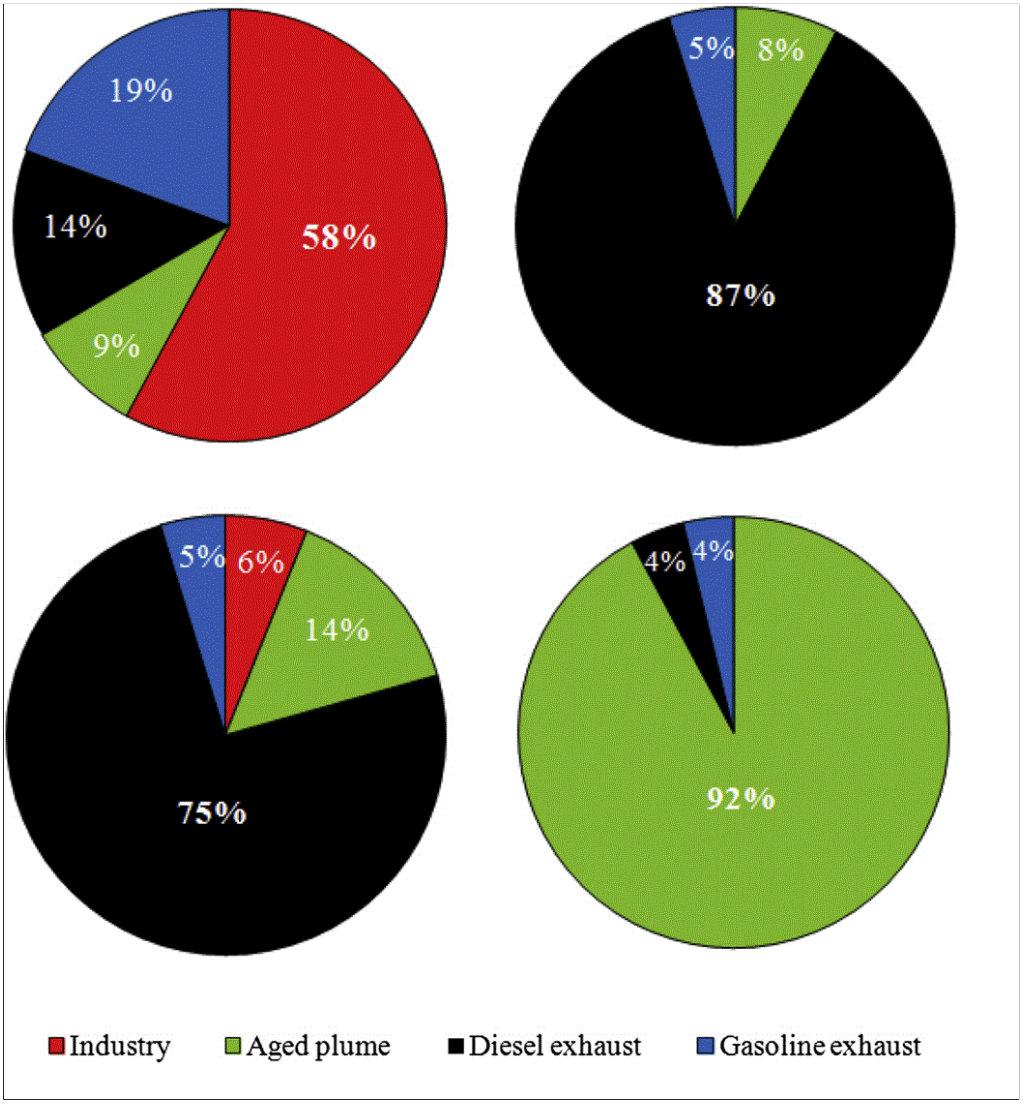
2) Diurnal variations of aromatics were strongly inter-correlated , suggesting similar emission sources (mainly from vehicular activities). Since aromatics are relatively reactive with OH, all aromatics reach daily maxima before noon and are consumed rapidly in the afternoon.

3) All the oxygenated VOCs (OVOCs) observed with the PTR-MS, except methanol, showed similar diurnal patterns and strong photochemical production during the daytime. The hourly average of methanol is mainly affected by the development of the planetary boundary layer. The high level of background methanol is attributed to vegetation and the electronics industry.

4) The hourly average profile for acetonitrile at Parque Morelos shows little variation during the day with an average concentration close to the background level in the free troposphere (0.1-0.2 ppbv). This may be an indication that the site was not affected by biomass burning during the observation period. However, individual episodes of biomass burning may still be important.

5) A source apportionment analysis of VOC (as well as NO_x, SO_2, and NO_z) data using PMF (positive matrix factorization) analysis indicated the predominance of four profiles: 1) local industrial emission, 2) gasoline vehicle exhaust, 3) diesel vehicle exhaust, and 4) aged plumes due to regional background and/or long-range transport. Methanol, acetone, propene, acetaldehyde, and alkyl acetate were the predominant VOCs for the industrial emissions profile (e.g., electronics industry and solvent usage). The source apportionment (Figure 7) resulted in about 60% contribution (in terms of carbon content) from the industrial source to VOC emissions. In addition, the diesel vehicle emission contributed over 70% to NO_x and SO_2. An independent conditional probability function analysis indicated that industrial source did not show significant tendency with wind direction, while both gasoline and diesel engine

emissions were associated with air masses passing over cross - border ports, and aged plumes were strongly associated with NW winds. [Zheng et al., 2013].



6)

Figure 7. Source apportionment of VOCs (top left), NO_x (top right), SO_2 (bottom left) and NO_z (bottom right) at Parque Morelos, Tijuana during the Cal-Mex 2010 campaign [Source: Zheng et al., 2013a].

7) The results from the canisters and benzene, toluene, ethylbenzene, and xylene (BTEX) measurements obtained by the INECC team indicate that the most abundant VOCs were aromatics, olefins and acetylene. In all sites these compounds comprised over 80% of VOCs observed. The most abundant aromatic compounds were toluene, benzene and C_8-aromatics (the sum of xylene, ethylbenzene and benzaldehyde), whereas isoprene was the most abundant olefin compound. The daily profile for isoprene at Parque Morelos measured from

PTR-MS clearly followed the solar radiation intensity; the increase of isoprene concentration after midday suggests a natural biogenic contribution. The isoprene concentration is low in Tijuana due to the lack of vegetation in this arid area (Zheng et al., 2013a).

8) Toluene/benzene ratios demonstrated the influence from local traffic at Parque Morelos and the impacts of nighttime industrial sources, whereas at Metales y Derivados the observed VOC ratios indicated the impacts of industrial sources.

9) The observed formaldehyde (HCHO) mixing ratio varied between 1.0 ppbv and 13.7 ppbv, with an average daily maximum of 6.3 ± 2.6 ppbv that occurred around 10 AM and a minimum of 2.8 ± 1.3 ppbv around midnight (Zheng et al., 2013b). The early onset of the HCHO daily maximum (~ 3 hr before the solar noon) indicated the presence of primary HCHO emission and a fast photolysis loss. The estimated contribution of OH radical production from HCHO photolysis relative to that from O_3 photolysis results in a ratio from 0.8 to 18 with the highest values around traffic rush hours. Overall, anthropogenic activities (especially the transportation sector) in Tijuana contributed substantially to primary HCHO emission and thus played a dominant role in regulating the OH radical budget, especially for the relatively low O_3 concentration in the area.

3.4. Particulate matter

During Cal-Mex 2010, extensive measurements of PM were taken using several complementary methods at various sites; this is given in Table 3.

PM10 and PM2.5

1) A comparison of PM10 annual averages for 2005-2009 shows lower PM10 concentrations in all San Diego sites compared to Tijuana sites (Figure 8). Comparison of the monthly average concentrations also indicates that PM10 levels in Tijuana are lower between May and August but higher between October and December. Therefore, the observation period of the Cal-Mex field study corresponded to the season with the lowest PM concentration.

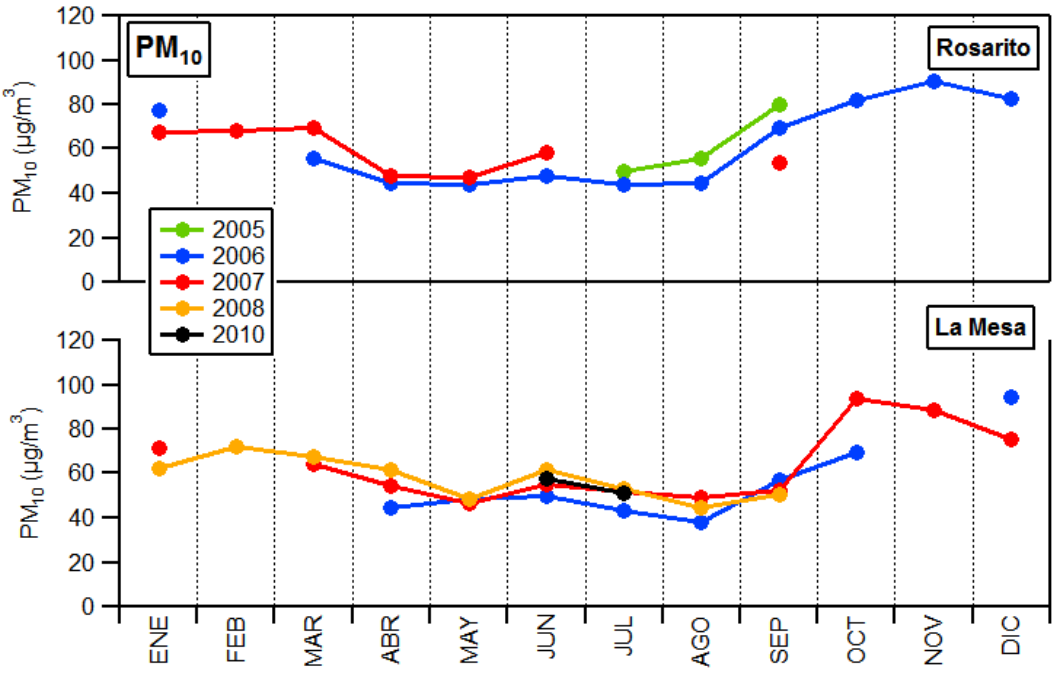


Figure 8. Monthly average of PM10 concentrations in Rosarito and La Mesa from 2005 to 2010.

2) Diurnal PM2.5 and PM10 temporal concentration profiles were both well correlated at Valle de Las Palmas but the correlations were not high in Metales y Derivados. At Metales y Derivados, La Mesa, and Valle de Las Palmas, PM10 concentrations were best correlated after late morning and afternoon during East-Southeast plume transport events. However, PM10 concentrations at Valle de Las Palmas were higher in the afternoon, when local winds come from the Northwest and under plume transport conditions to the East and Southeast. On the contrary, PM2.5 concentrations in the three sites were not correlated. The findings suggest that transport of PM10 occurs along Tijuana under East-Southeast transport conditions, whereas local sources determine PM2.5 concentrations.

3) Average PM10 concentrations from 24-hr gravimetric samples in Parque Morelos and Metales y Derivados were both 32 µg/m^3, whereas PM2.5 24-hr average concentrations were 17 µg/m^3 and 19 µg/m^3 at Parque Morelos and Metales y Derivados, respectively. These concentration averages are below current air quality standards for Mexico. Fine PM (PM2.5) was mainly apportioned by fuel oil and biomass combustion and secondary aerosols, and road traffic. Coarse PM (PM2.5-PM10) was mainly apportioned by a mineral source (sum of road dust resuspension, construction emissions and natural soil) and fresh and aged sea salt. The road traffic contributes more than 60% of the fine elemental carbon and almost 40% of the fine organic matter. The averagePM2.5/PM10 ratios were very similar at both sites (0.59 and 0.54 at Metales y Derivados and Parque Morelos, respectively), ranging from 0.45 to

0.74, the lowest being recorded at Parque Morelos and the highest at Metales y Derivados [Minguillón et al., 2013].

4) The PM10 OC and EC concentrations in Tijuana were 3.8-4.5 μg/^{m3} and 1.0-1.3 μg/m^3, respectively; whereas the PM2.5 OC and EC concentrations were 3.2-3.6 μg/m^3 and 0.9-1.0 μg/m^3, respectively [Minguillón et al., 2013]. These values are lower than reported in Mexico City during the MILAGRO campaign [Molina et al., 2010 and references therein].

5) The PM10 sulfate and nitrate concentrations registered in Tijuana (3.5 μg/m^3 and 2.1-2.2 μg/m^3, respectively) [Minguillón et al., 2013] were also lower than those in Mexico City during the MILAGRO campaign (5 μg/m^3 and 3.5 μg/m^3, respectively) [Querol et al., 2008].

6) An instrument inter-comparison showed high correlations for particle number concentrations, with large concentrations of particles in the fine size range.

7) Particle fluxes measured by eddy covariance were particle number fluxes were higher than those observed in other urban studies, likely due to differences in tower height and size range of particle counters employed as well as the possibility that vehicles and industries in the border region are more polluting than those encountered in study areas with stricter emissions controls [Klapmeyer et al., 2013].

Black carbon, organic carbon, Polycyclic Aromatic Hydrocarbons (PAHs), and sub-micron particles

During Cal-Mex, several complementary techniques were used to measure black carbon (BC) at different sites in Tijuana and also in the US site along the border. In addition, particle-bound PAHs and active surface were measured at various sites during the campaign by MCE2 and VT using EcoChem monitors.

Four sets of black carbon were obtained by VT: one on the US side (Otay Mesa) and three in Tijuana (Parque Morelos, UTT, and el Trompo) using the Aethalometer aboard the VT Flux Lab. Black carbon was also measured using a SP2 instrument, whereas non-refractory (NR) organic and inorganic aerosol mass fragments were obtained using an Aerosol Chemical Speciation Monitor (ACSM), and organic aerosol functional groups were collected during the campaign and analyzed with FTIR by the UCSD/SIO team. Black carbon was also measured using Aethalometers at three locations by the SDSU team in the US border at San Ysidro: Duty Free Store (DF) near San Ysidro crossing, Sunset School (SS) and Tijuana River Estuary (TR). Measurements of black carbon using Aethalometers in the CECyTE and UABC monitoring sites were also obtained by UABC-TIJ and MCE2 teams during the campaign.

1) Black carbon concentrations were more than two times higher, on average, in Tijuana compared to San Diego. BC was strongly correlated with CO at three sites in Tijuana (Parque Morelos, UTT, and El Trompo) but only weakly correlated at Otay Mesa along the US border [Shores et al., 2013]. The strong correlation between black carbon and CO observed in the three different sites in Tijuana suggests that on the Mexican side of the border, black carbon originates mainly from mobile sources (responsible for nearly all CO emissions). On the other hand, the weaker correlation at Otay Mesa suggests that other sources of black carbon may be influencing this site (see Figure 9).

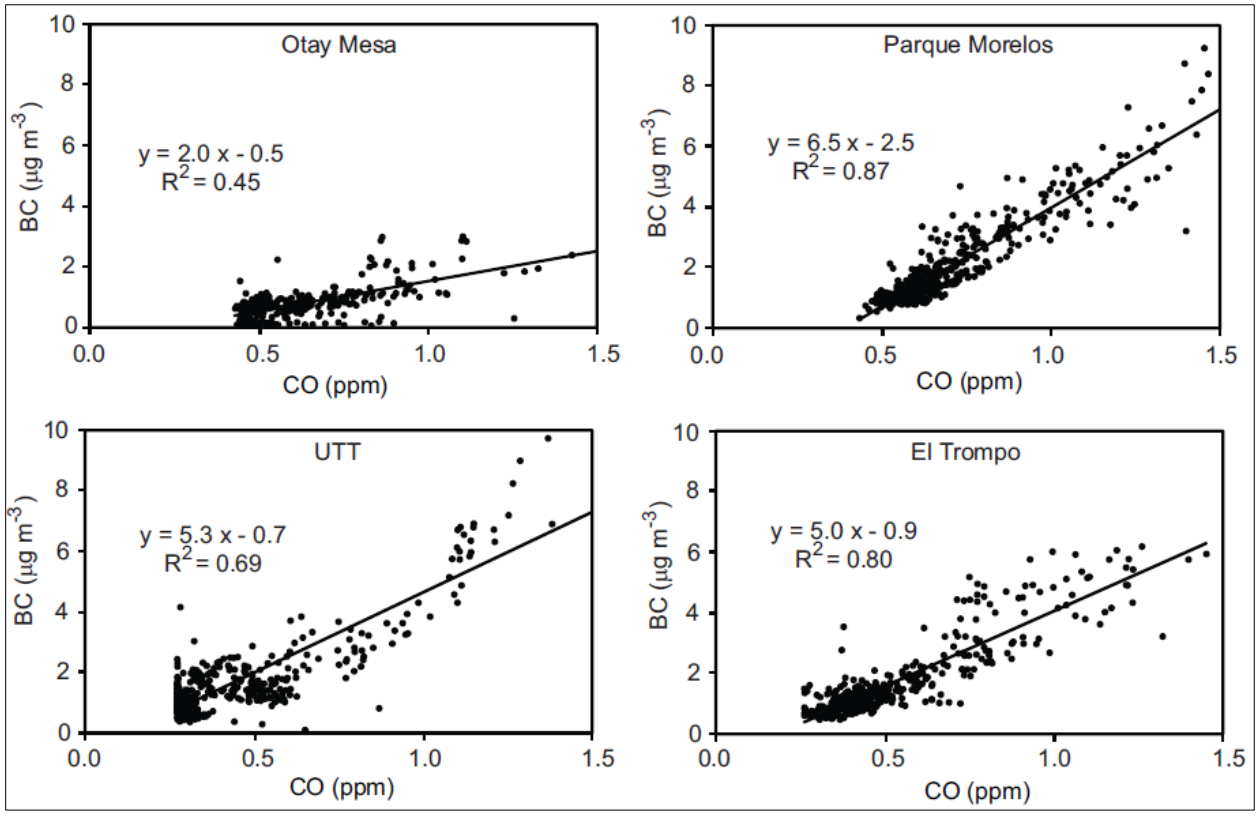


Figure 9. BC and CO were strongly correlated at three sites in Tijuana (Parque Morelos, UTT, and El Trompo) and less so along the US border (Otay Mesa) [Source: Shores et al., 2013].

2) Patterns in concentrations and wind suggest that BC in Tijuana was usually of local origin. Under typical summertime conditions such as those observed during the study, transport from Tijuana into the US was common, crossing the border in a northeasterly direction [Shores et al., 2013].

3) High black carbon particle number concentrations were observed in Parque Morelos; the number concentrations were highest during the weekdays on average, but elevated concentrations were observed on weekend evenings. Correlations with organic aerosol

markers and components suggests that these elevated concentrations were attributed to vehicular emissions (weekday mornings) and burning activities (weekend evenings) [Takahama et al., 2013a].

4) The average mass concentration of non-refractory PM1 (sulfate, nitrate, ammonium, chloride, and organic compounds) at Parque Morelos during Cal-Mex was 5.8 μg/m^3 and the average submicron organic mass concentration was 3.3 μg/m^3, which are relatively low compared to Mexico City and Los Angeles. However, the distribution of the functional groups of the organic mass in Tijuana was very similar to those cities, with alkanes and acids being the largest fractions [Takahama et al., 2013b]. The low concentrations are likely the result of the Parque Morelos location being upwind of many of the urban emissions of Tijuana and also the measurement taking place in May and June, a time of historically low PM levels.

5) Source apportionment results suggested that 40% of the organic mass concentration at Parque Morelos was from vehicular sources [Takahama et al., 2013b]. Simulations with the HYSPLIT trajectory model and chemical composition measurements suggest that as much as 60% of the oxygenated organic aerosol observed in Tijuana may have originated from the Southern California Air Basin (easterly winds from Pacific Ocean), in agreement with the large observed O/C ratios and the similar functional group composition.

6) Levels of surface-bound polycyclic aromatic hydrocarbons (SPAHs), BC, and aerosol active surface (AS) showed substantial daily spatial inter-variability and marked concentration profiles consistent with an overall pattern induced by daily anthropogenic activities. Higher SPAH and BC correlations were observed for smaller (0.3-0.5 μm) particles than for larger (0.5-10 μm) particles [Zavala et al., 2013].

7) Frequent high BC and SPAH concentrations of short duration at night suggest the presence of nighttime combustion sources, including ones that may be associated with clandestine activities.

8) A striking change in the relative proportions of BC/AS and SPAH/AS between morning and late-afternoon periods was observed at all sites. This change may be caused by a shift in predominant emission sources with higher PAH/BC emission ratios induced by daily activities at the border crossing (north-bound traffic is heavier than the south-bound).

9) Analysis with scanning electron microscopy indicates a large fraction of carbon-rich particles at Parque Morelos. The morphology analysis and association with K, Na, Si, Fe and Cl suggest the influence of biomass burning. In Metales y Derivados a large contribution of spherical particles with silicon oxide was observed. These particles may originate from high

temperature combustion industrial sources. Particles with lead oxide with irregular morphology were observed at Metales y Derivados.

Aerosols optical properties

A comprehensive set of properties of ambient submicron aerosols was measured in Tijuana including the chemical compositions, optical properties, the particle size, size - resolved effective density, hygroscopicity, and volatility [Levy et al., 2013].

1) The PM1 mass loading was dominated by organic aerosols (37%) and BC (27%), and there was little new particle formation or particle growth during the day. Measured particle effective density, hygroscopicity, and volatility exhibited size dependence and distinct diurnal trends. Both effective density size distribution and hygroscopicity measurements indicated that smaller particles (< 81 nm) were largely internally mixed, while larger particles (> 151 nm) were largely externally mixed. Hygroscopicity and volatility were strongly size dependent, with increasing hygroscopicity and volatility for particles with increasing size. Smaller particles exhibited a uni-modal hygroscopicity distribution, while larger particles typically exhibited a bi-modal distribution (non- hygroscopic and hygroscopic modes). In contrast, all particles exhibited bi-modal volatility distribution (non-volatile and volatile modes).

2) Dry submicron aerosol scattering and total extinction coefficients were measured at Parque Morelos during the campaign with Cavity Ring–Down Spectrometer and a nephelometer; the measured optical properties are size resolved [Levy et al., 2013]. The average extinction, scattering, and absorption coefficients were 86.0, 63.0, and 23.0 Mm^{-1}, respectively, with maxima occurring in the morning and minima near sunset. High extinction and absorption coefficients were concurrent with high fine PM and BC concentrations. The average single scattering albedo (SSA) at 532 nm was 0.75, ranging from 0.71 to 0.78. Low values of SSA occurred around both 7-8 AM and 7-9 PM, consistent with the local traffic rush hours. The average SSA values observed in Tijuana were much lower than those in many highly populated US cities and comparable to those in Mexico City obtained during MILAGRO Campaign [Molina et al., 2010], indicating the presence of a significant fraction of absorptive aerosols (freshly emitted black carbon) in Tijuana

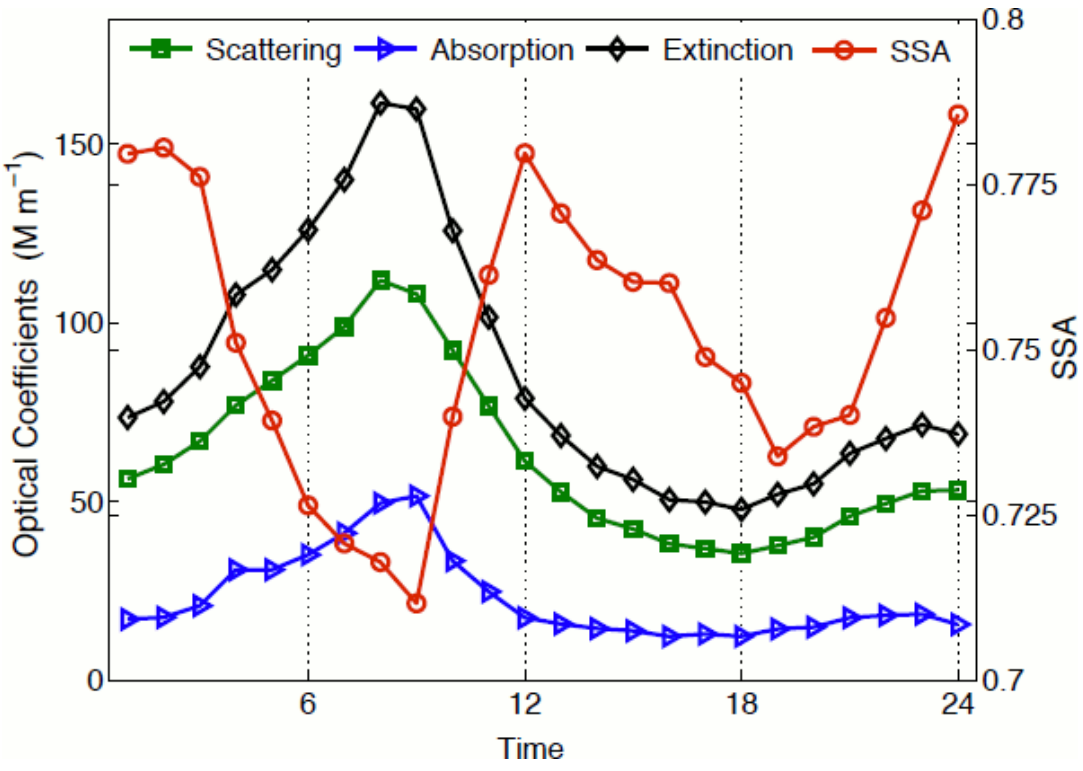


Figure 10. Average diurnal variations of aerosol extinction, scattering and absorption coefficients, and aerosol single scattering albedo during the observational period [Source: Levy et al., 2013].

3) The WRF-CHEM model is able to reproduce the observed temporal variations of the organic, nitrate and ammonium aerosols at Parque Morelos, but often overestimates the observed nitrate and ammonium aerosols in the early morning, which might be caused by the uncertainties of simulated meteorological fields, such as temperature and water vapor [Bei et al., 2013b].

4) The WRF-Chem model simulates reasonably well the observed black carbon concentrations in the US sites, but substantially underestimates the observation in the Mexico sites. Aerosol absorption from black carbon leads to 4-10% ozone reduction in the urban area of Mexico in the morning, but the impacts of aerosols become insignificant in the afternoon when ultraviolet (UV) radiation scattering compensates or even dominates UV absorption by aerosols in the boundary layer [Li et al., 2013].

Bioparticles

1) In samples taken in 9 sites across Tijuana, air concentration of airborne bacteria were highest in the Tijuana river area with relatively intense human and animal activities (average 40,000 CFUs) while the lowest microbial pollution was found near the coastal upwind site. Several potential pathogens, like Staphylococcus (32% average overall) and other common Gram-positive bacteria, were detected in several areas in Tijuana [Hurtado et al., 2013].

2) Measurements of microbial concentrations were highest in summer months and lowest in winter months, and showed large temporal and spatial variability among the various sites, indicating the importance of local biological sources of fungus, yeast, and bacteria. Bioaerosols characterization, source identification, and dispersion pattern are useful tools to correlate chemical and biological air quality with public health [Hurtado et al., 2013].

Border Crossings

1) Results from BC measurements obtained at various sites near the border crossings for February, March, April, May, June and November of 2010 show large differences in BC concentrations between nighttime and daytime periods, as well as seasonal variations, with May and June having the lowest BC concentrations. Concentrations of BC and ultrafine particles were higher for sites closer to the border crossings [Quintana et al., 2013].

2) Statistically significant correlations were found between daytime BC concentrations (30-min averages) and waiting time (the approximate time that a vehicle has to wait in line before northbound crossing the border) [Quintana et al., 2013].

3) Daily average concentration profiles of BC in three Tijuana sites (CECYTE, UABC, UTT) were very different from those obtained in three San Diego sites (TJ River estuary, San Ysidro store at border, and elementary school on San Ysidro). Sites in Tijuana showed much higher average BC concentrations than the sites in San Diego during the Cal-Mex campaign [Castillo et al., 2013]. However, data from other months in San Ysidro during 2010 indicate that at other times of the year, BC concentrations are much higher, with a night time regional increase in BC recorded [Quintana et al., 2013].

4) Fixed site measurements made at the San Ysidro port of entry (POE) pedestrian entry gate border recorded concentrations of BC averaging 7 $\mu g/m^3$, 1 nitro-pyrene (1-NP) averaging 2.0 $pg/m^3$and ultrafine particles averaging 40,000 particles/cc [Galaviz et al., 2013].

5) When personal air monitoring was conducted on pedestrians standing in line to cross northbound at the San Ysidro POE, subjects who crossed the border in pedestrian lanes had a 6-fold increase in personal exposure to 1-NP (1.7 ± 2.3 vs 0.22 ± 0.21 pg/m^3, $p<0.01$), a 3 fold increase in exposure to CO (2.8 ± 1.8 vs 1.0 ± 0.79 ppm, $p<0.01$), and a 2 fold increase in exposure to gravimetric PM2.5 (39 ± 30 vs 21 ± 11 μg/m^3, $p<0.01$), vs. non-border commuters [Galaviz et al., 2013]. This indicates that border crossings may be a source of exposure to persons who cross as well contributing to local and regional pollution. Reducing the time that vehicles idle while waiting to cross is a target for intervention.

4. FUTURE RESEARCH TOPICS

Meteorology

The uncertainties in meteorological modeling in the California-Mexico border region are still large, such as the discrepancies in simulating the shift time between sea-breeze and land-breeze. Questions still remain. How can the data assimilation methods improve the simulation? What are the impacts of small-amplitude meteorological initial errors on air quality simulations in the border region? What are the predominant local wind patterns in the border region for other seasons? How do the predominant synoptic conditions connect with local topographical features for inducing the dispersion patterns in the San Diego-Tijuana air basin?

Emissions

The emissions inventory is a powerful tool for the design and evaluation of emission-based air quality improvement program. However, characterizing and quantifying the emissions of both gaseous pollutants and primary PM is a difficult task in any major urban area, but it presents a particular challenge in the California-Mexico border cities such as Tijuana, characterized by a growing population and rapidly changing economic and social conditions. These changes impact both the quantity and speciation of gaseous and PM emissions, making the development of accurate emissions inventories a fast moving target. Uncertainties in the emissions inventories can be reduced by: 1) continuously improving and updating the local activity and source databases that are used during the emissions estimation process; 2) obtaining locally representative emissions factors for the most important emission sources in the region; and 3) applying modeling and top-down emission evaluation techniques.

Several studies can also be designed to address specific research topics on mobile sources in Tijuana that would greatly benefit the characterization of human health and climate impacts in the border. These include improved quantification of the following:

1) contribution of diesel-powered trucks and buses at the border crossings to particulate matter, aromatics, NO_x, and black carbon emissions;

2) contributions from the prevailing idling and stop-and-go driving conditions of vehicles crossing the border;

3) toxic substances from on-road gasoline-powered vehicles;

4) contributions of poorly-maintained, high emitters, and "chocolate" vehicles to the emissions burden in the border region;

5) contribution of poorly-maintained light-duty delivery trucks and small mulit-passenger transportation vehicles to emissions in Tijuana.

The analysis of data obtained during Cal-Mex also highlighted the need for a better understanding of the emission characteristics of additional sources, including:

1) emissions from fuel and biomass burning activities during nighttime in the urban area;

2) extent and contribution of illegal night-time burning activities associated with industrial areas at suburban East Tijuana;

3) contribution of emissions from brick production and burning of livestock waste from Tecate to air quality in Tijuana;

4) chemical composition of organic compounds (e.g. styrene, formaldehyde, acetaldehyde, methanol, etc.), NO_x, and SO_2 emitted by industrial sources;

5) contributions from resuspended road dust;

6) contribution of currently allowed prescribed 'grass' burns conducted by the Fire Department in the Tijuana area to summer emissions.

Gaseous Species

The role of VOCs in determining the chemistry and photochemistry in the urban area is of primary importance. Results from Cal-Mex suggest that HCHO plays an important role in regulating the OH radical budget in Tijuana. However, there may be additional contributions from higher aldehydes and other VOCs to the radical budget, particularly at the downwind areas. Therefore an important research topic is to evaluate the contribution to the HO_x radical production from photolysis of higher aldehydes, ozone, and other VOCs. Given the importance of aldehydes in the radical budget, it is important to understand the contributions of primary

versus secondary aldehydes to the observed concentration in the region. It is also important to better characterize the sources of aromatics due to their abundance in ambient VOCs and important roles in O_3 and secondary organic aerosol formation.

Sensitivity studies show that the biogenic emissions have substantial contributions to high ozone concentrations at sites above 500 m. It will be important to quantify the impacts of biogenic VOCs to the formation of secondary pollutants at regional scales. In addition, it is necessary to better understand the contributions from gaseous (including VOCs) precursors to secondary organic and inorganic aerosol formation. For example, an evaluation of biogas and VOCs emission from East Tijuana landfill should be made. These research topics can be pursued with the regional air quality models that are currently being evaluated with data obtained during Cal-Mex.

Particulate Matter

Despite the use of several complementary PM techniques during Cal-Mex, some questions remain unanswered and should be the focus of further research. For example, the fraction of dust due to resuspension from roads vs. natural sources is unclear. There is a need for characterizing the dust source regions and the soil characteristics for those regions. The identities of industrial sources of metals and organic aerosols remain unclear. High time-resolution quantitative analyses of dust and metals may yield very useful information for source identification.

The observed PM2.5 concentrations measured in various sites were not well correlated, although in some sites the correlations were better; this highlights the importance of local sources on PM2.5 levels. The relative contribution of primary emitted and condensed semi-volatile material in the particle phase to the observed PM2.5/PM10 ratio throughout the year needs to be further investigated. Seasonal changes of ambient temperature suggest that the condensed contribution would be time-dependent for organics and inorganics (e.g., ammonium nitrate); variation in emission patterns throughout the year may also influence this ratio. Chemical analysis of PM1 and variations of concentration profiles of PM2.5 suggests that secondary organic aerosol formation in the afternoon was not large. The contribution of secondary aerosol formation to fine particle mass should be explored by the current models in the region as well as the impact of gas-particle partitioning.

The fact that the largest concentrations of PM (2.5 and 10) were found in Valle de Las Palmas, suggests that PM transport might have regional effects. The impact of the urban PM emissions on the rural sites should be investigated.

Several surprising results of the study merit further attention. There appeared to be a very small contribution of local secondary organic aerosol to submicron particles. There were also very

weak diurnal and weekly patterns in fine particle concentrations. It would be important to understand if these characteristics are site specific and what factors control them.

The occurrence of significant seasonal differences in meteorology and emissions that contribute to seasonal differences in population exposures should be investigated.

High concentrations of black carbon were observed in Tijuana using several complementary measurement techniques at different sites; but sources of the high concentrations observed around midnight remains unclear. The large data sets on the evolution and optical properties of aerosols measured during the field study remained to be evaluated and used in model studies to assess the impacts on air quality and climate.

The identity of specific PM, bounded and gas phase PAHs and oxidation by-products that predominantly contribute to PAH levels observed in the border region remains to be investigated.

Other topics for further study include the spatial and temporal variability of microbial concentrations in particles in Tijuana and the contributions from specific sources (e.g., wastewater treatment plant, landfill, Tijuana River, etc.) to the observations.

An important future research topic is the integration of the data obtained from Cal-Mex with the extensive ground-and aircraft-based measurements from CalNex, to better constrain the gaseous and particulate emissions and to assess the cross border transport of pollutants.

Chemical analysis of the organic aerosol fraction of dry PM1 shows that much of is highly oxygenated (i.e., photochemically aged), suggesting that over 60% of the organic aerosol at Parque Morelos is transported from somewhere further out than San Diego. Backtrajectory analysis suggests that the air is north-easterly most of the time, and pollution from Los Angeles and the South Coast Air Basin may be a significant contributor to the organic aerosol and possibly sulfate aerosol concentrations at the site. However, analysis in PM variability across Tijuana implicates local sources as the determining factor in other locations, so constraining the relative contributions of transported and locally-emitted aerosols across the region would be important for understanding how activity on both sides of the border will affect PM concentrations and health.

Toxicity studies of PM10, PM2.5 and BC focusing in oxidative potential evaluation as a measure of toxicity related to PAHs and trace metals content, in urban and suburban areas are also needed.

Health impacts of air pollution in Tijuana

Exposures: Research is needed on contributions of exposures to residents of Tijuana in various microenvironments (home, work, transportation, schools, etc.) in order to characterize exposure profiles and identify persons at highest risk, in order to target interventions effectively.

Health impacts: Health studies should be conducted on sensitive subpopulations (for example children, pregnant women, pre-existing cardiovascular disease) in various regions of Tijuana. For example, playground concentrations of PM and NO_2 at schools across Tijuana and incidence and exacerbation of asthma. These would help quantify impacts and characterize magnitude of health and economic benefits of intervention measures.

5. POLICY IMPLICATIONS

Ambient Monitoring

1) It is important to guarantee the long term continuity of ambient observations and data quality controls through the institutional strengthening of the ambient monitoring network. These include the expansion of the current monitoring network to cope with the population growth and urban expansion in Tijuana, as well as the increase of the number of pollutants and parameters measured.

   Measurements with chemical specificity to further determine the contributions from various source types would be useful. AMS/ACSM type measurements would be expensive, but at least some elemental composition that would allow for source apportionment.

2) Due to current urban development plans in Valle de las Palmas, it will be beneficial to establish a monitoring station there and to consider the implementation of efficient mass transit modes.

3) Currently only PM10 is routinely measured in Tijuana, yet the results show that fine particles are an important component of PM in the region. Continuous measurements of PM2.5, as well as submicron particles (PM1) should be included in the local ambient monitoring network because of the adverse health impacts.

4) The addition of measurements of black carbon in the monitoring network capabilities would be highly beneficial. For example, the routine measurements of black carbon could be very useful for the evaluation of the effectiveness of a control emission strategy targeting combustion related sources.

5) Increased pollutant exposure to persons living or working near major traffic routes, especially border crossing region, has been documented. However, these risks may not be fully reflected in the current monitoring networks since sites are positioned at a distance from roads in accordance with conventional site selection criteria. There is therefore the need for additional monitoring via special studies.

6) A substantial component of PM2.5 in the northern region of Tijuana was shown to be from emissions transported from Los Angeles and San Diego; aged local plumes also indicate an important VOC and NO_x origin from the southern California. The interactions of these regional emissions with local emissions may cause unexpected results and these should be taken into account in locating and interpreting monitoring sites. Special studies targeting transport of pollution from Long Beach and Los Angeles are needed to quantify this contribution and its frequency. Efforts should be made to work with cross-border authorities to reduce these emissions.

Emissions

1) Emissions sources and patterns in the San Diego-Tijuana change continuously due to intricate relations between human activities and external emission drivers (e.g., available technology, local economy, population growth, etc.). Thus, there is a need to regularly update and improve the local emissions inventories in the border region to address emerging environmental concerns.

2) The suggested continuous improvement of the local emissions inventory should consider promoting studies to determine local emission factors, reducing uncertainties in databases of activity data, as well as including emissions of additional key pollutants (e.g. black carbon).

3) Emissions from mobile sources in Tijuana are of major importance. Studies indicate that regulations and governmental programs that promote: 1) identification and removal of on-road high-emitter vehicles (including the Inspection and Maintenance Program), 2) increase of the renewal rate of the local vehicle fleet, 3) increase of usage rates of public transport, 4) creation of an energy-efficient public transportation system, and 5) transition to cleaner and more energy-efficient fuels, should be favored for reducing emissions.

4) Chocolate cars are a unique feature of the on-road vehicle fleet in Tijuana. Studies directed towards the characterization of pollutant emissions from chocolate cars would be highly beneficial for identifying their impacts.

5) The large mass fraction of PM of geological origin in Tijuana indicates that actions targeting dust re-suspension and road paving can be beneficial in reducing ambient PM loadings.

6) The Cal-Mex study results indicate that emissions from industrial sources can contribute substantially to ambient levels of VOCs in Tijuana. Thus, the enforcement of environmental regulations for industries will benefit the air quality in the region. In addition, there is a need to better characterize industrial emissions, including source-specific VOC species profiles with special consideration of those VOCs that are toxic and/or contribute to ozone formation and secondary particulate formation.

7) Modeling study investigations indicate that anthropogenic emissions from California contribute more to O_3 formation in the San Diego-Tijuana border region. Therefore emission regulation and reduction should be addressed and coordinated not only locally, but also regionally.

8) Biomass burning in Tijuana and Tecate (mainly grassland and bushes) was commonly observed during the field study and the results indicate that they may contribute to particulate matter and PAHs in the region. Enforcement of regulations regarding grassfires and other open burning is needed to reduce their emissions and the practice of permitted Fire Department burns should be scrutinized.

9) It would be worthwhile to work with border agencies on policies that might reduce the volume of idling traffic, both passenger cars and cargo trucks, at the border crossings.

Capacity Building and Outreach

1) The continuous efforts for updating and improving the monitoring network and the estimated emissions will require enhancing local technical capacities of environmental agencies.

2) Addressing environmental issues requires a holistic approach and multi-stakeholder participation. This could include establishing a working group of technical and policy oriented leaders to create a broad-based strategy for communication and outreach among the data base developers, decision makers, air quality policy groups, atmospheric and health researchers, integrated assessment analysts, and the general public. In addition, characterizing the uncertainties in the data used and the model analysis is also an important part of the communications.

3) The spatial and temporal nature of pollutants associated with adverse health effects such as PM2.5 should be monitored, and the potential to issue population alerts warning sensitive

subpopulations such as elderly and asthmatic children should be evaluated, especially for the most polluted areas.

4) Additional monitoring data is needed to facilitate studies that would quantify the economic and public health burden of air pollution, supporting future policy decisions.

CONCLUSIONS

Although substantial progress has been made in achieving the Border 2012 goals, air quality is still a major concern throughout the California-Mexico border region. The pressures associated with industrial and population growth, the increase in the number of old vehicles, differences in governance and regulatory frameworks, and topographic and meteorological conditions present a challenging context in which to address air quality management. These same factors also present many opportunities for binational cooperation.

The Cal-Mex 2010 Campaign is the first intensive study to investigate the cross-border transport of emissions and the impacts on regional air quality. Even though the field campaign was limited in scope, this field study has generated an extensive data set that will take years to analyze and evaluate fully. Nevertheless, many interesting results are emerging and have already added to our understanding of the transport of pollutants within the San Diego-Tijuana Air Basin and have provided valuable new information about the air quality in Tijuana.

Table 1. Cal-Mex 2010 ground sites gas–phase measurements

Measurement	Technique	Sample interval (s)	Accuracy at high S/N (±1–sigma)	Precision at low S/N (±1–sigma)
H_2SO_4	Atmospheric pressure NO_3^- chemical ionization mass spectrometry (API-CIMS)	30	36%	0.004 pptv
Methanol, acetonitrile, formaldehyde, isoprene, acetaldehyde, acetone, methyl ethyl ketone, and aromatics	Proton-transfer-reaction mass spectrometry (PTR-MS)	300	25%; (40-80% for formaldehyde due to RH change)	< 400 pptv (3.0 ppbv for methanol and 1.2 ppbv for formaldehyde)
CO_2, CO, NO_x	Infrared absorption (CO_2 and CO) and chemiluminescence (NO_x)	60[(a)]	2%, 5%, 5%	0.5 ppmv, 0.04 ppmv, 0.05 ppbv
column NO_2	Differential Optical Absorption Spectroscopy	300		2.67E15 molecules/cm^2 [(b)]
O_3	UV absorption	60		0.6 ppb[(c)]
NO/NO_x	Chemiluminescence (non-specific for NO_2)	60		0.4 ppb[(c)]
CO	Infrared gas filter correlation	60		0.04 ppm[(d)]
SO_2	Pulsed UV fluorescence	60		1 ppb[(e)]
NO_y-HNO_3	Chemiluminescence with dual external converters and nylon filter	60		0.5 ppb[(c)]
NO_2 and peroxyacetyl nitrate (PAN)	Luminol chemiluminescence	One instantaneous sample every 5 minutes		1 ppb[(f)]
CH_4 and NMHC	GC-FID	One sample every 70 s		20 ppb CH4 150 ppb NMHC [(g)]
Benzene, toluene, ethylbenzene, o-xylene, m-xylene	Gas-chromatography Retention TENAX	15 minutes		0.004[(h)]

Hg	Atomic Fluorescence	60[i]		0.2 ng/m^{3}[(i)]

[(a)]Faster (0.1-1 s) data available upon request.

[(b)]Detection limit at 2sigma.

[(c)]Low detection limit with range of 500 ppb and ±10% expected precision.

[(d)]Low detection limit with range of 50 ppm and ±0.1 ppm expected precision.

[(e)]Low detection limit with range of 500 ppb and 1% reading expected precision.

[(f)]Low detection limit with range of 500 ppb and 20% expected precision.

[(g)]Low detection limit with range of 20 ppb and 2% of measured value expected precision.

[(h)]Low detection limit with range of 300 ppb and 10% of measured value expected precision.

[(i)]Low detection limit with range of 1000 ppm and 10% of measured value expected precision.

Table 2. Cal-Mex 2010 ground sites aerosol measurements

Measurement	Technique	Sample interval	Accuracy at high S/N (±1–sigma)	Precision at low S/N (±1–sigma)
Submicron organic functional groups and total organic mass	Fourier Transform Infrared Spectroscopy (FTIR)	2.2 to 4.3 hrs	21% (Total organic mass)	10-130 ng/m^3
Elemental composition	X-ray fluorescence (XRF)	2.2 to 4.3 hrs	8-41%, 68% (Cl)	0.3-75 ng/m^3
Submicron non-refractory NH_4^+, NO_3^-, SO_4^{2-}, Cl^- and organic composition	Aerosol Chemical Speciation Monitor (ACSM)	15 to 30 min	20-25%	13-200 ng/m^3
Single-particle refractory black carbon mass and coating state	Single-particle soot photometry (SP2)	5 min	20% for time-averaged mass conc.	<100% detection efficiency for particles <0.7 fg
Single-particle morphology and composition	X-ray spectromicroscopy (STXM-NEXAFS)	Single-particle	[*Takahama et al.*, 2010]	
$PM_{2.5}$ trace elements composition	Acid digestion followed by ICP-MS analysis	24 hours	< 20%	depends on the element
$PM_{2.5}$ EC/OC content	CM5014 analyzer (UIC, Joliet, IL)	12 hours	10%	3 ng/m^3
Size distributions 0.03–0.4 µm (RH<10%)	DMA-CPC (TSI 3081 and 3760A)	2 min	10%	1 cm^{-3}
Aerosol density (RH<10%: 46, 81, 151, and 240 nm)	Aerosol particle mass analyzer (APM)	10 min	5%	0.05 g cm^{-3}
Optical extinction (RH<10%: 532 nm)	Cavity ring-down spectroscopy	90 s	1%	0.5 Mm^{-1}
Optical Scattering (RH<10%: 450, 550, and 700 nm)	TSI 3563 nephelometer	90 s	1%	0.5 Mm^{-1}
$PM_{2.5}$, particle number (3-	Light scattering, diffusion charging,	60 s[(a)]	50%, 10%, 20%,	1 µg m^{-3}, 1 cm^{-3}, 10 mm^2

1000 nm), active surface area, total polycyclic aromatic hydrocarbons, black carbon	aerosol photoemission, light absorption		20%, 10%	m^{-3}, 10 ng m^{-3}, 0.1 µg m^{-3}
Black carbon particle mass	Light absorption by suspended aerosol particles at two wavelengths: 880 nm (black carbon) and 370 nm (UV-PM)	5 min	5.2%[(b)] r^2 =0.92 against EC Quartz filter	5.2%[(b)]
PM2.5, particle mass	TEI personal DataRAM nephelometer	60 s	±5% of reading [(c)]	±0.2% of reading [(d)]or ±0.0005 mg/m^3
PM1, particle mass	Tapered element oscillating microbalance	10 min	0.1[(e)]µg/m^3	
PM0.1, particle count	Condensation particle counter	60 s	*5%*	±3–12%

[(a)]Faster (1 s) data available upon request.

[(b)]Personal communication Tony Hansen, Magee Scientific, Oakland, CA.

[(c)]Accuracy referred to gravimetric calibration with SAE Fine (ISO Fine) test dust (mmd = 2 to 3 µm, □g = 2.5, as aerosolized).

[(d)]Precision/repeatability (2-sigma) at constant temperature and full battery voltage.

[(e)]Low detection limit with range of 0 to 1,000,000 µg/m^3 and expected precision of 2.0 µg/m^3 (1-hour), 1.0 µg/m^3 (24-hour)

Table 3. PM measurements during Cal-Mex 2010 Field Campaign

Pollutant	Site	Average concentration $\mu g/m^3$	Dates in 2010	Instrument/ method	Group	Notes
PM2.5[a]	Metales y Derivados	18.6	May 17 to June 27	Quartz Filter /gravimetric	CENICA	Filter sample every three days, 17 samples total
PM2.5 [a]	Parque Morelos	17.3	May 17 to June 27	Quartz Filter /gravimetric	CENICA	Filter sample every three days, 17 samples total
PM2.5-PM10 [a]	Metales y Derivados	13.8	May 17 to June 27	Quartz Filter /gravimetric	CENICA	Filter sample every three days, 17 samples total
PM2.5-PM10 [a]	Parque Morelos	15.1	May 17 to June 27	Quartz Filter /gravimetric	CENICA	Filter sample every three days, 17 samples total
PM10 [a]	Metales y Derivados	32.4	May 17 to June 27	Quartz Filter /gravimetric	CENICA	Filter sample every three days, 17 samples total
PM10 [a]	Parque Morelos	32.4	May 17 to June 27	Quartz Filter /gravimetric	CENICA	Filter sample every three days, 17 samples total
EC in PM10 [a]	Metales y Derivados	1	May 17 to June 27	Quartz Filter /Thermo optical	CENICA, IDAEA	Filter sample every three days, 17 samples total
EC in PM10 [a]	Parque Morelos	1.3	May 17 to June 27	Quartz Filter /Thermo optical	CENICA, IDAEA	Filter sample every three days, 17 samples total
OC in PM10 [a]	Metales y Derivados	3.8	May 17 to June 27	Quartz Filter /Thermo optical	CENICA, IDAEA	Filter sample every three days, 17 samples total
OC in PM10 [a]	Parque Morelos	4.5	May 17 to June 27	Quartz Filter /Thermo optical	CENICA, IDAEA	Filter sample every three days, 17 samples total
EC in PM2.5 [a]	Metales y Derivados	0.9	May 17 to June 27	Quartz Filter /Thermo optical	CENICA, IDAEA	Filter sample every three days, 17 samples total
EC in PM2.5 [a]	Parque Morelos	1	May 17 to June 27	Quartz Filter /Thermo optical	CENICA, IDAEA	Filter sample every three days, 17 samples total
OC in PM2.5 [a]	Metales y Derivados	3.2	May 17 to June 27	Quartz Filter /Thermo optical	CENICA, IDAEA	Filter sample every three days, 17 samples total
OC in PM2.5 [a]	Parque Morelos	3.6	May 17 to June 27	Quartz Filter /Thermo optical	CENICA, IDAEA	Filter sample every three days, 17 samples total
BC [b]	Parque Morelos	1.08	May 18 to June 30	Single Particle Soot Photometer/ Thermal	UCSD-SIO	Measured every 15 minutes intervals

Pollutant	Site	Average concentration μg/m^3	Dates in 2010	Instrument/ method	Group	Notes
				radiation		
BC in PM0.6 [c]	Parque Morelos	2.87 ± 2.65	May 15 to June 30	CRDS[c], nephelo-meter	Texas A&M	Derived by absorption from extinction and scattering. Sampling 2 minutes intervals.
BC in PM1[c]	Parque Morelos	3.22 ± 2.33	May 15 to June 30	DMA, CPC/ Volatility	Texas A&M	Derived from volatility tandem assuming non-volatile volume for BC
PM0.6 [c]	Parque Morelos	10.39 ± 7.61	May 15 to June 30	APM	Texas A&M, UCSD-SIO	Derived from the particles' mass to charge ratio
PM1.0 [b, c]	Parque Morelos	13.04 ± 7.94	May 15 to June 30	ACSM	Texas A&M, UCSD-SIO	Non-refractory PM1. 15-30 minutes time resolution
OA [b, c]	Parque Morelos	3.54	May 15 to June 30	ACSM	Texas A&M, UCSD-SIO	Non-refractory PM1. 15-30 minutes time resolution
NO_3 [b, c]	Parque Morelos	1.64	May 15 to June 30	ACSM	Texas A&M, UCSD-SIO	Non-refractory PM1. 15-30 minutes time resolution
SO_4 [b, c]	Parque Morelos	0.81	May 15 to June 30	ACSM	Texas A&M, UCSD-SIO	Non-refractory PM1. 15-30 minutes time resolution
NH_4 [b, c]	Parque Morelos	0.92	May 15 to June 30	ACSM	Texas A&M, UCSD-SIO	Non-refractory PM1. 15-30 minutes time resolution
Chloride [b, c]	Parque Morelos	0.24	May 15 to June 30	ACSM	Texas A&M, UCSD-SIO	Non-refractory PM1. 15-30 minutes time resolution
BC [d]	Parque Morelos	2.2 ± 2.5	May 29 to June 7	AE-51 aethalometer	VT	Instrument placed 10 m above ground between 7:00 and 17:00 PST and at ground level during the evenings
BC [d]	Otay Mesa	0.8 ± 0.6	May 21-27	AE-51 aethalometer	VT	Instrument placed 10 m above ground between 7:00 and 17:00 PST.
BC [d]	UTT	1.9 ± 1.7	June 8-15	AE-51 aethalometer	VT	Instrument placed 10 m above ground between 7:00 and 17:00
BC [d]	El Trompo	1.7 ± 1.6	June 17-22	AE-51 aethalometer	VT	Instrument placed 10 m above ground between 7:00 and 17:00 PST and at ground level in

Pollutant	Site	Average concentration μg/m^3	Dates in 2010	Instrument/ method	Group	Notes
						PQM during the evenings
BC [e]	TJ River Estuary	0.34	May 28 to July 3	AE-42 aethalometer/ absorption	UABC-SDSU	5 minutes intervals. Measured by light absorption
BC [e]	TJ River Estuary	0.22	June 18 - 22	AE-42 aethalometer/ absorption	UABC-SDSU	5 minutes intervals. Measured by light absorption
BC [e]	TJ River Estuary	0.31	June 22 - 25	AE-42 aethalometer/ absorption	UABC-SDSU	5 minutes intervals. Measured by light absorption
BC [e]	San Ysidro School	0.61	May 28 to July 3	AE-42 aethalometer/ absorption	UABC-SDSU	5 minutes intervals. Measured by light absorption
BC [e]	San Ysidro School	0.39	June 18 - 22	AE-42 aethalometer/ absorption	UABC-SDSU	5 minutes intervals. Measured by light absorption
BC [e]	San Ysidro School	0.51	June 22 - 25	AE-42 aethalometer/ absorption	UABC-SDSU	5 minutes intervals. Measured by light absorption
BC [e]	Store near Border Crossing	0.68	May 28 to July 3	AE-42 aethalometer/ absorption	UABC-SDSU	5 minutes intervals. Measured by light absorption
BC [e]	Store near Border Crossing	0.51	June 18 - 22	AE-42 aethalometer/ absorption	UABC-SDSU	5 minutes intervals. Measured by light absorption
BC [e]	Store near Border Crossing	0.64	June 22 - 25	AE-42 aethalometer/ absorption	UABC-SDSU	5 minutes intervals. Measured by light absorption
BC [e]	UABC	2.66	May 28 to July 3	AE-42 aethalometer/ absorption	UABC-SDSU	5 minutes intervals. Measured by light absorption
BC [e]	UABC	1.91	June 18 - 22	AE-42 aethalometer/ absorption	UABC-SDSU	5 minutes intervals. Measured by light absorption
BC [e]	CECYTE	3.13	May 28 to July 3	AE-42 aethalometer/ absorption	UABC-SDSU	5 minutes intervals. Measured by light absorption
BC [e]	CECYTE	2.97	June 18 - 22	AE-42 aethalometer/ absorption	UABC-SDSU	5 minutes intervals. Measured by light absorption
BC [e]	CECYTE	3.8	June 22 - 25	AE-42 aethalometer/ absorption	UABC-SDSU	5 minutes intervals. Measured by light absorption
BC [e]	CECYTE (no grass burning)	2.82	May 28 to July 3	AE-42 aethalometer/ absorption	UABC-SDSU	5 minutes intervals. Measured by light absorption
BC [e]	CECYTE (no grass burning)	2.64	June 18 - 22	AE-42 aethalometer/ absorption	UABC-SDSU	5 minutes intervals. Measured by light absorption

Pollutant	Site	Average concentration μg/m^3	Dates in 2010	Instrument/ method	Group	Notes
BC [e]	UTT	3.81	June 22 - 25	AE-42 aethalometer/ absorption	UABC-SDSU	5 minutes intervals. Measured by light absorption
BC [e]	UTT	4.01	May 28 to July 3	AE-42 aethalometer/ absorption	UABC-SDSU	5 minutes intervals. Measured by light absorption
BC [e]	UTT	6.36	June 22 - 25	AE-42 aethalometer/ absorption	UABC-SDSU	5 minutes intervals. Measured by light absorption
BC [f]	Site 1 (near San Ysidro LPOE)	0.7	April, May, June, 2010	AE-42 aethalometer	SDSU	5 minutes intervals. Measured by light absorption. Includes non-CalMex periods.
BC [f]	Site 2 (near Chula Vista downtown)	0.6	April, May, June, 2010	AE-42 aethalometer	SDSU	5 minutes intervals. Measured by light absorption. Includes non-CalMex periods.
BC [f]	site 4 (TJ River Estuary)	0.4	April, May, June, 2010	AE-42 aethalometer	SDSU	5 minutes intervals. Measured by light absorption. Includes non-CalMex periods.
PM2.5[f]	Site 1 (near San Ysidro LPOE)	19.2	April, May, June, 2010	RAMs (pDRs)/Light scattering	SDSU	Personal passive monitors. Includes non-Cal-Mex periods
PM2.5[f]	Site 2 (near Chula Vista downtown)	12.5	April, May, June, 2010	RAMs (pDRs)/Light scattering	SDSU	Personal passive monitors. Includes non-Cal-Mex periods.
PM2.5[f]	site 4 (TJ River Estuary)	11.0	April, May, June, 2010	RAMs (pDRs)/Light scattering	SDSU	Personal passive monitors. Includes non-Cal-Mex periods

[a] Minguillon et al., 2013.
[b] Takahama et al., 2013. ACSM: Aerosol Chemical Speciation Monitor.
[c] Levy et al., 2013. CRDS: Cavity ring-down spectrometer; DMA: Differential Mobility Analyzer; CPC: Condensation Particle Counter; OA: Organic Aerosol; APM: Aerosol Particle Mass Analyzer.
[d] Shores et al., 2012.
[e] Castillo et al., 2013.
[f] Quintana et al., 2013. pDRs: personal Data-RAM.

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Appendix A

List of Participants

Insitution	Principal investigator/ coordinator	Participants (researchers and students)
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Appendix B

List of Publications

Published

Bei, N., Li, G., Zavala, M., Barrera, H., Torres, R., Grutter, M., Gutierrez, W., Garcia, M., Ruiz-Suarez, G., Ortinez, A., Gutierrez, Y., Alvarado, C., Flores, F., Molina, L.T., (2013a). Meteorological overview and plume transport patterns during Cal-Mex 2010. Atmospheric Environment. 70, 477-489.

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