Sources and Transport of Black Carbon at the United States-Mexico Border near San Diego-Tijuana

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Abstract

Black carbon (BC), a major component of soot, is a byproduct of incomplete combustion of carbonaceous fuels, such as diesel and biomass. It has significant climate effects due to its ability to absorb solar radiation across a wide spectral range; the magnitude of this radiative forcing is estimated to be second only to carbon dioxide. It also has worrisome health effects due to its high porosity and ultrafine size that allow it to adsorb other potentially carcinogenic species in the vapor phase and easily deposit into the respiratory system. Reducing BC emissions and impacts requires an improved understanding of its sources and their spatial and temporal distributions. This problem is of special interest at the US-Mexico border, where air quality is poor and the potential for cross-border transport creates an imperative for binational cooperation in designing air quality management strategies.

The overall objective of this research is to assess emissions of BC and its transport in the US-Mexico border region. The specific goals of this research are to characterize the spatial and temporal variability in BC concentrations and emissions in the border region, to identify potential source areas of BC emissions, and to characterize the cross-border transport of BC and assess its impact on local and regional air quality. As part of the Cal-Mex 2010 field campaign in the border cities of San Diego and Tijuana, we measured BC concentrations at three locations in Mexico and one in the US. BC was measured continuously with an aethalometer, and these measurements were used in conjunction with particle dispersion simulations conducted with the

Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model. Three-dimensional wind fields from Weather Research and Forecasting (WRF) model output, supplied by the Environmental Protection Agency (EPA), were used to drive HYSPLIT. Probabilistic analysis of HYSPLIT modeling results produced residence time analysis and concentration field analysis plots, which can be used to assess sources and transport of pollutants.

BC concentrations at Parque Morelos, the campaign's supersite, averaged 2.1 μg m^{-3} and reached a maximum value of 55.9 μg m^{-3} near midnight. This average value is comparable to that found in large American cities like Los Angeles and similarly sized Mexican cities like Mexicali. The maximum value is extremely high for anywhere in the world, and similar events were observed on other nights, too, possibly due to illicit industrial emissions. Strong diurnal patterns in BC were observed at all four sites, with peak hourly concentrations occurring in the morning rush hour around 8:00. BC was strongly correlated with carbon monoxide, a tracer for gasoline-powered vehicle emissions, at all three of the Mexican sites, where R^2 values were 0.71-0.86, but was weakly correlated at the American site, where R^2 was 0.13.

Modeling results were assessed by both wind roses and residence time analyses and indicated that winds were typically westerly, due to onshore flow typical in this region, except at Parque Morelos where they were southerly. The consistency of the winds typically resulted in concentration field analyses that mirrored residence time analyses. Generally, BC in Tijuana appeared to originate within the city, as backward simulations showed transport from the US into Mexico at only one site. The majority of the backward and forward trajectory analyses indicated, however, that there was often transport from Tijuana into the US, sometimes directly from the south but often entering in a northeasterly direction east of San Diego-Tijuana and sometimes as far east as Imperial County at the eastern edge of California.

Emissions of BC from Tijuana and the neighboring resort city of Rosarito are estimated to be 380-1470 metric tons yr^{-1}, at most 3% of California's total statewide emissions and 10-38% of San Diego County's. Modeling results indicate that most emissions of BC from Tijuana are transported into the US. Due to BC's relatively long atmospheric lifetime, these particles can travel long distances into the country. BC is increasingly being recognized as an important pollutant with respect to climate change, and reducing BC emissions presents an opportunity for achieving an immediate and significant impact on warming. As air quality management strategies in the US begin to address BC, the contribution of neighboring countries like Mexico will have to be considered carefully.

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The following thesis may have been written by the author, but that should in no way imply that he was the singular force behind its creation. Nothing in modern times exists in a bubble, independent of contributions from those past and present, and this thesis is no exception. It could not have been done without the help of countless people, and not necessarily limited to those who appear as co-authors.

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Chapter 1

1.0 Introduction

Black carbon (BC) is a combustion byproduct of critical concern due to its effects on climate, air quality, and human health. By absorbing both direct and reflected solar radiation over a wide spectral range, BC particles have been shown to have a significant impact on the radiative forcing of regional and global climates (Ramanathan and Carmichael, 2008). BC also has worrisome health effects due to its high porosity and ultrafine size (10 to 80 nm) that allow it to adsorb other potentially carcinogenic species in the vapor phase and easily deposit into the respiratory system. Due to BC's significant impact on climate and its relatively short atmospheric lifetime, reducing its emissions presents an opportunity to achieve an immediate and cost-effective impact on climate change. Modeling results have indicated that reductions of BC emissions may slow global warming more than would reductions of carbon dioxide emissions (Jacobson, 2002).

1.1 Air Pollution Issues at the United States-Mexico Border

Growing population and industrial activity along the US-Mexico border, shown in Figure 1.1, have created environmental stresses in both countries (Chow et al., 2000). The border region comprises 14 pairs of inter-dependent "sister-cities" containing 90% of the 14 million border area residents, and the population and industrial development in this region are expected to increase. Since the passage of the North American Free Trade Agreement in 1993, the border region has undergone a rapid increase of industrial complexes (maquiladoras), transportation activity, and aging of the vehicle fleet (Shi et al., 2009).

The most pervasive pollutants found in the sister-cities are ozone and particulate matter (PM_{10}). San Diego-Tijuana exceeded the 8-hour air quality standard for ozone (80 ppb) on average 15 days per year from 2001 to 2005. The 24-hour air quality standard for PM_{10} (150 μg m^{-3}) was exceeded on average 7 days per year from 2001 to 2005 (US EPA and SEMARNAT, 2005). Because there are no air quality standards for BC, it is not routinely monitored, but given the status of ozone and PM_{10}, it is likely that BC is also problematic.

Figure 1.1. US-Mexico border region (reproduced from US EPA and SEMARNAT, 2005).

1.2 Research Objectives and Approach

Identification of sources of BC and understanding of its transport are needed to develop strategies for reducing its emissions and impacts. The overall objective of this research is to assess emissions of BC and its transport in the California-Mexico border region. The assessment is based on measurements of BC collected by a mobile laboratory during the Cal-Mex 2010 field campaign and on trajectory modeling. The specific objectives of the research are:

(1) to characterize the spatial and temporal variability in BC concentrations and emissions in the border region;

(2) to identify potential source areas of BC emissions; and

(3) to characterize the cross-border transport of BC and assess its impact on local and regional air quality.

BC concentrations were measured by light absorption with an aethalometer (Magee Scientific AE-51) at four sites, three in Mexico and one in the US. Three-dimensional wind fields from Weather Research and Forecasting (WRF) model results provided by the Environmental Protection Agency (EPA) were used to simulate forward and backward particle trajectories using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model. Trajectories were simulated every hour and tracked for 24 subsequent hours. Particle coordinates were assigned to a grid to develop probabilistic representations of air transport using the residence time analysis (RTA) technique. The results of the RTA were then weighted by respective BC concentrations at the release hour to develop concentration field analyses (CFA) to determine source regions of BC. These analyses allow assessment of whether BC is transported across the international border.

1.3 Black Carbon

Carbonaceous particulate matter suspended in the atmosphere can be broadly divided into two categories based on a particle's impact on solar radiation. Organic carbon mainly scatters light, while BC, also referred to as elemental carbon, absorbs solar radiation. BC is usually associated with soot, the black particulate matter formed as a byproduct of the combustion of organic materials, such as coal, wood, fuel oil, paper, and refuse. BC is more precisely defined

based on analytical considerations: “it is the portion of combustion emissions that is insoluble in both polar and non-polar solvents, and stable in air or oxygen at temperatures up to approximately 350 - 400°C, and it is strongly optically absorbing.” It is operationally defined as the light-absorbing component of particles (Hansen, 2003).

1.3.1 Climate Effects

BC absorbs solar radiation over a wide spectral range. Recent modeling results indicate that BC is the second largest contributor to global climate change after carbon dioxide. The radiative forcing of BC has been estimated to be +0.9 W m^{-2} (with a range of +0.4 to +1.2 W m^{-2}, where a positive value implies warming), 55% that of carbon dioxide’s forcing and larger than the forcing from other greenhouse gases like methane and nitrous oxide (Ramanathan and Carmichael, 2008). This absorption can offset the cooling effect of other aerosols like sulfates (Beegum et al., 2009). BC has a much shorter lifetime in the atmosphere compared to other greenhouse gases, one week at most versus 100 years or more for carbon dioxide, so it offers an immediate opportunity through reductions in emissions to reduce warming.

At the regional scale, BC is suspected to perturb regional hydrologic cycles. The surfaces of fresh BC particles are hydrophobic, but these surfaces can be oxidized over time such that the particles become cloud condensation nuclei. This phenomenon is claimed to be significant enough in South Asia to disturb rainfall patterns over the tropical Indian Ocean and surrounding areas. Increased summer flooding in south China, increased drought in north China, and moderate cooling of China and India have also been blamed on the massive emissions of BC from the combustion of biofuels and coal (Ramanathan and Carmichael, 2008), which is particularly common in households in China and India (Menon et al., 2002).

BC is also suspected to be a major contributing factor to the retreat of over two thirds of the Himalayan glaciers. When BC deposits on snow and ice surfaces, the albedo may be sufficiently reduced to accelerate thawing. Modeling of emissions from South and East Asia has shown that the Himalayan region is the receptor for these sources. BC is estimated to contribute to a localized warming of about 0.6 ºC, roughly equivalent to that attributable to greenhouse gases (Ramanathan and Carmichael, 2008).

1.3.2 Human Health Effects

BC is usually associated with ultrafine particles smaller than 0.1 μm, and ultrafine particles have been shown to be more harmful to human health than larger particles, as the former are more efficiently retained in the peripheral regions of the lungs. Exposure of alveolar macrophages to particles found in urban air induces a series of cytotoxic effects, such as the production of oxygen radicals and the release of various cytokines that are likely responsible for inflammatory responses (Calcabrini et al., 2004). BC inhaled at high concentrations can cause chronic pulmonary inflammation, pulmonary fibrosis, and lung tumors in exposed rats. The lungs have a natural clearing ability, but this can be overwhelmed when the deposition rate of inhaled particles is greater than the clearance rate (Renwick et al., 2000).

Due to its high porosity and specific surface area, BC also has the ability to adsorb other species in the vapor phase, including many potentially carcinogenic organics, such as polycyclic aromatic hydrocarbons (PAHs). In effect, BC serves as the nuclei of agglomerated particles which are coated by adsorbed hydrocarbons. Due to their small size, BC particles are easily deposited into the respiratory system. Thus, BC particles can act as the vehicles for delivery of harmful compounds adsorbed on their surfaces (Jiang et al., 2005).

Approximately half of the world depends on biofuels, whose combustion produces BC, for home cooking and heating. This is particularly true in developing countries like India and China, where ~75% of households utilize biofuels. The World Health Organization (WHO) estimates that nearly two million premature deaths can be attributed to the effects of indoor smoke each year. The WHO ranks indoor smoke as the fourth leading cause of health problems in developing countries, behind access to clean drinking water, unsafe sex, and malnutrition. Indoor smoke disproportionately affects women and children in developing countries, as they tend to spend the most time indoors while cooking (Barnes et al., 1994).

1.3.3 Sources, Concentrations, and Fate

BC is produced during the incomplete combustion of carbonaceous fuels, with the most important sources being fossil fuels (diesel and coal), biomass (deforestation and crop residue burning), biofuels (dung and wood), and wildfires (Penner et al., 1993). The first three sources are anthropogenic and believed to be the major inputs of global BC, though forest fire emissions can have significant local effects (Ramanathan and Carmichael, 2008). According to the most recent global inventory of BC, the annual emissions of BC are (for 1996) ~8 Tg yr^{-1}, with about 20% from biofuels, 40% from fossil fuels, and 40% from open biomass burning (Bond et al., 2004). The uncertainty in the published estimates for BC emissions is at least ±50% on a global scale (Ramanathan and Carmichael, 2008). Chow et al. (2010) developed a bottom-up inventory for BC in California and estimated that the state emitted about 47,250 metric tons of BC in 2006. This inventory does not consider contributions from Mexico, as the level of detail necessary to conduct such an analysis was not available.

Figure 1.2 shows an estimate of global and US distributions of BC sources (Battye et al., 2002). In the US, fuel combustion is the dominant source of BC. Globally, however, biomass burning represents the majority of BC emissions due to its widespread use in heating homes and cooking food, as well as open burning of forests to create pasture and cropland.

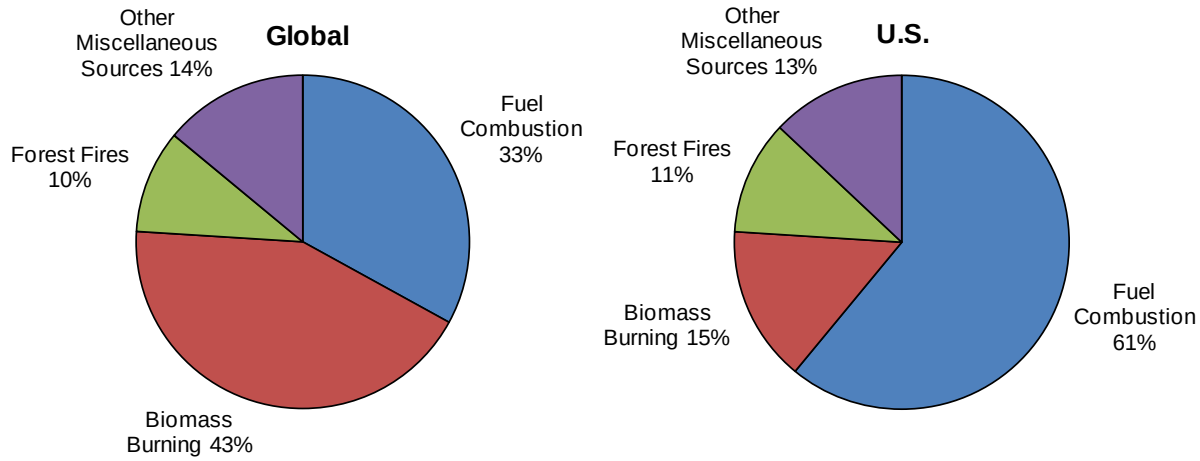

Figure 1.2. Estimated global and US distribution of BC emissions.

Ambient BC concentrations typically vary from 0.2 to 2.0 µg m^{-3} in rural areas and from 1.5 to 20 µg m^{-3}, 10 times higher, in urban areas. BC concentrations exceeding 10 µg m^{-3} are common in some urban locations. BC measurements from a series of major studies in North America are shown in Table 1.1 (US EPA, 1996; Chow et al., 2000; Kelly et al., 2006).

Table 1.1. Daily Average Black Carbon Concentrations in Selected Cities in North America

Location	Date	BC (µg m^{-3})
East		
Philadelphia [a]	August 1994	0.8
Roanoke [a]	Winter 1988/1989	1.5
West		
Los Angeles [a]	Summer 1987	2.4
Los Angeles [a]	Fall 1987	7.3
San Joaquin [a]	1988-1989	3.2
Phoenix [a]	Winter 1989/1990	7.5
Calexico[b]	1992-1993	2.5
Mexicali*[b]	1992-1993	3.8
Calexico[c]	March 2002	4.7
Mexicali*[c]	March 2002	7.5
Central		
Albuquerque [a]	Winter 1984/1985	2.1
Denver [a]	Winter 1987/1988	4.4
Chicago [a]	July 1994	1.3
El Paso[c]	March 2002	1.9
Ciudad Juarez*[c]	March 2002	7.1

[a]US EPA (1996)

[b]Chow et al. (2000)

[c]Kelly et al. (2006)

*In Mexico

As BC is chemically inert and in the ultrafine size range (10 to 80 nm), the major removal mechanism from the atmosphere is wet deposition. Compared to other types of particles, BC has a relatively long lifetime in the lower troposphere (1 week in dry climates, 40 hours in wet climates), and as such it is capable of traveling long distances (Beegum et al., 2009).

1.4 Black Carbon at the US-Mexico Border

At the US-Mexico border, industrial activity is largely concentrated on the Mexican side. While most raw materials originate elsewhere, this activity can consume large amounts of solvents and fuels and concomitantly produce large amounts of air pollutant emissions. In addition, the large amount of transport of goods across the border suggests that the fraction of diesel-powered vehicles in the region is greater than average. Diesel fuel combustion is a major source of BC, while gasoline combustion produces negligible amounts of BC.

Despite the accelerating environmental stresses near the US-Mexico border, only a few studies have been conducted on the cross-border transport of pollutants, and none of these have considered BC. The previous work does suggest, however, that cross-border transport may be important. The US National Park Service concluded that significant amounts of aerosols are transported from Mexico into Big Bend National Park in southwest Texas (Malm et al., 1990). Another study assessed the contribution of cross-border pollution on visibility degradation in national parks in an effort to evaluate the potential success of EPA's Regional Haze Rule (RHR). The results indicated that accounting for cross-border transport of aerosols was critical, and that the original goals of the RHR were unattainable from domestic emission reductions alone (Park et al., 2006). Table 1.1 includes two sister-city pairs (El Paso-Ciudad Juarez and Calexico-Mexicali) in which BC concentrations were 3.8 and 1.5 times higher, respectively, in the Mexican cities than in their American counterparts.

Furthermore, the amounts and types of emissions on either side of the border may differ dramatically because of cross-border differences in industrial activities, socioeconomic status, and environmental regulations. Previous work (Zavala et al., 2009) comparing emissions in Mexicali and Austin showed that on a per vehicle basis, the Mexicali fleet was significantly more

polluting than the fleets of other cities, probably due to the older age of the vehicles. BC emissions originating in Mexico could therefore be a potentially important contribution to the total inventory in the US.

1.5 Cal-Mex 2010 Research Campaign

The states of California in the US and Baja California in Mexico share a common air basin along 200 km of the international border and include two of the 14 sister-city pairs (San Diego-Tijuana and Calexico-Mexicali). Due to the industrial activity along the border, as well as the intense traffic of heavy-duty vehicles associated with trade through the crossings, these two sister-city pairs account for the highest observed ozone and aerosol concentrations in the urban areas of the entire border region. From 2001 to 2005, ozone concentrations exceeded both the binational 8-hour ozone standard of 80 ppb and the annual PM_{10} standard of 50 μg m^{-3} (US EPA and SEMARNAT, 2005). There exists, therefore, mutual interest among the bordering nations in understanding the chemical and physical properties of the pollutants that originate in this region, as well as their transformations and impacts on climate and health.

The Cal-Mex 2010 research campaign was a collaborative effort between numerous research groups in the US and Mexico to study air quality and climate change issues affecting the common air basin shared by the states of California and Baja California. The campaign team measured a comprehensive suite of pollutants from May to July 2010 at a central fixed site in Tijuana and several surrounding sites. The campaign team measured gases, aerosols, and meteorological parameters, as well as surface-atmosphere exchange fluxes by eddy covariance. Results from this campaign are intended to guide government officials and inform

the development of air quality management strategies to reduce adverse human health, ecosystem, and climate impacts.

1.6 Benefits of Reducing Black Carbon Emissions

The relatively short atmospheric lifetime of BC compared to other greenhouse gases presents an opportunity for emissions reductions to have an immediate impact on climate change, as opposed to reductions of carbon dioxide which would not be noticed for decades. In addition, a substantial portion of the global BC emission inventory comes from the combustion of biofuels to cook food and heat homes (20% globally, but nearly 50% in developing countries like China and India). As this combustion typically occurs indoors, reducing BC emissions could also have extraordinary benefits for human health. Many affordable technologies already exist that would greatly reduce BC emissions, such as energy-efficient and smokeless cookers (Zhi et al., 2009). Compared to the complex technological, economic, and political considerations of reducing or capturing carbon dioxide, attacking BC emissions may represent a preferable strategy for improving both the climate and human health.

1.7 References

Barnes, D., Openshaw, K., Smith, K.R., van der Plas, R., 1994. What makes people cook with improved biomass stoves? Work Bank Technical Paper 242.

Battye, W., Boyer, K., Pace, T.G., 2002. Methods of improving global inventories of black carbon and organic carbon particulates. 11th International Emission Inventory Conference.

Beegum, S.N., Moorthy, K.K., Babu, S.S., Satheesh, S.K., Vinoj, V., Badarinath, K.V.S., Safai, P.D., Devara, P.C.S., Singh, S., Vinod, Durnka, U.C., Pant, P., 2009. Spatial distribution of aerosol black carbon over India during pre-monsoon season. Atmospheric Environment 43, 1071-1078.

Bond, T.C., Streets, D.G., Yarber, K.F., Nelson, S.M., Woo, J.H., Klimont, Z., 2004. A technology-based global inventory of black and organic carbon emissions from combustion. Journal of Geophysical Research-Atmospheres 109.

Calcabrini, A., Meschini, S., Marra, M., Falzano, L., Colone, M., De Berardis, B., Paoletti, L., Arancia, G., Fiorentini, C., 2004. Fine environmental particulate engenders alterations in human lung epithelial A549 cells. Environmental Research 95, 82-91.

Chow, J.C., Watson, J.G., Green, M.C., Lowenthal, D.H., Bates, B., Oslund, W., Torres, G., 2000. Cross-border transport and spatial variability of suspended particles in Mexicali and California's Imperial Valley. Atmospheric Environment 34, 1833-1843.

Chow, J.C., Watson, J.G., Lowenthal, D.H., Chen, L.W.A., Motallebi, N., 2010. Black and Organic Carbon Emission Inventories: Review and Application to California. Journal of the Air & Waste Management Association 60, 497-507.

Hansen, A.D.A., 2003. The Aethalometer. Magee Scientific Co.

Jacobson, M.Z., 2002. Control of fossil-fuel particulate black carbon and organic matter, possibly the most effective method of slowing global warming. Journal of Geophysical Research 107, D19. doi: 10.1029/2001JD001376.

Jiang, M., Marr, L.C., Dunlea, E.J., Herndon, S.C., Jayne, J.T., Kolb, C.E., Knighton, W.B., Rogers, T.M., Zavala, M., Molina, L.T., Molina, M.J., 2005. Vehicle fleet emissions of black carbon, polycyclic aromatic hydrocarbons, and other pollutants measured by a mobile laboratory in Mexico City. Atmospheric Chemistry and Physics 5, 3377-3387.

Kelly, K., Wagner, D., Lighty, J., Nunez, M.Q., Vazquez, F.A., Collins, K., Barud-Zubillaga, A., 2006. Black carbon and polycyclic aromatic hydrocarbon emissions from vehicles in the United States-Mexico border region: Pilot study. Journal of the Air & Waste Management Association 56, 285-293.

Malm, W.C., Gebhart, K.A., Henry, R.C., 1990. An Investigation of the Dominant Source Regions of Fine Sulfur in the Western United-States and Their Areas of Influence. Atmospheric Environment Part a-General Topics 24, 3047-3060.

Menon, S., Hansen, J., Nazarenko, L., Luo, Y.F., 2002. Climate effects of black carbon aerosols in China and India. Science 297, 2250-2253.

Park, R.J., Jacob, D.J., Kumar, N., Yantosca, R.M., 2006. Regional visibility statistics in the United States: Natural and transboundary pollution influences, and implications for the Regional Haze Rule. Atmospheric Environment 40, 5405-5423.

Penner, J.E., Eddleman, H., Novakov, T., 1993. Towards the Development of a Global Inventory for Black Carbon Emissions. Atmospheric Environment Part a-General Topics 27, 1277-1295.

Ramanathan, V., Carmichael, G., 2008. Global and regional climate changes due to black carbon. Nature Geoscience 1, 221-227.

Renwick, L.C., Donaldson, K., Clouter, A., 2001. Impairment of alveolar macrophage phagocytosis by ultrafine particles. Toxicology and Applied Pharmacology 172, 119-127.

Shi, C.N., Fernando, H.J.S., Yang, J., 2009. Contributors to ozone episodes in three US/Mexico border twin-cities. Science of the Total Environment 407, 5128-5138.

United States Environmental Protection Agency (EPA), 1996. Air quality criteria for particulate matter. EPA/600/P-95/001.

United States Environmental Protection Agency (EPA) and Secreteria de Medio Ambiente y Recursos Naturales (SEMARNAT), 2005. Border 2012: US Mexico Environmental Program Indicators Report.

Zavala, M., Herndon, S.C., Wood, E.C., Jayne, J.T., Nelson, D.D., Trimborn, A.M., Dunlea, E., Knighton, W.B., Mendoza, A., Allen, D.T., Kolb, C.E., Molina, M.J., Molina, L.T., 2009. Comparison of emissions from on-road sources using a mobile laboratory under various driving and operational sampling modes. Atmospheric Chemistry and Physics 9, 1-14.

Zhi, G.R., Peng, C.H., Chen, Y.J., Liu, D.Y., Sheng, G.Y., Fu, J.M., 2009. Deployment of Coal Briquettes and Improved Stoves: Possibly an Option for both Environment and Climate. Environmental Science & Technology 43, 5586-5591.

Chapter 2

Sources and Transport of Black Carbon at the United States-Mexico Border near San Diego-Tijuana

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2.1 Abstract

At international border areas that suffer from poor quality, assessment of pollutant sources and transport across the border is important for designing effective air quality management strategies. As part of the Cal-Mex 2010 field campaign at the US-Mexico border in San Diego and Tijuana, we measured black carbon (BC) concentrations at three locations in Mexico and one in the United States. The measurements were intended to support the following objectives: to characterize the spatial and temporal variability in BC concentrations and emissions in the border region, to identify potential source areas of BC emissions, and to characterize the cross-border transport of BC and assess its impact on local and regional air quality. BC concentrations at Parque Morelos, the campaign's supersite, averaged 2.1 μg m^{-3} and reached a maximum value of 55.9 μg m^{-3}. This average value is comparable to levels in large American cities like Los Angeles and similarly sized Mexican cities like Mexicali. The maximum value occurred near midnight, and similar incidents were observed on nearly half of the overnight monitoring periods.

BC and carbon monoxide (CO) were strongly correlated at the Mexican sites. The BC/CO ratio was ~3 times higher in Tijuana than in Mexico City, suggesting that gasoline-powered vehicles in Tijuana emit more BC than is typical or that diesel vehicles comprise a relatively high proportion of the vehicle fleet. Tijuana's emissions of BC are estimated to be 380-1470 metric tons yr^{-1}. BC measurements were used in conjunction with modeled wind fields to simulate forward and backward particle trajectories. Generally, BC in Tijuana appears to originate locally, as backward simulations showed transport from the US into Mexico at only one site. The majority of the trajectory analyses indicate that there is often transport from Tijuana into the US, crossing the border in a northeasterly direction to the east of San Diego-Tijuana and sometimes as far east as Imperial County at the eastern edge of California. These results suggest that any air quality management strategies considering BC should account for contributions from the border region, as BC is chemically inert in the atmosphere and can travel up to thousands of kilometers.

2.2 Introduction

Growing population and industrial activity along the US-Mexico border have led to environmental stresses in both countries (Chow et al., 2000). The border region comprises 14 pairs of inter-dependent "sister-cities" containing 90% of the 14 million border area residents. Since the passage of the North American Free Trade Agreement in 1993, the border region has experienced a rapid increase of manufacturing plants (maquiladoras), transportation activity, and age of the vehicle fleet (Shi et al., 2009). Continued growth in the population and industrial development in this region is expected to strain environmental resources, including air quality. Between 2001 and 2005, the sister-city pair of San Diego-Tijuana exceeded the 8-h air quality standard for ozone of 80 ppb on average 15 days per year and the 24-h standard for coarse

particulate matter (PM_{10}) of 150 µg m^{-3} on average 7 days per year (US EPA and SEMARNAT, 2005).

Although less information is available about BC compared to the criteria pollutants, which have national standards, it is of increasing concern because of its impacts on both climate and health. Its radiative forcing is estimated to be +0.9 W m^{-2} (with a range of +0.4 to +1.2 W m^{-2}), second only to carbon dioxide (Ramanathan and Carmichael, 2008), and it has been linked to respiratory and cardiovascular health effects (Peters et al., 2000; Gauderman et al., 2004; Kim et al., 2004; Gold et al., 2005; O'Neill et al., 2005). Because of these dual effects and because of its shorter lifetime in the atmosphere compared to carbon dioxide, it is an excellent target for emissions reductions (Jacobson, 2010). Given the status of ozone and PM_{10} in the US-Mexico border cities, it is likely that BC is also problematic in the region.

Air quality and pollutant emissions have been found to differ in the short distance across the US-Mexico border. Two studies of BC in the sister-city pair of Calexico-Mexicali found that BC was ~1.5 times greater in Mexicali, which is on the Mexican side of the border, and that Mexicali exceeded the PM_{10} standard 23 times during the study, while Calexico only exceeded the standard three times (Chow et al., 2000 and Kelly et al., 2006). Kelly et al. (2006) also measured BC in the sister-city pair of El Paso-Ciudad Juarez and found that it was ~3.8 times higher in Ciudad Juarez, which is on the Mexican side of the border. Previous work comparing motor vehicle emissions in Mexicali and Austin, Texas showed that Mexicali's fleet is significantly more polluting than that of other cities, probably due to the older average age of the vehicles (Zavala et al., 2009). Only a few studies have been conducted on the cross-border transport of pollutants, and none have considered BC. The previous work does suggest, however, that cross-border transport is likely to have significant impacts on air quality (Malm et al., 1990 and Park et al., 2006).

Reducing BC emissions and improving air quality in the border region require an improved understanding of BC's spatial patterns, sources, and transport. The overall objective of this research is to assess emissions of BC and its transport in the California-Mexico border region. The assessment is based on measurements of BC and carbon monoxide (CO) at four sites during the Cal-Mex 2010 field campaign, and on trajectory modeling of particle transport. The specific objectives of the research are to characterize the spatial and temporal variability in BC concentrations and emissions in the border region, to identify potential source areas of BC emissions, and to characterize the cross-border transport of BC and assess its impact on local and regional air quality.

2.3 Experimental

2.3.1 Field Campaign

Measurements were conducted as part of the Cal-Mex 2010 field campaign, a multi-institutional collaborative effort between scientists and agencies in the US and Mexico, whose main objective was to improve the understanding of emissions and air quality along the California-Mexico border. The campaign was designed to complement the large CalNex 2010 study of air quality and climate change in California. The campaign ran for six weeks in June and July 2010 and focused on the sister-city pair of San Diego-Tijuana.

The measurements described in this research were conducted at four urban locations: a parking lot near a major border crossing in Otay Mesa, California (32.55º N, 116.94º W, 158.0 m msl); a municipal park, Parque Morelos, in central Tijuana, Mexico (32.50º N, 116.94º W, 43.0 m msl); the Universidad de Technológica de Tijuana in southeast Tijuana (32.36º N, 116.83º W, 159.1

m msl); and a museum, El Trompo, in central Tijuana (32.49º N, 116.94º W, 47.0 m msl) just several hundred meters away from Parque Morelos. Measurements took place on 21-27 May at Otay Mesa, 29 May-7 June at Parque Morelos, 8-15 June at the Technológica de Tijuana (UTT), and 17-22 June at El Trompo. A map of the monitoring locations is shown in Figure 2.1.

2.3.2 BC and CO Measurements

A mobile laboratory designed to conduct eddy covariance measurements was deployed during the Cal-Mex 2010 research campaign. It was equipped with a comprehensive suite of fast-response instruments for gases and particles, including an aethalometer (AE-51, Magee Scientific, Berkeley, CA) that measures BC. The aethalometer determines the mass concentration of BC particles by light absorption at a wavelength of 0.88 µm. The instrument continuously collects particles on a filter and measures the change in its transmittance. The mass concentration is obtained from the incremental attenuation between two subsequent measurements using the known mass absorption cross-section of BC (16.6 m^2 g^{-1} at 0.88 µm). When connected to the supplemental pump, the aethalometer is advertised to employ a flow rate of 1 l min^{-1} in order to support a 1-s response time, but in our experience, the actual flow rate is ~0.4 l min^{-1}.

During the daytime, between ~8:00-18:00, BC was sampled from the top of the mobile laboratory's mast, 15 m above ground, and the aethalometer was programmed to record at 1-s intervals. During the nighttime, when the mobile laboratory was not deployed, BC was instead sampled at a height of 2 m above ground, and the aethalometer was programmed to record at 1-min intervals. At Otay Mesa, power was not available at nighttime, so measurements were not

possible. At El Trompo, power was also not available at nighttime, so measurements were taken at nearby Parque Morelos.

CO was measured by infrared absorption (Teledyne 300E, Thousand Oaks, CA). Although the instrument was calibrated in accordance with the manufacturer's recommendations prior to initiating measurements at each sampling location, measurements suggested that an additional offset was needed. We compared our CO measurements against those of three other groups, some co-located and others at routine air quality monitoring sites in Tijuana, and determined that an offset of +0.7 ppm was optimal.

2.3.3 Modeling

To evaluate transport across the US-Mexico border, as well as identify potential source areas, particle dispersion simulations were conducted using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model, version 4 (Draxler, 1992). Three-dimensional wind fields from Weather Research and Forecasting (WRF) model output, supplied by the Environmental Protection Agency (EPA), were used to drive HYSPLIT. The WRF data were available every hour on a 4-km grid with 35 vertical levels. To assess potential source areas and cross-border transport, 24-h backward and forward trajectories were constructed for every hour of BC measurements. For each trajectory, 100 particles were released at 15 m above ground and tracked hourly for 24 subsequent hours. Model simulations for Otay Mesa were conducted only for daytime hours. Model simulations for El Trompo utilized nighttime data taken from nearby Parque Morelos.

The default parameters of HYSPLIT were used except for the minimum mixing depth (kmix0). This parameter is related to the typical vertical resolution of the meteorological data, which is

assumed to be 25 hPa near the surface. The default value of 250 m indicates that the model cannot infer a mixed layer depth of less than 250 m (Draxler, 1998). The WRF data provided by EPA had a vertical resolution greater than that assumed by HYSPLIT, and therefore kmix0 was reduced to 100 m.

To visualize results from the particle dispersion simulations, residence time and concentration field analyses (Ashbaugh et al., 1985; Seibert et al., 1994; de Foy et al., 2007) were prepared. Each set of released particles was tracked hourly, and particle coordinates were assigned to the nearest grid cell. Summing these backward and forward trajectories over a grid produces a time exposure image that indicates where the wind was coming from or going to, respectively, over multiple hours. The residence time analysis (RTA) is a grid of probabilities that represent the likelihood that an air parcel traveled through the cell.

The concentration field analysis (CFA) is the product of the RTA and average hourly BC concentration at the monitoring location corresponding to each hour of particle release in the model. The CFA thus weights each hourly emission cycle by pollutant concentration and can reveal potential source areas or transport paths associated with high pollutant levels (Thornhill et al., 2008). One limitation to the CFA is that the method is not able to distinguish between different points along the release path. As such, the method is sensitive to direction but not distance (de Foy et al., 2007).

Probabilities were normalized to the 99^{th} percentile to reduce bias from BC concentration outliers. Backward trajectory analyses were plotted over a 50 km x 50 km area on a linear scale. Forward trajectory analyses were plotted over a larger 150 km x 150 km area on a log scale, as probability values decreased rapidly away from the receptor site. Finally, mapping software

(Surfer, Golden Software, Golden, CO) was used to develop contours based on each grid cell's RTA or CFA probability value.

2.4 Results

2.4.1 BC

Figure 2.2 displays time series of BC concentrations, 10-min averages, at the four monitoring sites. The highest concentrations were observed at Parque Morelos, which averaged 2.1 ± 1.8 μg m^{-3} during the campaign. The averages at Otay Mesa, UTT, and El Trompo were 0.8 ± 0.6, 1.9 ± 1,7, and 1.8 ± 1.5 μg m^{-3}, respectively. The average at Otay Mesa is for daytime measurements only.

Strong diurnal patterns were observed at all four sites, with average peak hourly concentrations of 1.2 μg m^{-3} occurring at 7:00 at Otay Mesa on the US side of the border and 4.5, 3.8, and 4.9 μg m^{-3} occurring at 8:00 at Parque Morelos, UTT, and El Trompo, respectively, on the Mexican side. There was no obvious day-of-week dependence of the hourly peaks, although those at Parque Morelos and El Trompo were slightly higher on weekends. Typically, such concentrations would be lower on weekends in urban areas, but massively increased use of Parque Morelos (a popular, ~4-km^2 park that features picnic areas, a lake, a zoo, children's rides, and a food court) on Saturdays and Sundays probably resulted in increased emissions on those days.

Large spikes in BC were observed during six of the sixteen overnight sampling events at Parque Morelos and one of the six nights at UTT. The maximum 1-min concentrations ranged from 12

to 56 μg m^{-3}, with an average peak of ~26 μg m^{-3}. The maximum 10-min concentrations ranged from approximately 8 to 46 μg m^{-3}, with an average peak of ~18 μg m^{-3}. The peaks tended to occur between 22:00 and 1:00 and lasted from 4 to 28 min, with an average duration of ~13 min (with the extent of the peak defined by half of the maximum concentration). For the ambient atmosphere, these levels are extremely high, comparable to occupational exposures in workplaces dominated by diesel engine exhaust emissions, such as bus repair shops and tollbooths (Groves et al., 2000 and Lewne et al., 2007). As hypothesized for some pollutants in Mexico City (Fortner et al., 2009), the nighttime peaks may be due to increased industrial activity. Some illegal emissions are suspected to occur at nighttime because they are more likely to escape detection.

Figure 2.3 shows the correlations between BC and CO at each of the sites. Because motor vehicles are the source of almost all CO emissions, this relationship illuminates whether BC emissions are likely to be associated with vehicles or with other sources. BC and CO were strongly correlated at all of the Mexican sites, where R^2 values were 0.71-0.86, but weakly correlated at the American site, where R^2 was 0.13.

BC/CO ratios were also calculated for each site from ~8:30 to 10:00, the morning hours when emissions were fresh and not yet subject to photochemical processing. This ratio has been suggested to depend on the mix of incomplete combustion sources and also fleet age and condition (Kirchstetter et al., 1999 and Baumgardner et al., 2002). The average BC/CO ratios and standard deviations at Otay Mesa, Parque Morelos, UTT, and El Trompo were 1.2 ± 0.6, 2.6 ± 1.0, 3.8 ± 1.7, and 3.0 ± 1.1 μg m^{-3} ppm^{-1}, respectively. The ratio was at least 50% lower at Otay Mesa compared to the Mexican sites.

2.4.2 Meteorology

Based on the WRF model output, wind roses were generated for each of the monitoring locations during the dates when measurements were conducted there. Shown in Figures 2.4-2.8, the wind roses indicate a mainly westerly direction, consistent with onshore flow typical of this region. At Otay Mesa, winds were most often from the west and southwest, but winds from all directions except the northeast were fairly common. The strongest winds observed during the campaign were from the west at Otay Mesa. At Parque Morelos, winds were more consistent and originated from the southwest and west-southwest, with the strongest winds from the southwest. At UTT, the majority of the winds were west-northwesterly with contributions from the southwest and west-southwest. Strong winds were evenly distributed across these directions at UTT. At El Trompo, winds usually originated from the west and west-northwest, while the strongest winds were from the southwest. Finally, a shift in wind direction was observed on most days, particularly at Otay Mesa and UTT, with daytime winds tending to be southwesterly and even southeasterly and shifting toward westerly and northwesterly at nighttime.

2.4.3 Residence Time Analyses and Concentration Field Analyses

Figure 2.4 shows the wind rose, BC concentration rose, residence time analysis plot, and BC concentration field analysis plot for backward trajectories at Otay Mesa. The winds were predominantly from the west and southwest, and the RTA shows the majority of air parcels originating directly from the west. The concentration rose shows that BC originated from various directions; the highest concentrations, those above 1.3 μg m^{-3}, were not associated with any particular wind direction. The CFA closely resembles the RTA. As the winds were consistently

from the west, weighting the probability of each grid cell by concentration had a limited effect. BC observed here was probably emitted by local sources, not surprising given the large amount of traffic passing through this area.

Figure 2.5 is the same as Figure 2.4 but for Parque Morelos. While the wind rose indicates that the winds were from the southwest, the RTA indicates that the area around Parque Morelos was often an inflection point, where southerly winds turned westerly and southwesterly. Examination of wind field vectors confirmed these modeling results. As at Otay Mesa, the RTA and CFA were very similar. Sources to the immediate southwest of Parque Morelos included motor vehicle traffic along a major highway, Via Rápida.

Figure 2.6 shows an RTA and CFA for overnight hours when large spikes were measured at Parque Morelos (29 May 22:00 - 30 May 2:00, 30 May 20:00 - 23:00, 31 May 21:00 - 22:00, 2 June 23:00 - 3 June 1:00, and 4 June 20:00 - 5 June 2:00). This analysis shows that while the majority of the winds were southerly, as shown in Figure 2.5, BC spikes were consistently associated with more westerly transport. For contrast, Figure 2.6 also shows an RTA and CFA for overnight hours when spikes of BC were not observed at Parque Morelos (1 June 22:00 – 2 June 2:00, 5 June 22:00 – 6 June 2:00, and 6 June 22:00 – 7 June 2:00). This analysis shows that overnight winds were often northeasterly during these periods.

Figure 2.7 is the same as Figure 2.4 but for UTT. The wind rose indicates that the winds were predominantly westerly, but the concentration rose indicates that the highest BC concentrations, though infrequent, were associated with southeasterly winds. A federal highway connecting Tijuana and Tecate lies to the southeast, and its vehicle traffic may have been the cause of elevated BC concentrations. The RTA shows the majority of air parcels originating directly from the west. The CFA shows a similar result but with slightly greater contributions from the

southeast as well as the northwest, back toward the center of Tijuana, as UTT is located at the southeastern edge of the city.

Figure 2.8 is the same as Figure 2.4 but for El Trompo. The wind rose indicates that the winds were predominantly westerly and northwesterly, but the RTA shows that the majority of the winds were only from the northwest. The strong winds from the southwest are also evident in the RTA. The concentration rose indicates that the highest BC concentrations were evenly distributed. The CFA is thus similar to the RTA, except southwesterly winds were not a factor, as the strong winds from that direction were not associated with high BC concentrations. As both Parque Morelos and El Trompo were located within the same cell of the WRF modeling grid, differences between the two locations are due to the timing of the measurements. Those at El Trompo took place more than a week later than those at Parque Morelos, and wind patterns were evidently different then.

Figure 2.9 shows the modeling results for forward trajectories at all sites. As weighting by BC concentrations had little effect on the CFA plots, only RTA plots are shown. At Otay Mesa, winds were distributed among several directions, but northwesterly winds did transport air parcels from the US into Mexico. At Parque Morelos, the winds were predominantly from the south, and the forward trajectories show that air moved northward across the international border. Transport then continued north into the US, several kilometers past Otay Mesa, before proceeding to the east. At UTT and El Trompo, winds were predominantly from the west and crossed the border into the US in a northeasterly direction.

2.5 Discussion

Average concentrations of BC in Tijuana ranged from 1.8 to 2.1 μg m^{-3}, comparable to those in similarly sized Mexican cities like Mexicali and larger American cities like Los Angeles (US EPA, 1996 and Chow et al., 2000). The average value of BC at Otay Mesa (0.8 μg m^{-3}) was ~61% less than the average daytime (7:00-18:00) concentration at the Mexican sites, despite Otay Mesa's proximity to a major border crossing ~200 m the southwest. However, this border crossing was limited to passenger vehicles only, mostly light-duty gasoline-powered vehicles, which typically emit very low amounts of BC (Thornhill et al., 2010). Heavy-duty diesel trucks, which typically emit much higher amounts of BC, crossed the border at a different location to the east and downwind.

The large spikes in BC observed at Parque Morelos around midnight likely originated nearby, as the sudden, significant, and short-lived patterns suggest that the emissions did not have time to be diluted. Backward trajectory modeling and concentration field analysis of these BC spikes indicate that the source is to the west-southwest of the site. As previously mentioned, one hypothesis is that the spikes are associated with clandestine industrial activity. On nights when spikes of BC were not observed, winds were mostly northeasterly, so large emissions may still have been occurring even though spikes in BC were not observed. In a model of industrial air pollution generation in Tijuana (Obee et al., 1998), Parque Morelos falls within the industrial pollution area identified as La Mesa Corridor. It is likely that the source of the BC observed at midnight originated from this area.

The BC/CO ratio of 3.1 μg m^{-3} ppm^{-1} in Tijuana, averaged across the three sites, fell within the range of those found elsewhere in the world: 6.0, 4.1, and 1.3 μg m^{-3} ppm^{-1} in Tokyo, Japan (Kondo et al., 2006); Fort Meade, Maryland (Chen et al., 2001); and Mexico City (Subramanian

et al., 2010), respectively. The ratio at Otay Mesa was ~2.6 times lower than at the Mexican sites. While BC concentrations at Otay Mesa were indeed lower (~61%) on average than at the Mexican sites, CO concentrations at Otay Mesa were relatively high (~2.8 times greater than the Mexican average), thus producing the low BC/CO ratio. As discussed earlier, the segregation of passenger vehicles, which are usually gasoline-powered, from heavy-duty diesel trucks at the Otay Mesa border crossing helps to explain why BC concentrations were low, CO concentrations were high, and the two pollutants were poorly correlated.

Nearly all CO emissions are usually attributed to gasoline-powered vehicles, while BC emission factors are much higher in diesel-powered vehicles (Thornhill et al., 2010). While this suggests that the relationship of BC to CO is most dependent on the fraction of fuel that is diesel, some factors can complicate this relationship, such as decreased combustion efficiency related to geographic and socioeconomic factors that tend to increase emissions of both pollutants, but in unknown proportions (Baumgardner et al., 2002). In addition, BC emissions have been found to be significant from gasoline-powered motor vehicles under some conditions, such as cold-start ignition, hard acceleration, and fuel-rich combustion (Robert et al., 2007 and Kleeman et al., 2008). Nevertheless, these results seem to suggest that gasoline-powered vehicles in Tijuana emit more BC than those in Mexico City or that diesel-powered vehicles comprise a larger proportion of the fleet.

BC in Tijuana appears to originate locally, as the modeling results indicate that there is typically not much transport across the border from the US into Mexico. Backward trajectory modeling at El Trompo and forward trajectory modeling at Otay Mesa did indicate that northwesterly winds occasionally transport air parcels into Mexico. The majority of the backward and forward trajectory analyses indicate, however, that there is usually transport from Tijuana into the US, sometimes directly from the south but often entering in a northeasterly direction east of San

Diego-Tijuana and sometimes as far east as Imperial County at the eastern edge of California. The sister-city pair of Imperial Valley-Mexicali has the worst PM_{10} problem of all the border region's metropolitan areas, exceeding the standard on average ~49 days per year between 2001-2005 (US EPA and SEMARNAT, 2005). BC transport from Tijuana may be a contributing factor to this problem.

Total emissions of BC in Tijuana can be estimated based on current knowledge of CO emissions and the BC/CO ratio measured during the field campaign. According to the most recent official emission inventory, CO emissions in Tijuana and the neighboring resort city of Rosarito were 299,691 metric tons yr^{-1} in 1998 (Gobierno del Estado de Baja California et al., 2000). Collaborators in the Cal-Mex 2010 field campaign estimate the emission inventory of CO to have been 77,216 metric tons yr^{-1} in 2005, a decrease of 74% from 1998 that may either be real or an artifact of changes in methods used to develop the inventory. The uncertainty associated with either estimate of CO emissions is unknown. The BC/CO ratio observed at three sites in Tijuana in units of mass of BC per mass of CO is 0.0049 ± 0.0004 g BC g^{-1} CO. Tijuana's emissions of BC, estimated as the product of the city's CO emissions and the BC/CO ratio, are thus 1470 ± 120 or 380 ± 30 metric tons per year, depending on which estimate of CO emissions is used. Nearly all of this is transported into California, but it is at most 3% of the estimated statewide BC emissions of 47,250 metric tons yr^{-1} (Chow et al., 2010). If the spatial distribution of BC emissions in California is proportional with population, then emissions in San Diego County are ~3900 metric tons yr^{-1}, and Tijuana-Rosarito's contribution to BC emissions would be 10-38% of San Diego's.

The dominant source of uncertainty in this analysis is the fidelity of the wind fields produced by the WRF model. At Parque Morelos, winds measured by the mobile laboratory's anemometer differed from model predictions. Observed winds were generally from the northwest, as opposed

to the southwest. At the other three sites, the observations and predictions were generally in agreement. Additionally, this analysis is based on just one month of the year. The climate in this area is relatively steady throughout the year, but different meteorological patterns occur on occasion and would produce different conclusions regarding pollutant transport.

2.6 Conclusions

An analysis of the spatial and temporal variations of BC concentrations in the border region near San Diego-Tijuana was conducted using continuous measurements from a network of four monitoring locations: Otay Mesa in the US and Parque Morelos, UTT, and El Trompo in Mexico. The average values of BC at the sites were 0.8, 2.1, 1.9, and 1.8 μg m^{-3}, respectively. The strong correlation of BC with CO at the Mexican sites suggests that motor vehicles are a dominant source. BC/CO ratios ranged from 1.2 to 3.8 μg m^{-3} ppm^{-1} and were highest at the Mexican sites. Ratios in Tijuana were ~3 times higher than in Mexico City, suggesting that gasoline-powered vehicles emit more BC than is typical or that diesel vehicles comprise a larger proportion of the fleet. BC and CO correlated poorly at Otay Mesa likely because traffic was limited to gasoline-powered vehicles. Large spikes of BC as high as 56 μg m^{-3} (1-min average) were observed around midnight during several of the overnight monitoring periods and may stem from a nearby industrial park to the west-southwest of Parque Morelos. BC emissions in Tijuana and Rosarito were estimated to be 380-1470 metric tons yr^{-1}, less than half the amount emitted in San Diego County.

BC measurements were used in conjunction with forward and backward trajectory modeling to assess potential source regions and cross-border transport of BC. Winds were typically westerly, due to onshore flow typical in this region, except at Parque Morelos where they were

southerly. The consistency of the winds typically resulted in concentration field analyses that mirrored residence time analyses. Generally, BC in Tijuana appears to originate locally, as RTAs and CFAs do not show significant transport into the city. The majority of the trajectory analyses indicate that there is often transport from Tijuana into the US, sometimes directly from the south but often entering in a northeasterly direction east of San Diego-Tijuana and sometimes as far east as Imperial County at the eastern edge of California. Therefore, the majority of BC emissions in Tijuana are probably transported into the US. These results suggest that any air quality management strategies considering BC should account for contributions from the border region, as BC is inert in the atmosphere and can travel up to thousands of kilometers.

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2.8 References

Ashbaugh, L.L., Malm, W.C., Sadeh, W.Z., 1985. A Residence Time Probability Analysis of Sulfur Concentrations at Grand-Canyon-National-Park. Atmospheric Environment 19, 1263-1270.

Baumgardner, D., Raga, G., Peralta, O., Rosas, I., Castro, T., Kuhlbusch, T., John, A., Petzold, A., 2002. Diagnosing black carbon trends in large urban areas using carbon monoxide measurements. Journal of Geophysical Research-Atmospheres 107.

Calcabrini, A., Meschini, S., Marra, M., Falzano, L., Colone, M., De Berardis, B., Paoletti, L., Arancia, G., Fiorentini, C., 2004. Fine environmental particulate engenders alterations in human lung epithelial A549 cells. Environmental Research 95, 82-91.

Chen, L.W.A., Doddridge, B.G., Dickerson, R.R., Chow, J.C., Mueller, P.K., Quinn, J., Butler, W.A., 2001. Seasonal variations in elemental carbon aerosol, carbon monoxide and sulfur dioxide: Implications for sources. Geophysical Research Letters 28, 1711-1714.

Chow, J.C., Watson, J.G., Green, M.C., Lowenthal, D.H., Bates, B., Oslund, W., Torres, G., 2000. Cross-border transport and spatial variability of suspended particles in Mexicali and California's Imperial Valley. Atmospheric Environment 34, 1833-1843.

Chow, J.C., Watson, J.G., Lowenthal, D.H., Chen, L.W.A., Motallebi, N., 2010. Black and Organic Carbon Emission Inventories: Review and Application to California. Journal of the Air & Waste Management Association 60, 497-507.

de Foy, B., Lei, W., Zavala, M., Volkamer, R., Samuelsson, J., Mellqvist, J., Galle, B., Martinez, A.P., Grutter, M., Retama, A., Molina, L.T., 2007. 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. Atmospheric Chemistry and Physics 7, 781-801.

Draxler, R.R., 1992. Hybrid single-particle lagrangian integrated trajectories (HY-SPLIT): version 3.0 - user's guide and model description. NOAA Technical Memorandum ERL-ARL-195.

Draxler, R.R., Hess, G.D., 1998. Description of the HYSPLIT 4 modeling system. NOAA Technical Memorandum ERL-ARL-224.

Fortner, E.C., Zheng, J., Zhang, R., Knighton, W.B., Volkamer, R.M., Sheehy, P., Molina, L., Andre, M., 2009. Measurements of Volatile Organic Compounds Using Proton Transfer Reaction - Mass Spectrometry during the MILAGRO 2006 Campaign. Atmospheric Chemistry and Physics 9, 467-481.

Gauderman, W.J., Avol, E., Gilliland, F., Vora, H., Thomas, D., Berhane, K., McConnell, R., Kuenzli, N., Lurmann, F., Rappaport, E., Margolis, H., Bates, D., Peters, J., 2004. The effect of air pollution on lung development from 10 to 18 years of age. New England Journal of Medicine 351, 1057-1067.

Gobierno del Estado de Baja California, Gobierno Municipal de Tijuana, Instituto Municipal de Planeación, Gobierno Municipal de Playas Rosarito, Delegacón Federal Semarnap, SEMARNAP, 2000. Programa Para Mejorar la Calidad del Aire: Tijuana-Rosarito 2000-2005.

Gold, D.R., Litonjua, A.A., Zanobetti, A., Coull, B.A., Schwartz, J., MacCallum, G., Verrier, R.L., Nearing, B.D., Canner, M.J., Suh, H., Stone, P.H., 2005. Air pollution and ST-segment depression in elderly subjects. Environmental Health Perspectives 113, 883-887.

Groves, J.Cain,, J.R., 2000. A survey of exposure to diesel engine exhaust emissions in the workplace. Annals of Occupational Hygiene 44, 435-447.

Jacobson, M.Z., 2010. Short-term effects of controlling fossil-fuel soot, biofuel soot and gases, and methane on climate, Arctic ice, and air pollution health. Journal of Geophysical Research 115, D14209. doi: 10.1029/2009JD013795.

Kelly, K., Wagner, D., Lighty, J., Nunez, M.Q., Vazquez, F.A., Collins, K., Barud-Zubillaga, A., 2006. Black carbon and polycyclic aromatic hydrocarbon emissions from vehicles in the United States-Mexico border region: Pilot study. Journal of the Air & Waste Management Association 56, 285-293.

Kim, J.J., Smorodinsky, S., Lipsett, M., Singer, B.C., Hodgson, A.T., Ostro, B., 2004. Traffic-related air pollution near busy roads - The East Bay children's respiratory health study. American Journal of Respiratory and Critical Care Medicine 170, 520-526.

Kleeman, M.J., Riddle, S.G., Robert, M.A., Jakober, C.A., 2008. Lubricating oil and fuel contributions to particulate matter emissions from light-duty gasoline and heavy-duty diesel vehicles. Environmental Science & Technology 42, 235-242.

Kirchstetter, T.W., Harley, R.A., Kreisberg, N.M., Stolzenburg, M.R., Hering, S.V., 1999. On-road measurement of fine particle and nitrogen oxide emissions from light- and heavy-duty motor vehicles. Atmospheric Environment 33, 2955-2968.

Kondo, Y., Komazaki, Y., Miyazaki, Y., Moteki, N., Takegawa, N., Kodama, D., Deguchi, S., Nogami, M., Fukuda, M., Miyakawa, T., Morino, Y., Koike, M., Sakurai, H., Ehara, K., 2006. Temporal variations of elemental carbon in Tokyo. Journal of Geophysical Research-Atmospheres 111, D12205. doi: 10.1029/2005JD006257.

Lewne, M., Plato, N., Gustavsson, P., 2007. Exposure to particles, elemental carbon and nitrogen dioxide in workers exposed to motor exhaust. Annals of Occupational Hygiene 51, 693-701.

Malm, W.C., Gebhart, K.A., Henry, R.C., 1990. An Investigation of the Dominant Source Regions of Fine Sulfur in the Western United-States and Their Areas of Influence. Atmospheric Environment Part a-General Topics 24, 3047-3060.

O'Neill, M.S., Veves, A., Zanobetti, A., Sarnat, J.A., Gold, D.R., Economides, P.A., Horton, E.S., Schwartz, J., 2005. Diabetes enhances vulnerability to particulate air pollution - Associated impairment in vascular reactivity and endothelial function. Circulation 111, 2913-2920.

Park, R.J., Jacob, D.J., Kumar, N., Yantosca, R.M., 2006. Regional visibility statistics in the United States: Natural and transboundary pollution influences, and implications for the Regional Haze Rule. Atmospheric Environment 40, 5405-5423.

Peters, A., Liu, E., Verrier, R.L., Schwartz, J., Gold, D.R., Mittleman, M., Baliff, J., Oh, J.A., Allen, G., Monahan, K., Dockery, D.W., 2000. Air pollution and incidence of cardiac arrhythmia. Epidemiology 11, 11-17.

Ramanathan, V., Carmichael, G., 2008. Global and regional climate changes due to black carbon. Nature Geoscience 1, 221-227.

Renwick, L.C., Donaldson, K., Clouter, A., 2001. Impairment of alveolar macrophage phagocytosis by ultrafine particles. Toxicology and Applied Pharmacology 172, 119-127.

Robert, M.A., VanBergen, S., Kleeman, M.J., Jakober, C.A., 2007. Size and composition distributions of particulate matter emissions: Part 1 - Light-duty gasoline vehicles. Journal of the Air & Waste Management Association 57, 1414-1428.

Seibert, P., Kromp-Kolb, H., Baltensperger, U., Jost, D.T., Schikowski, M., 1994. Trajectory analysis of high-alpine air pollution data. Air Pollution Modelling and its Application X, 595-596.

Shi, C.N., Fernando, H.J.S., Yang, J., 2009. Contributors to ozone episodes in three US/Mexico border twin-cities. Science of the Total Environment 407, 5128-5138.

Subramanian, R., Kok, G.L., Baumgardner, D., Clarke, A., Shinozuka, Y., Campos, T.L., Heizer, C.G., Stephens, B.B., de Foy, B., Voss, P.B., Zaveri, R.A., 2010. Black carbon over Mexico: the effect of atmospheric transport on mixing state, mass absorption cross-section, and BC/CO ratios. Atmospheric Chemistry and Physics 10, 219-237.

Thornhill, D.A., de Foy, B., Herndon, S.C., Onasch, T.B., Wood, E.C., Zavala, M., Molina, L.T., Gaffney, J.S., Marley, N.A., Marr, L.C., 2008. Spatial and temporal variability of

particulate polycyclic aromatic hydrocarbons in Mexico City. Atmospheric Chemistry and Physics 8, 3093-3105.

Thornhill, D.A., Williams, A.E., Onasch, T.B., Wood, E., Herndon, S.C., Kolb, C.E., Knighton, W.B., Zavala, M., Molina, L.T., Marr, L.C., 2010. Application of positive matrix factorization to on-road measurements for source apportionment of diesel- and gasoline-powered vehicle emissions in Mexico City. Atmospheric Chemistry and Physics 10, 3629-3644.

United States Environmental Protection Agency (EPA), 1996. Air quality criteria for particulate matter. EPA/600/P-95/001.

United States Environmental Protection Agency (EPA) and Secreteria de Medio Ambiente y Recursos Naturales (SEMARNAT), 2005. Border 2012: US Mexico Environmental Program Indicators Report.

Zavala, M., Herndon, S.C., Wood, E.C., Jayne, J.T., Nelson, D.D., Trimborn, A.M., Dunlea, E., Knighton, W.B., Mendoza, A., Allen, D.T., Kolb, C.E., Molina, M.J., Molina, L.T., 2009. Comparison of emissions from on-road sources using a mobile laboratory under various driving and operational sampling modes. Atmospheric Chemistry and Physics 9, 1-14.

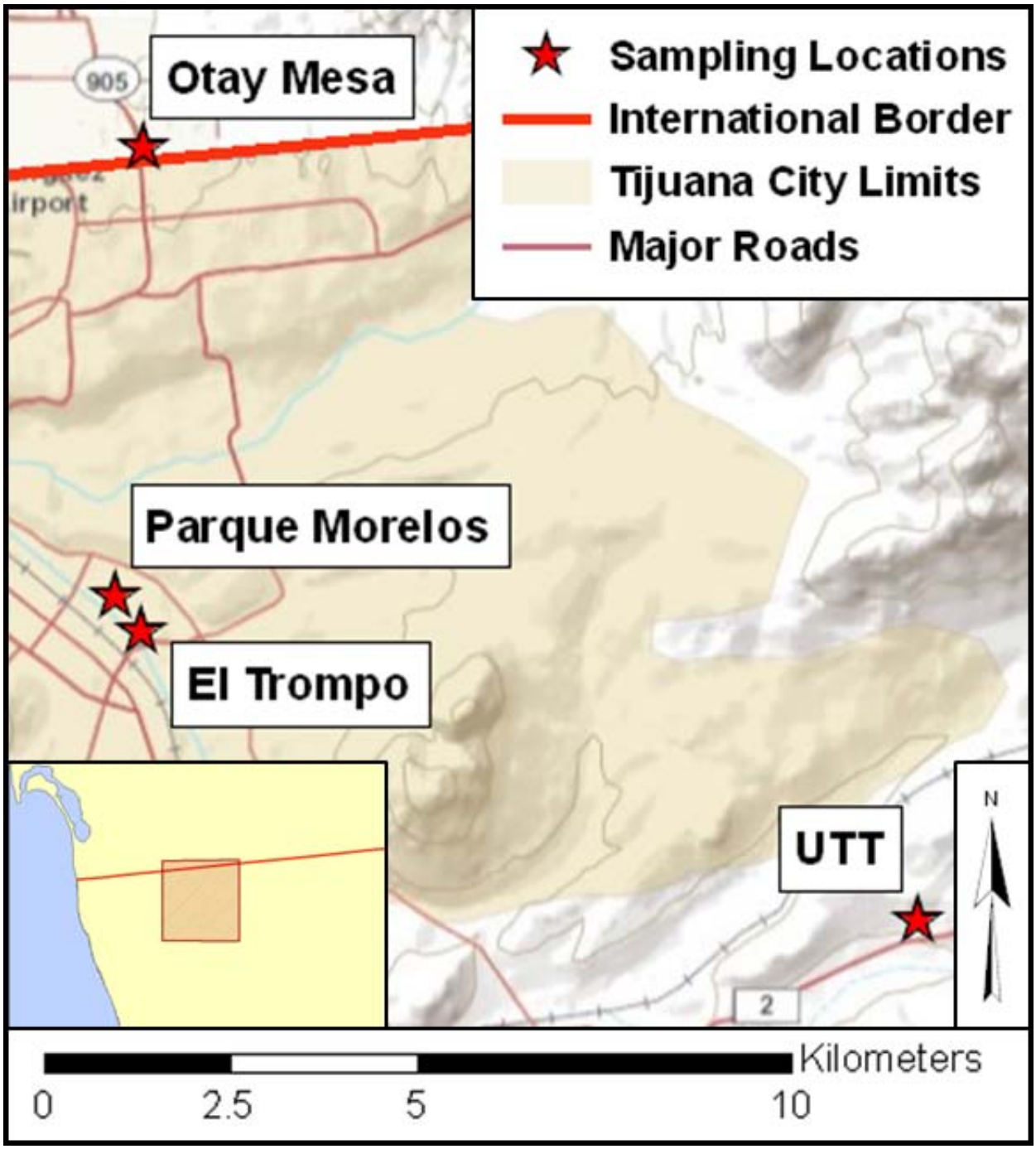

Figure 2.1. Map showing sampling locations.

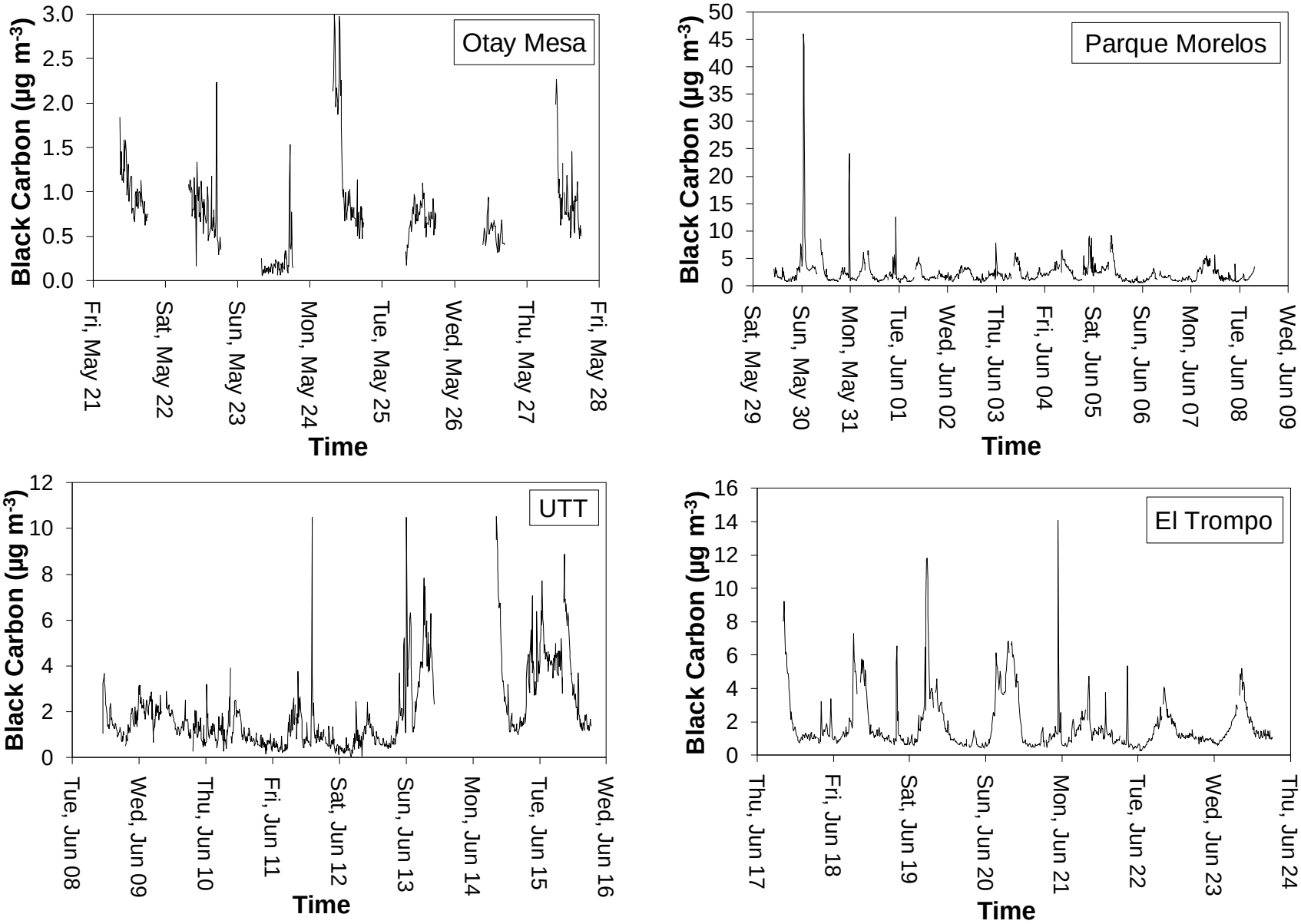

Figure 2.2. 10-min average BC concentrations at each site. Tick marks on the x-axes correspond to midnight.

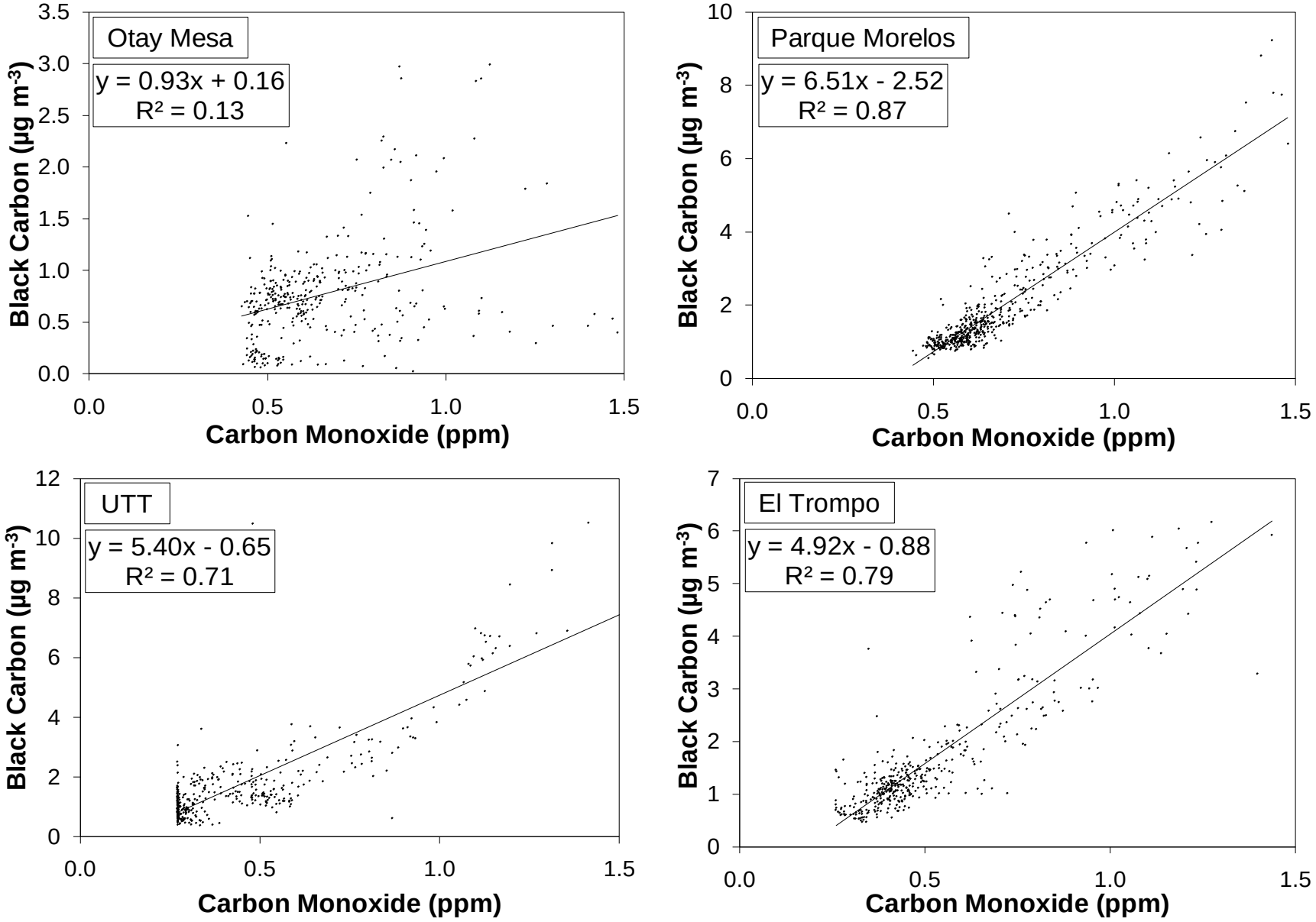

Figure 2.3. BC v. CO at each site.

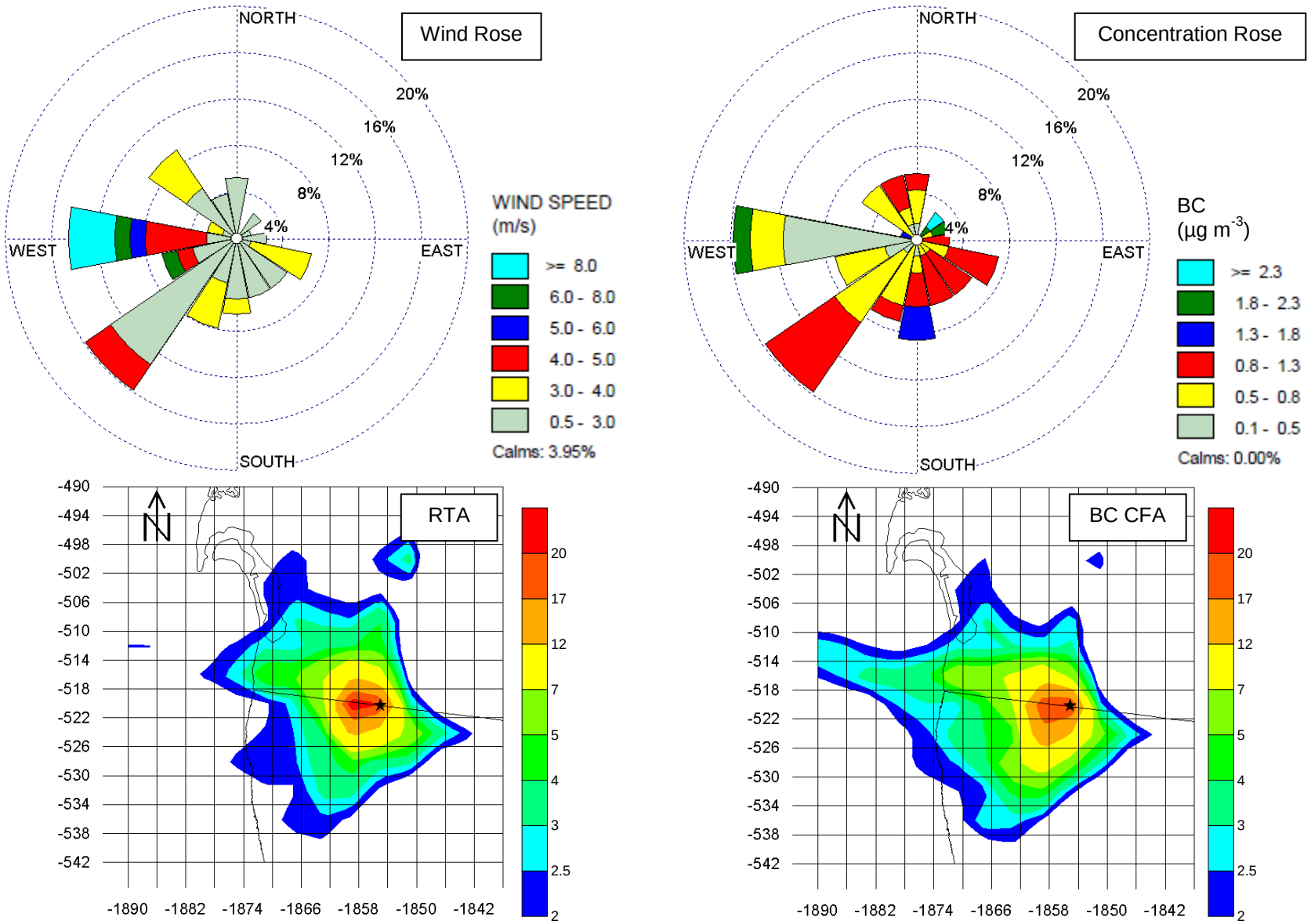

Figure 2.4. Wind rose, BC concentration rose, RTA, and BC CFA for backward simulations at Otay Mesa. Axes labels on maps are in kilometers, relative to the center of the map projection.

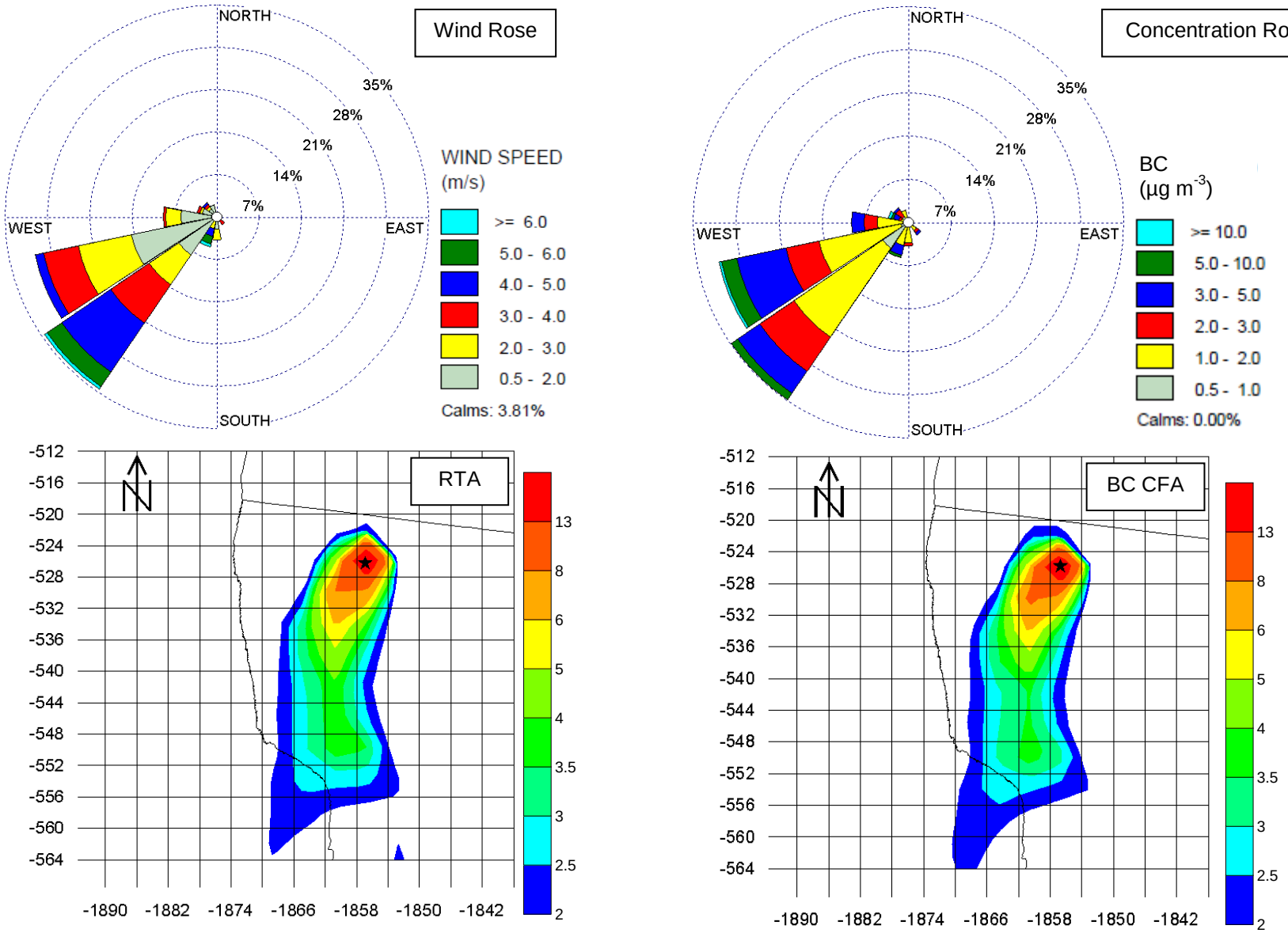

Figure 2.5. Wind rose, BC concentration rose, RTA, and BC CFA for backward simulations at Parque Morelos. Axes labels on maps are in kilometers, relative to the center of the map projection.

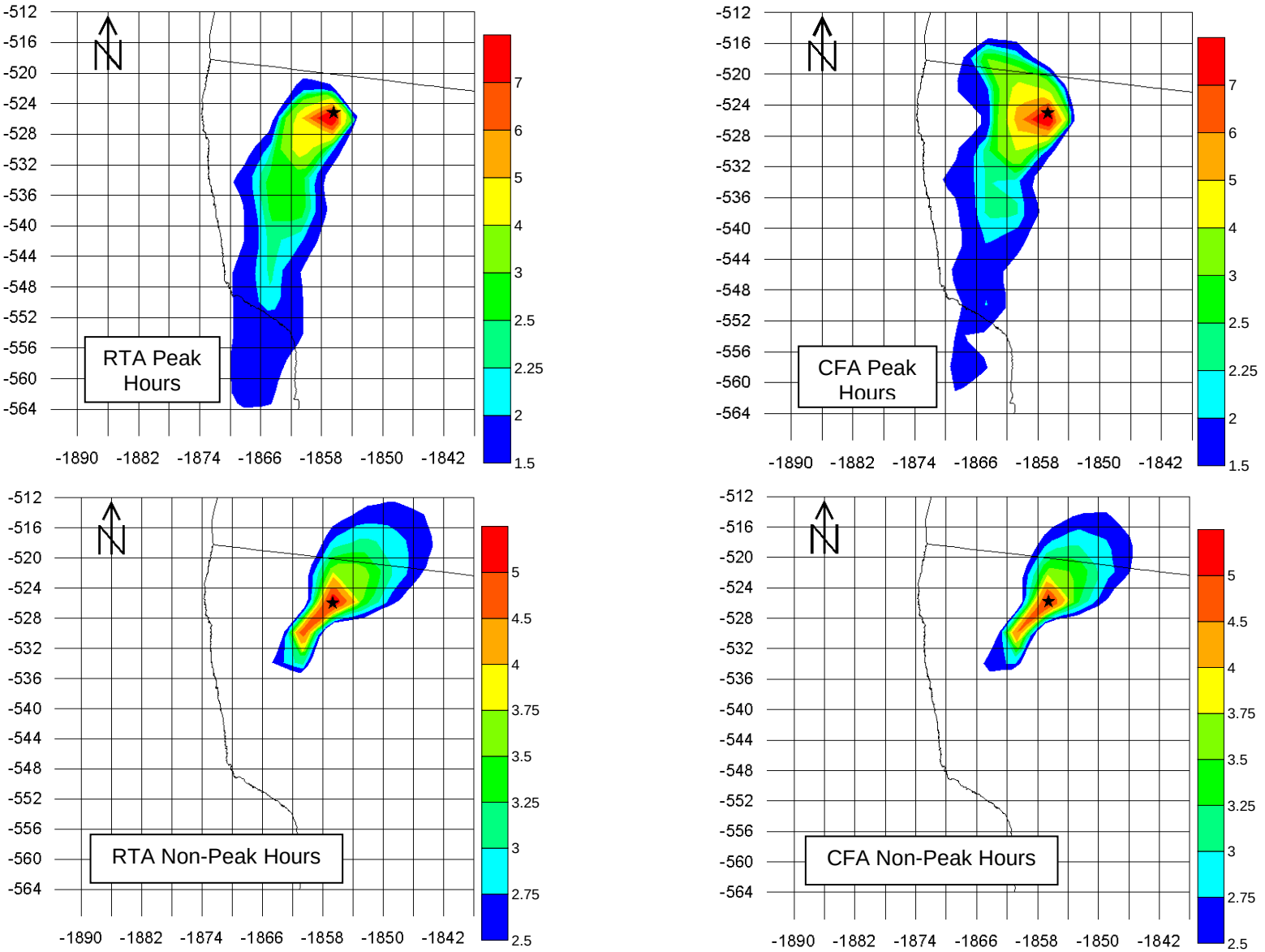

Figure 2.6. RTAs and CFAs for BC during peak hours and non-peak hours at Parque Morelos. Axes labels on maps are in kilometers, relative to the center of the map projection.

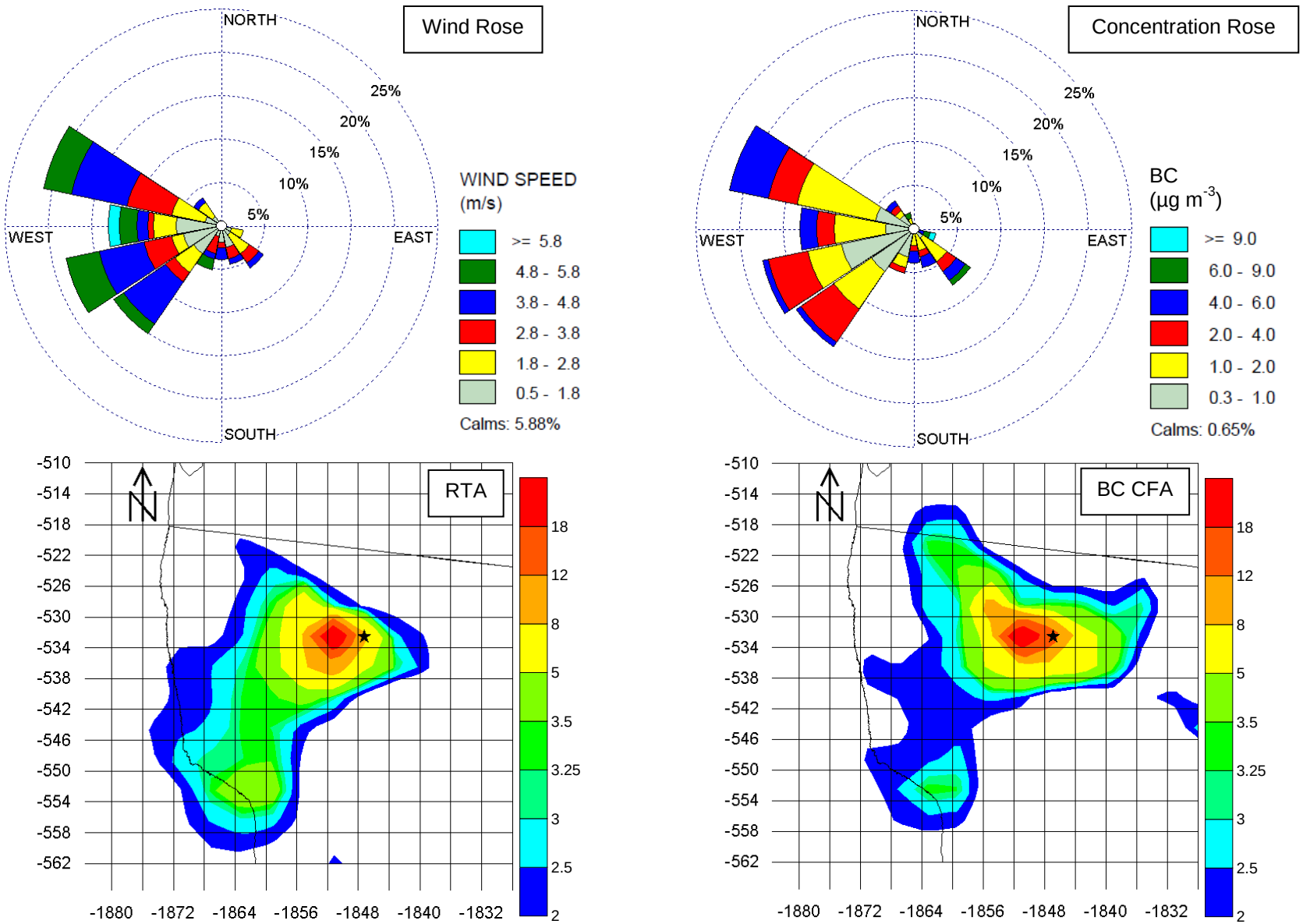

Figure 2.7. Wind rose, BC concentration rose, RTA, and BC CFA for backward simulations at UTT. Axes labels on maps are in kilometers, relative to the center of the map projection.

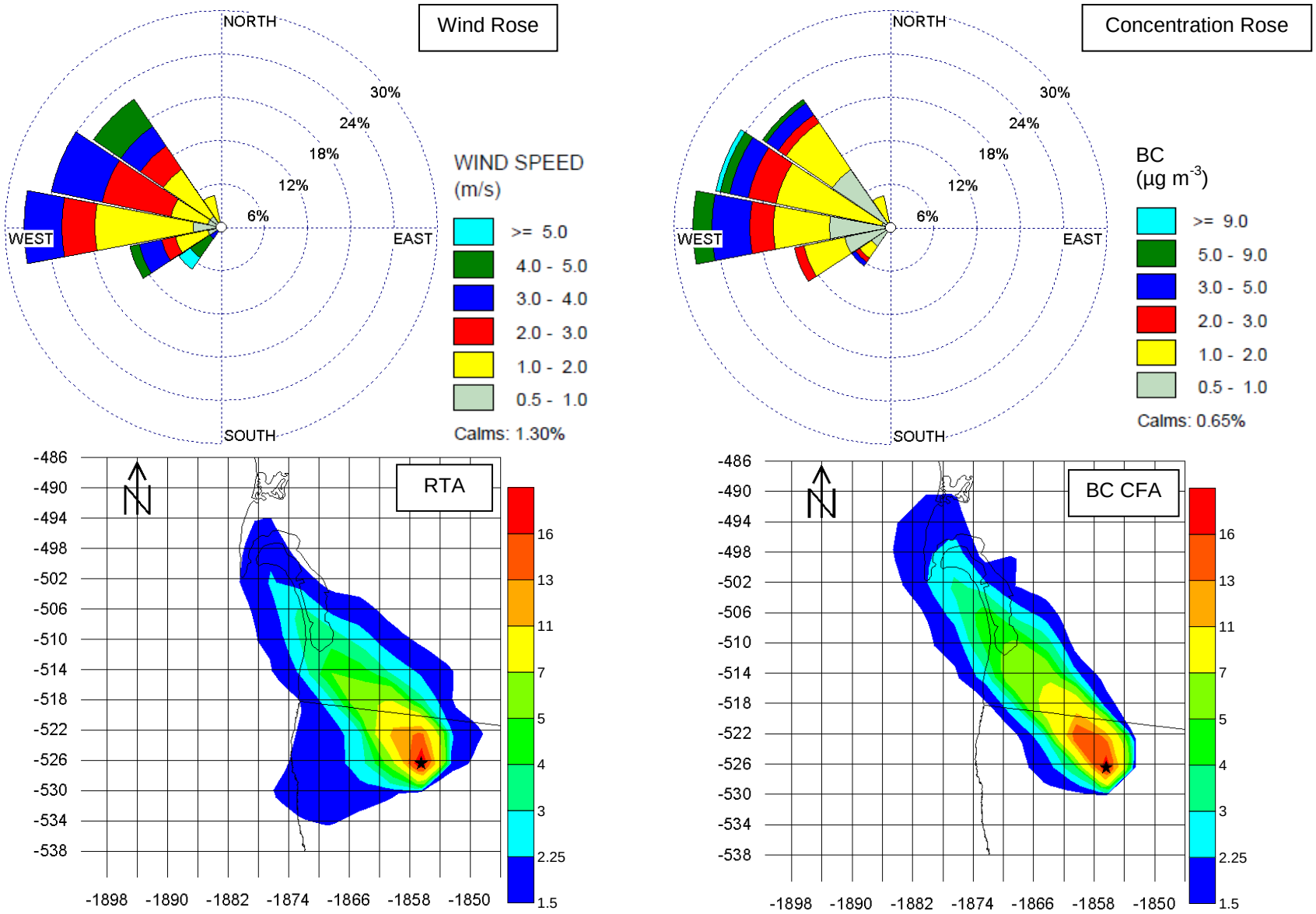

Figure 2.8. Wind rose, BC concentration rose, RTA, and BC CFA for backward simulations at El Trompo. Axes labels on maps are in kilometers, relative to the center of the map projection**.**

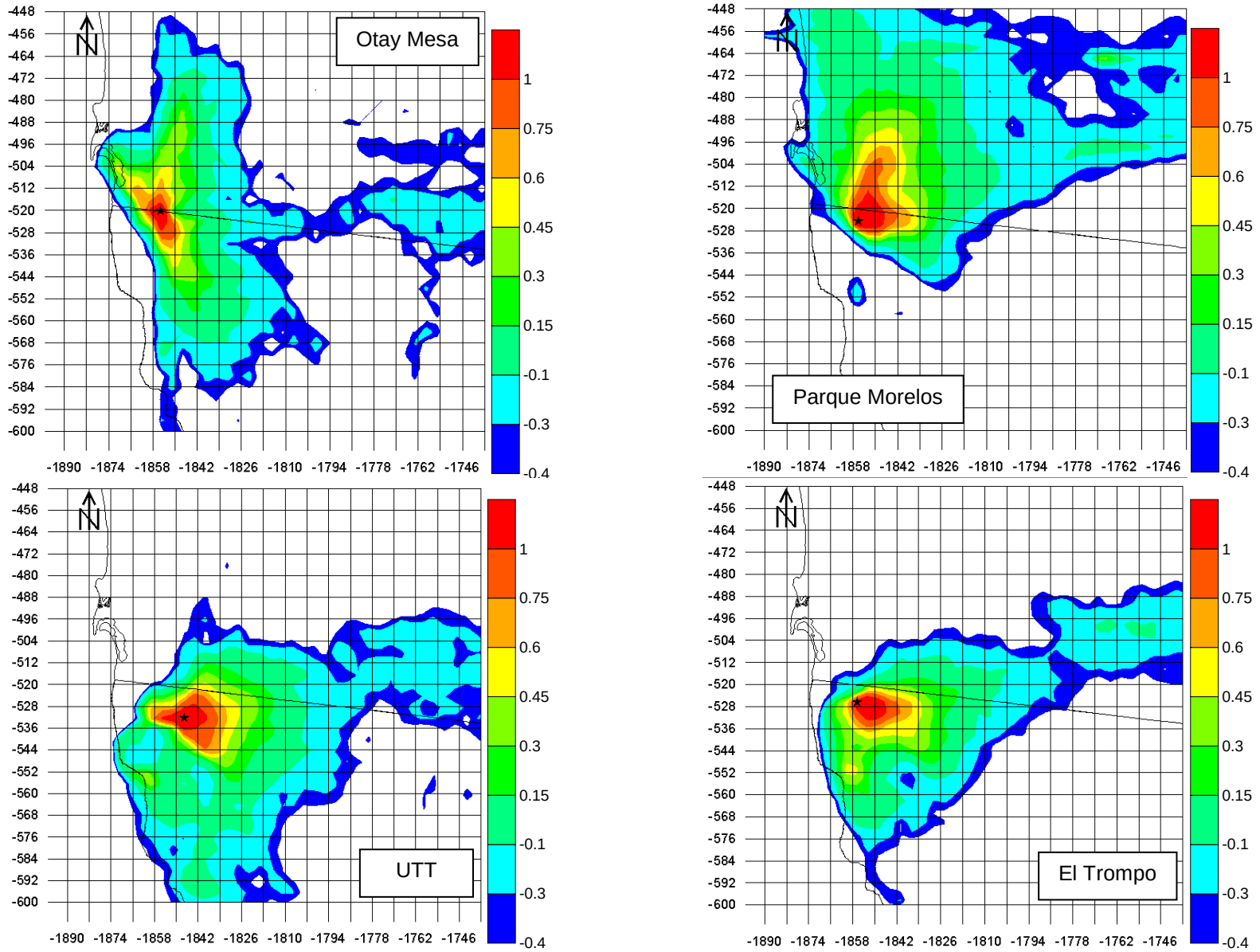

Figure 2.9. Forward RTAs at each site. Axes labels on maps are in kilometers, relative to the center of the map projection**.**

Chapter 3

Conclusions

The analysis of spatial and temporal variations of BC concentrations in the border region near San Diego-Tijuana during the Cal-Mex 2010 field campaign has led to the following deductions:

- BC concentrations in Tijuana are comparable to similarly sized Mexican cities like Mexicali and larger American cities like Los Angeles. Extremely high concentrations of BC were observed around midnight and may be the result of industrial activity seeking to avoid attention.

- BC correlated well with CO at the Mexican sites, but not well at the American site. The segregation of traffic into passenger vehicles and heavy-duty diesel trucks at the American site likely created the low BC and high CO concentrations, as the measurement site was located downwind of the passenger vehicle crossing but upwind of the truck one. In addition, the BC/CO ratio was significantly higher at the Mexican sites and higher in Tijuana than in Mexico City, which suggests that gasoline-powered vehicles emit more BC than is typical or that diesel vehicles comprise a larger proportion of the fleet in Tijuana.

- Tijuana's emissions of BC, estimated as the product of the city's CO emissions and the BC/CO ratio, are 380-1470 metric tons yr^{-1}. Nearly all of these emissions are transported into California but are at most 3% of the estimated statewide BC emissions, and if the spatial distribution of BC emissions in California is proportional with population, Tijuana-

Rosarito's contribution to BC emissions would be 10-38% of San Diego's. The variation of this estimate is due to uncertainty associated the CO emission inventory.

From the analysis of potential source areas of BC emissions, we concluded that:

- BC measured at the Mexican sites typically appears to have originated from within Tijuana, as there was only occasional transport into Mexico from the US. The generally consistent westerly air flow typical of this region indicates that most sources were west of the monitoring sites. The high concentrations of BC around midnight were also found to originate from the west and west-southwest of Parque Morelos, probably from industrial sources in the La Mesa corridor.

Finally, from the characterization of cross-border transport of BC and its impact on local and regional air quality, we concluded that:

- Forward trajectories from Tijuana typically travel into the US, often crossing the border in a northeasterly direction, into Imperial County, California. As such, most of the BC emissions in Tijuana will be transported into the US, and air quality management strategies in the US that consider BC should take into account the heavily industrialized border region.