

Modeling Air Quality during the California Regional PM₁₀/PM_{2.5} Air Quality Study (CRPAQS) using the UCD/CIT Source Oriented Air Quality Model - Part I. Base Case Model Results

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Abstract

A comprehensive air quality modeling project was carried out to simulate size and composition resolved airborne particulate matter concentrations in northern and central California using the pollutant concentration and meteorological data collected during the California Regional PM₁₀/PM_{2.5} Air Quality Study (CRPAQS) from December 15, 2000 to January 7, 2001. Measured 24-hr average PM_{2.5} concentrations during this time period exceeded 180 $\mu\text{g m}^{-3}$ at Bakersfield, making it the most severe PM_{2.5} air quality episode ever recorded in the United States with a rigorous measurement database to support modeling. In this paper, the UCD/CIT source oriented air quality model is used to predict the concentrations of O₃, NO, NO₂, CO, elemental carbon (EC), organic compounds (OC), nitrate and PM_{2.5} mass concentration over a 24 day period using a horizontal resolution of 4 km \times 4 km to cover all of central California. This is the first rigorous evaluation of an air quality model in central California using the fine spatial resolution appropriate for the mountain-valley topography of the region combined with the relatively long multi-week time scales associated with winter stagnation events.

Fractional bias (FB) values were calculated at all sites on each day of the study to quantify model performance. The CO (FB=-0.5 to +0.3), O₃ (FB=-0.5 to +0.25), NO (FB=-0.9 to -0.1) and NO₂ (FB=0 to +0.4) concentrations predicted by the UCD/CIT model are in good agreement with observations at most monitoring stations throughout the Valley. Measured and predicted maximum O₃ concentrations in the northern portion of the domain are only 40 ppb (close to background levels). Measured O₃ concentrations in the southern portion of the domain near Bakersfield are slightly greater (50 ppb) but model predictions are consistently lower than this value possibly due to missing VOC emissions in the emission inventory. The predicted PM_{2.5} concentrations (FB=-0.5 to +0.75) generally agree with observations at Bethel Island, Sacramento, Fresno and Bakersfield spanning the entire length of the model domain. PM_{2.5} concentrations are over-predicted at the remote monitoring site Angiola in the central portion of the domain. Part of the over-prediction is due to excess fugitive dust emissions. CO, NO, EC and OC were all under-predicted at Angiola, indicating possible missing combustion sources in the emission inventory. The regional nitrate (FB=-1.5 to +1.25) formation dynamics were correctly reproduced by the model simulation but imperfect wind fields cause differences between the predicted vs. measured spatial distribution of nitrate during the last several days of simulation leading to the broader range of fraction bias. Overall, the results of the current study confirm the ability of the air quality model to capture the major features of a severe particulate air pollution event in northern and central California providing a foundation for future studies on source apportionment and emissions control.

1 Introduction

California's central Valley spans a region approximately 700 km long and 250 km wide making it one of the largest contiguous air basins in the United States. The southern portion of the central Valley (referred to as the San Joaquin Valley (SJV)) suffers from elevated ozone (O_3) concentrations in the summer and high particulate matter (PM) concentrations in the winter. The central Valley is enclosed on the west by the coastal mountain range, on the east by the Sierra Nevada mountain range, and to the south by the Tehachapi Mountains (see Figure 1). This topography makes the central Valley susceptible to the production and accumulation of airborne pollutants when temperature stratification produces stable atmospheric conditions. The highest $PM_{2.5}$ concentrations usually occur in the winter when a high pressure system (the Great Basin High) reduces the ventilation in the Valley (Chow et al., 2006).

The California Regional $PM_{10}/PM_{2.5}$ Air Quality Study (CRPAQS) was a 13 month field campaign started in December 1999 that was designed to study the particulate pollution problem in the central Valley. Continuous measurements of gaseous CO, NO_x and O_3 were made at 100 locations throughout the Valley during CRPAQS. Four winter Intensive Operation Periods (IOPs) lasting 3-4 days each were carried out between December 2000 and February 2001 during which time large amounts of aerosol size distribution and chemical composition data were collected to support detailed modeling.

The source-oriented UCD/CIT air quality model was applied to simulate particulate air quality using the data collected during CRPAQS in order to further understand the formation processes of PM, to identify the sources that lead to the elevated PM concentrations, and to design efficient emission control strategies to reduce PM pollution. The purpose of this paper is to study the performance of the UCD/CIT air quality model during the CRPAQS episode for key gas- and particle-phase pollutants. The validation of the model results will provide higher confidence for the subsequent modeling studies of source apportionment of particulate matter, evolution of particle chemical and size distribution, pollutant formation process analysis and emission control strategies.

2 Model Description

The UCD/CIT model used in the current study has been applied in several previous studies in the South Coast Air Basin (SoCAB) and the SJV in California (Kleeman and Cass, 2001; Ying et al., 2004; Ying and Kleeman, 2006). A detailed description of the source-oriented UCD/CIT model is provided by Ying et al. (2004), Mysliwiec and Kleeman (2002) and Kleeman et al. (1997) so only a brief description of the model along with recent updates are summarized below.

The UCD/CIT model is a source-oriented air quality model for the direct source apportionment of both primary and secondary particulate matter. The SAPRC90 gas phase mechanism (Carter, 1990) is modified to independently track the formation of precursors of secondary particulate matter from different sources. The particle representation is expanded to allow gas-to-particle partitioning of the precursor gases from different sources. In this way, the sources that lead to the formation of secondary particulate matter can be directly determined. To allow direct source apportionment of primary particulate matter, the *source-oriented externally mixed aerosol* approach is employed whereby particles from different sources are tracked separately in the model simulation of emission, transport, gas-to-particle partitioning and deposition so that the particle source infor-

mation is retained. When necessary, the UCD/CIT model can also be configured to use an internal mixture particle representation, in which the particles emitted from different sources are lumped together before entering into the model simulation. In this configuration, the source apportionment capabilities for secondary particulate matter are unaffected, but primary source apportionment is accomplished using internal tracers. An on-line UV radiation calculation module, which considers the effect of aerosol loading, is used to directly determine the photolysis rates at each model time step (Ying and Kleeman, 2003). The particle coagulation process is simulated in the model using the method described in Herner et al. (2006). Since the current study is mainly focused on particle mass concentrations, formation of new particles due to nucleation is not considered in the model simulation.

The vertical turbulent diffusion coefficient (K_{zz}) in the model surface layer has a minimum value enforced based on landuse in each grid cell. The details of this formation can be found in the Supplementary Materials section.

3 Model Application

In this study, the UCD/CIT model is applied to simulate the air quality in the central Valley from December 15, 2000 to January 7, 2001. Figure 1 shows the surface elevation of the CRPAQS modeling domain. The model domain is divided horizontally into $4\text{km} \times 4\text{ km}$ grid cells, with 190 grid cells in each direction. The model domain is divided into 10 layers in the vertical with a total height of 5 km. The thickness of each layer starting from the surface layer is 35, 105, 140, 330, 390, 500, 500, 1000, 1000 and 1000 meters. The active computation domain, where the actual gas and particle simulations are carried out, is outlined by the dark lines. The UCD/CIT model was initially configured to use the internal mixture particle representation and the fog module was not fully activated in the base-case simulation. Particles were allowed to activate into fog droplets during periods when relative humidity exceeded 100%, but detailed oxidation chemistry was not enabled. The comparison of the results predicted by the internal mixture and external mixture is examined in (Ying et al., 2007). The effect of fog processing on the predicted particle size distribution will be discussed in a separate manuscript. In the following sections, the methods used to create the meteorology, emission and boundary conditions are described in detail.

3.1 Meteorological Fields

The meteorological fields (3D temperature, humidity and wind) that drive the UCD/CIT model are generated using the objective analysis method described by Goodin et al. (1979, 1980). Hourly vertical wind and virtual temperature profiles were collected at 20 stations during the entire modeling episode. Balloon soundings of relative humidity were measured at Oakland, Fresno and Bakersfield four times a day at 0500, 1000, 1600 and 2000 Pacific Standard Time (PST) during the three modeled IOPs (December 15-18, 2000; December 26-28, 2000; January 4-7, 2001). These humidity measurements were linearly interpolated in time to generate hourly humidity inputs for the objective analysis program. For the days without humidity measurement, the nearest IOP day was taken as a surrogate day for the 3D humidity fields. The virtual temperature measurements

from the profilers were corrected to ambient temperature with equation 1:

$$T = T_v \left(1.0 - \frac{RH \cdot e_s(T)}{p} \times 0.378 \right) \quad (1)$$

where T is the ambient temperature in K, T_v is the virtual temperature in K, p is the atmospheric pressure, $e_s(T)$ is the saturation vapor pressure at ambient temperature T , and RH is the relative humidity.

Surface measurements of hourly wind (120 stations), humidity (132 stations) and ambient temperature (192 stations) were taken throughout the portion of the modeling domain over land. These surface data were used by the objective analysis program to generate the meteorological fields for the first model layer to provide better regional details. There were no available observations of wind, temperature and humidity profiles over the Pacific Ocean. The results from a MM5 simulation performed by staff at the California Air Resources Board (CARB) were used as surrogate observations at 17 virtual stations outside the valley to provide the best possible estimate of meteorological conditions when direct measurements were not available. Previous studies have demonstrated that hybrid meteorology fields generated using both observations and MM5 predictions give better ozone air quality model performance for central California than MM5 fields alone (Jackson et al., 2006). The hourly mixing height fields used in the current study were generated by a surface energy balance scheme (Planton and Noilhan, 1988) that predicts the surface energy fluxes and the equations described by Garratt (1994) to predict the growth of the mixing height as a function of time.

3.2 Initial and Boundary Conditions

Surface concentrations of gas and PM pollutants were measured at over 80 locations during the study period. The measurements of surface pollutant concentration were interpolated in time to generate continuous series of hourly concentration values. The hourly pollutant concentration data was then interpolated spatially to generate air quality fields for the entire model domain using the objective analysis method described in Goodin et al. (1979). Details about the field measurements are described by Chow et al. (2006) and are not repeated here. Concentrations of HNO_3 and NH_3 were only available for five locations (Bodega Bay (BODB), Sacramento (SDP), Modesto (M14), Angiola (ANGI) and Bakersfield (BAC)). The details of the HNO_3 and NH_3 measurement are discussed by Herner et al. (2005). Non-methane hydrocarbon (NMHC) concentrations were measured at 5 stations during the three IOPs (Bodega Bay (BODB), Bethel Island (BTI), Fresno (FSF), Angiola (ANGI) and Sierra Nevada Foot Hill (SNFH)). Continuous $\text{PM}_{2.5}$ mass and nitrate measurements were taken at Bethel Island, Sacramento, Fresno, Angiola and Bakersfield sites throughout the entire wintertime CRPAQS episode. Filter based measurements of bulk particle mass and chemical composition were made by the Desert Research Institute. Size- and chemically-resolved PM measurements were taken during the IOPs, as described by Herner et al. (2005, 2006). These size resolved measurements, together with the real time $\text{PM}_{2.5}$ measurements, were used to interpolate the air quality fields for PM. Details about the procedures that were used to generate the PM fields are provided by Held et al. (2004) and are not repeated here. One $\mu\text{g m}^{-3}$ of sulfate with the size distribution measured at the Sequoia (SEQU) site (549 meters above sea level) was used to represent the approximate amount of background sulfate in the California atmosphere during

the winter season. The surface concentrations were scaled by a set of empirical vertical factors to specify the pollutant concentrations in the upper layers. The concentrations of elemental carbon (EC) and organic compounds (OC) are set to be high near the surface while much lower in the upper layers. The concentrations of secondary pollutants are set to be equal to the surface value up to 1000 meters and then linearly decreased to zero at the top of the model domain.

The boundary conditions for gas phase species are mainly set to be fixed values during the model calculation. In particular, the ozone concentration was set to a typical winter background concentration of 30 ppb at all four boundaries based on the measurements made by Brown et al. (2006). NO and NO₂ concentrations were set to be 1 ppb based on the NO measurements at the remote Angiola site 90 m above the surface. The PM boundary conditions were determined from the interpolated surface PM fields. The empirical vertical scaling factors used for the initial conditions are also used to set the PM boundary conditions aloft.

3.3 Emissions

The hourly emissions inventory with 4 km spatial resolution for the entire modeling episode was generated by CARB. Emissions of NO_x, SO_x, CO, NH₃, VOC, and PM from major point, area and mobile sources were transformed to model-ready inputs using the VOC and PM profiles measured during source tests (Kleeman et al., 1999, 2000; Schauer et al., 2002a,b, 2001; Schauer and Cass, 2000; Schauer et al., 1999a,b). Weekday and weekend variations of emissions are roughly represented in the emission inventory. A summary of the emission inventory can be found in a separate manuscript (Ying et al., 2008) for particle source apportionment and is not repeated here.

4 Results

The purpose of the current manuscript is to evaluate the UCD/CIT model performance for the prediction of gas and particle phase pollutant concentrations to verify the accuracy of input data and the model formulation. This study provides a solid foundation for future source apportionment and emissions control exercises. In the following sections, predicted gas- and particle-phase pollutant concentrations are compared with measured values using time-series analysis and x-y scatter plots. The model performance statistics are discussed in the following section.

One of the characteristics of winter stagnation episodes in central California is that the wind speeds are usually low and the wind direction varies frequently, making the accurate prediction of pollutant fields difficult. The stagnant wind conditions also create high pollutant concentration gradients near the major emission sources. Therefore, to better evaluate the model performance under these stagnant conditions, we not only compare the model predictions at the exact grid cell where the measurement was made but also search within grid cells around the air quality monitoring station to find the predicted concentration that best agrees with the observation.

4.1 Gas Phase Pollutants

Figure 2 shows the measured and predicted CO concentrations at five stations: Sacramento (SDP), Modesto (M14), Fresno (FSF), Visalia (VCS) and Bakersfield (BAC). Visalia is a rural site while other locations are urban. The five stations are all located in the central Valley, generally arranged

from north to south. The observed concentrations are shown as solid lines, the model predictions at the exact grid cell where the monitor was located are shown as dashed lines, and the crosses (x) indicate the best model results within a 10 km (2.5 grid cells) search radius. CO reacts relatively slowly under typical atmospheric conditions. The highest CO concentrations occur around mid-night each day because fresh combustion emissions are trapped in the shallow nighttime stagnation layer. The model successfully predicted the observed diurnal variation of the CO concentrations at all the urban sites. The peak concentrations at night are generally under-predicted, but better agreement can be found within a 10 km search radius. This indicates that the spatial distribution of CO concentrations might be slightly inaccurate due to uncertainties in the wind fields. At Visalia, the predicted concentrations show little diurnal variation because local sources are not present in the emissions inventory but the observed concentrations show clear diurnal variations. This is likely caused by some missing combustion sources that were left out of the emission inventory.

Figure 3 shows the measured and predicted O₃ concentrations at six stations from north to south in the central Valley. Peak ozone concentrations were generally less than 50 ppb during the cold winter stagnation episode. In urban locations, ozone concentrations are even lower due to the titration reaction with NO. The diurnal variation of the observed ozone concentration in the Valley is a combination of local removal of ozone due to dry deposition and chemical reactions, and a net gradient transport of background ozone from the upper atmosphere to the surface. The predicted ozone concentrations agree with observations at Sacramento, Modesto (M14), Visalia (VCS) and Angiola (ANGI) at most times during the 24 day episode. In Fresno, the predicted ozone peak concentrations are slightly lower than the observed values, but predicted concentrations that are in good agreement with measured values can usually be found within the 10 km search radius. At Bakersfield the model systematically under-predicts the ozone concentrations everywhere within 10 km search radius surrounding the observation site. Since the predicted CO and NO concentrations (see Figure 2 and 4) at Bakersfield match observations, it is likely that some VOC sources are missing from the emissions inventory that leads to the low reactivity of the atmosphere.

Figure 4 shows the measured and predicted NO concentrations at the same six stations shown in Figure 3. The model generally captures the diurnal variation of the NO concentrations at most locations. The model prediction agrees with observation best at Fresno (FSF). In Sacramento (SDP) and Modesto (M14) the predicted peak concentrations at night are slightly lower than the observed values. At Bakersfield (BAC), the predicted NO concentrations are slightly higher than the observed values. Concentrations that better match the observation can typically be found within the 10 km search radius at all sites except Visalia (VCS) and Angiola (ANGI). Sharp nighttime peaks in the measured NO concentrations at these remote locations are not predicted by the model because the emissions inventory does not include local NO sources around the measurement stations. The mechanism that produces the high nighttime concentrations of NO at Angiola is currently unknown.

Figure 5 shows the measured and predicted NO₂ concentrations at the same six stations shown in Figures 3 and 4. NO₂ is mainly produced in the atmosphere by the oxidation of NO by ozone. The averaged NO₂ concentrations during the study period vary from approximately 30% of the NO_x concentration in Bakersfield (BAC) where NO emissions are high, to 90% in Angiola (ANGI) where no significant NO_x sources exist. The predicted NO₂ concentrations agree with observation well at Modesto (M14), Fresno (FSF) and Visalia (VCS). Predicted daytime NO₂ concentrations are lower than nighttime values due to the photochemical dissociation reaction: $NO_2 + h\nu \rightarrow NO + O$. The nighttime NO₂ concentrations are generally over-predicted at

Sacramento (SDP), Angiola (ANGI) and Bakersfield (BAC). The measured NO₂ concentrations typically decline before midnight, while the predicted NO₂ concentrations keep increasing for a few more hours and then starts to decrease. The best NO₂ results found within 10km radius of the observation site were usually very close to the measured values.

4.2 Particulate Pollutants

Figure 6 shows the measured and predicted PM_{2.5} concentrations at Bethel Island (BTI), Sacramento (SDP), Fresno (FSF), Angiola (ANGI) and Bakersfield (BAC). The hourly PM_{2.5} mass concentrations were measured by Sonoma Technology, Inc. (Petaluma, CA) using Beta Attenuation Monitors (BAMs). Very high PM_{2.5} concentrations were observed during the episode. The predicted concentrations at BTI (panel a), located about 60 miles east of San Francisco, agree quite well with observations. The long term increase of PM_{2.5} throughout the entire model episode is correctly predicted although the diurnal variation is not reproduced very accurately in the last 12 days of the modeled episode.

Predicted and observed PM_{2.5} concentrations are in good agreement at the Sacramento (SDP) site (panel b). The diurnal variation of the PM_{2.5} behaves similarly to CO and NO in that the concentrations increase at night and decrease during the day. The diurnal variation is mainly driven by the decrease of vertical mixing and increased emission at night vs. enhanced vertical mixing during the day.

The diurnal variation of PM_{2.5} mass concentrations at Fresno (FSF) (panel c) are similar to those at Sacramento (SDP). Higher concentrations usually occur during the evening hours and decrease during the day. Excellent agreement is found between the predicted and observed concentrations in both diurnal and day-to-day variations. The gradual increase of PM concentrations in the 24-day model episode is also correctly predicted.

Predicted and measured concentrations of PM_{2.5} at the rural Angiola (ANGI) site are lower than at the urban locations in the study domain. PM_{2.5} concentrations are significantly over-predicted, especially at nighttime, in the first 14 days of simulation. In the last 10 days of the simulation, the PM_{2.5} concentrations are under-predicted at Angiola (ANGI). Large fluctuations in the measured PM_{2.5} concentrations were observed, with daytime concentrations generally higher than nighttime concentrations. The concentrations predicted by model simulations were lower during the day and higher at night. Further analysis of the model results revealed that a large fraction of the predicted PM_{2.5} is composed of particles from fugitive dust sources. A recent CARB document indicates that the PM_{2.5} fraction in the dust profiles are significantly over estimated (Gaffney, 2006). Part of the fugitive dust emission (wind blown dust) should actually be wind speed dependent but the current CARB emission estimation of wind blown dust does not include a wind speed dependence or any diurnal variation. Thus, the current PM_{2.5} emission inventory for dust particles might be over-predicted during evening hours and under-predicted during the day.

The observed diurnal variation of PM_{2.5} concentrations at Bakersfield (BAC) is similar to that at Sacramento (SDP) and Fresno (FSF) with higher concentrations measured at night and lower concentrations measured during the day. The diurnal variation is correctly predicted by the UCD/CIT model calculations. The concentrations predicted at the grid point containing the Bakersfield (BAC) monitoring site are slightly higher than the observed values, but good agreement with measured values is generally found within the 10 km search radius. This shows that the PM_{2.5} concentration gradient is quite significant near the Bakersfield (BAC) observation site. The com-

plex topography at the southern end of the Central Valley makes it difficult to generate accurate wind fields around Bakersfield (BAC).

Figure 7 compares the observed vs. predicted EC, OC and nitrate (N(V)) concentrations at Fresno (FSF), Angiola (ANGI) and Bakersfield (BAC). Filter measurements were taken at these locations 4 times each day during the IOPs. The open circles represent the comparison between the measured concentration and the predicted concentration in the grid cell containing the measurement site. The solid circles compare the measured value to the best prediction within the 10 km search radius around the measurement site. The solid line is the 1:1 line, while the two dashed lines represents a $\pm 20\%$ deviation from the 1:1 line. The EC and OC measurements were analyzed using a thermal-optical technique following the IMPROVE protocol (Chow et al., 2004b) while the EC and OC fractions used to generate the speciated emissions were measured using the NIOSH protocol (Schauer et al., 2003). These two protocols use different temperature ramps and thus yield slightly different results. It has been shown that EC determined using the IMPROVE protocol is approximately a factor of two higher than EC determined using the NIOSH protocol while the total carbon (EC+OC) concentrations are close to each other (Chow et al., 2001). Previous modeling studies in the SJV have therefore converted 50% of the measured IMPROVE EC to OC before comparison to NIOSH predictions of EC and OC (Held et al., 2004). This same approach is used in the current study to bring EC and OC measured using different techniques to a common basis for model evaluation.

At Fresno (FSF), the model slightly under-predicts EC, OC, and N(V) concentrations at the grid cell where measurements were made. Agreement between measured and predicted values increases greatly when the best prediction within 10km of the observation site is used. The majority of the OC and N(V) values are within 20% of the measured concentration in this case, with slight under predictions of EC still observed.

The UCD/CIT model significantly under-predicts EC and OC concentrations at Angiola (ANGI), matching the trends observed for CO and NO and further supporting the hypothesis that the emissions inventory around the Angiola monitoring site is incomplete. Nitrate concentrations were over predicted at Angiola (ANGI) during the first two IOPs and under predicted by a factor of two during the third IOP (January 4-7, 2001).

EC concentrations are over-predicted when observed concentrations are low and under-predicted when the observed concentrations are high at Bakersfield. OC concentrations are slightly over predicted at Bakersfield. Reasonable agreement between observed and predicted concentrations was generally found within the 10 km search radius. The difference between the predicted concentrations within the 10 km search radius reflects the sharp pollutant concentration gradients around Bakersfield (BAC). Nitrate is significantly under-predicted at Bakersfield (BAC) during the latter portion of the episode when the observed concentration is high. These high nitrate concentrations coincide with significant ozone production at Bakersfield.

An analysis of regional concentration fields shows that the predicted high nitrate concentrations in the model domain are transported to the north of Bakersfield earlier and faster than the observed pattern, leading to the under-prediction of nitrate. Figure 8 shows the calculated domain-wide maximum 24-hour average nitrate concentration as a function of time together with the maximum 24-hour average nitrate concentrations from continuous and filter-based measurements at Fresno (FSF), Angiola (ANGI) and Bakersfield (BAC). It has been shown that the continuous nitrate method yields lower concentrations than the filter-based measurements when nitrate concentrations are high due to the difference between the ambient temperature and the sampling temperature

of the real-time nitrate instrument (Chow et al., 2004a). It should be noted that the maximum nitrate concentrations measured at these three observation sites does not represent the true domain-wide maximum nitrate concentrations but the change in nitrate concentrations at these locations should be proportional to the change in the domain-wide maximum since nitrate production is a regional process. The model successfully predicted the increase of nitrate concentrations during the IOP2 (December 26 - December 28, 2000) and the subsequently elevated nitrate concentration in the early part of January 2001. This strong agreement between the measured and predicted trends suggests that the model correctly captures the dynamics of the gas phase nitrate precursor production and the thermodynamics for secondary aerosol formation. The under-prediction of nitrate at Bakersfield (BAC) and Angiola (ANGI) is more likely due to a distortion of the nitrate spatial distribution induced by the imperfect wind fields. A sensitivity analysis of the response of simulated nitrate concentrations around Bakersfield to key model parameters is presented by (Ying et al., 2008).

4.3 Model Performance

In this study, fractional bias (FB) (Equation 2) is used as a statistical measure for the model performance. $C_{p,i}$ and $C_{o,i}$ are the predicted and observed concentrations for the i^{th} data point, respectively. N is the number of total data points used in the FB calculation.

$$FB = \frac{2}{N} \times \sum \frac{C_{p,i} - C_{o,i}}{C_{p,i} + C_{o,i}} \quad (2)$$

Figure 9 shows the calculated FB for CO, O₃, NO, NO₂ and PM_{2.5} for all available stations within the model domain between December 15, 2000 and January 07, 2001 using a box-and-whisker plot (Tukey, 1977). Upper and lower bounds of the box represent 75% and 25% quartiles, respectively. Dark central bars represent median FB value, and upper and lower whiskers show the maximum and minimum FB values among all the available stations. No attempt was made to identify the outliers as all the observation data used in the analysis passed quality control checks. Approximately 70 stations were used in the O₃ FB calculations while 40 stations were used for CO, NO and NO₂ calculations. The five stations shown in Figure 6 were used to calculate the FB for PM_{2.5} mass concentrations. Only observed concentrations above threshold values were used in the FB calculation. The threshold for gas species was 5 ppb and for PM_{2.5} it was 1 $\mu\text{g m}^{-3}$. Panel (9a) shows that FB values for CO are generally within ± 0.5 and mostly less than zero, indicating slight under-predictions. The FB for O₃ (panel (9b)) spans a wider range, from -2 to 1. This partially reflects the inclusion of very low O₃ concentrations in the FB calculation. Typical threshold concentrations for O₃ FB calculations during actual photochemical smog episodes would be 50 ppb (greater than the maximum observed O₃ concentration during the current episode). The middle 50% FB values are within ± 0.5 for most of the days. Panel (9c) shows that FB values for NO have wide distributions among all the stations. The predicted concentrations are lower than observations most of the time, which leads to negative FB values. However, as can be seen from figure 5, predictions at major emission areas are in good agreement with observations. Most of the under-predictions occur at rural areas where there are no significant NO emission sources. The peak NO concentrations at most stations are also under-predicted, contributing to negative FB values. Panel (9d) shows that NO₂ FB values are generally within the range [-0.5,0.5] with median

values slightly higher than 0. Since only 5 stations were used to calculate $PM_{2.5}$ FB box-and-whisker plots, FB values for these 5 stations are shown directly in panel (9e). The FB values for $PM_{2.5}$ mass varies within [-1,1] at all times and within [-0.5,0.5] on most days. Generally speaking, $PM_{2.5}$ values are over-predicted during the first half of the simulation and under-predicted during the second half of the stagnation period.

Figure 10 shows the calculated FB for nitrate, EC and OC for ANGI, BAC and FSF during the three IOPs. Threshold values for nitrate, EC and OC were all set to be $1 \mu g m^{-3}$. Panel (10a) shows that for nitrate, predicted concentrations at FSF agree with observation very well, with FB values within [-0.5,0.5] for most days during all IOPs. The nitrate concentrations at BAC also agrees with observation quite well, with FB values within [-0.6,0.6] during IOP1 and IOP2. During IOP3, the FB values for Bakersfield are in the range of [-1.2,-1.5], indicating a significant under-prediction of nitrate. Nitrate concentrations at ANGI are slightly over-predicted during IOP1 and IOP2 but agree well with observation during the last two days of IOP3. Panel (10b) shows that EC concentrations at FSF and BAC agree with observation during most of the IOP days, with FB values within [-0.6, 0.6]. Panel (10c) shows that at Fresno and Bakersfield, OC concentrations also agree well with observation, with FB values within [-0.5,0.5] for most of the days. EC and OC concentrations at ANGI are significantly under-predicted, with large negative FB values.

5 Conclusions

The source-oriented UCD/CIT model was applied to study a three-week long winter stagnant air pollution episode in central California. The model successfully reproduced the major features of the air pollution episode including the high organic carbon concentrations near urban centers, the elevated nitrate concentrations in rural areas in the southern SJV and the near-background ozone concentrations throughout the Valley. Slow wind speed and unsteady wind direction is a common meteorological feature in the SJV during stagnant periods. This makes it difficult to accurately characterize the hourly-averaged wind field and thus the spatial distribution of the pollutants has inherent uncertainty. However, the close agreement between the predicted and observed concentrations at multiple locations for multiple pollutants builds confidence that the major chemical, physical and transport processes are reasonably represented by the model simulation so that the results are suitable for further size distribution simulation, source contribution analysis and control strategies evaluations.

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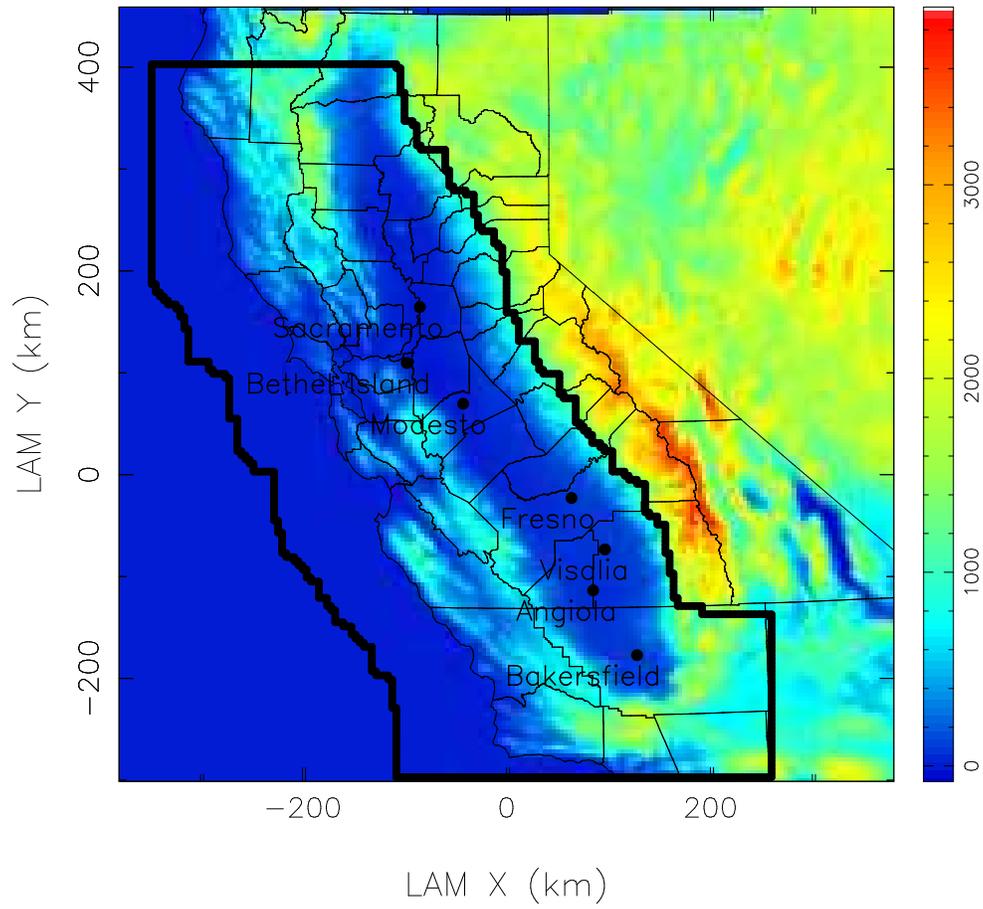


Figure 1: The surface elevation of the CRPAQS model domain. Units are in meters.

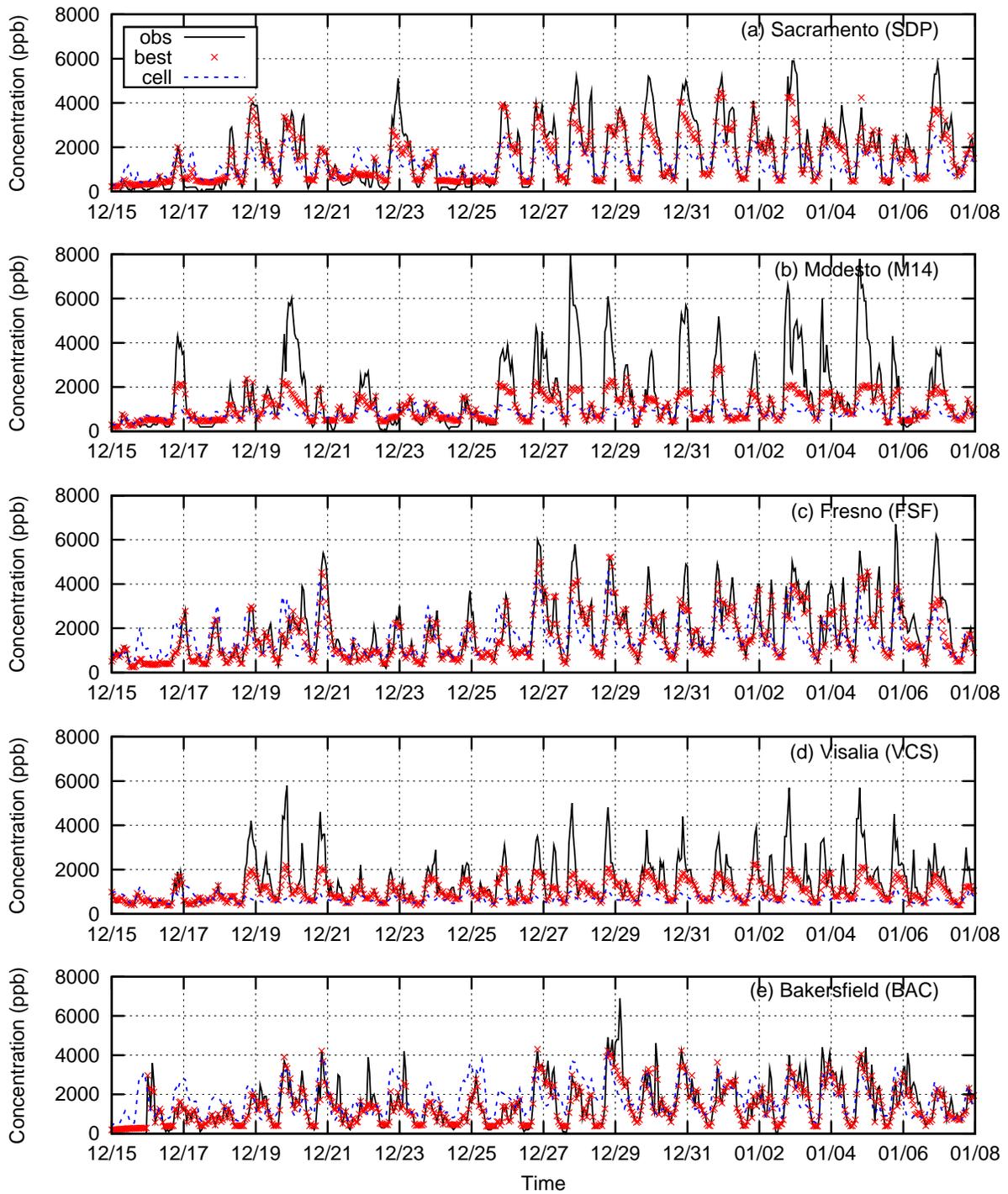


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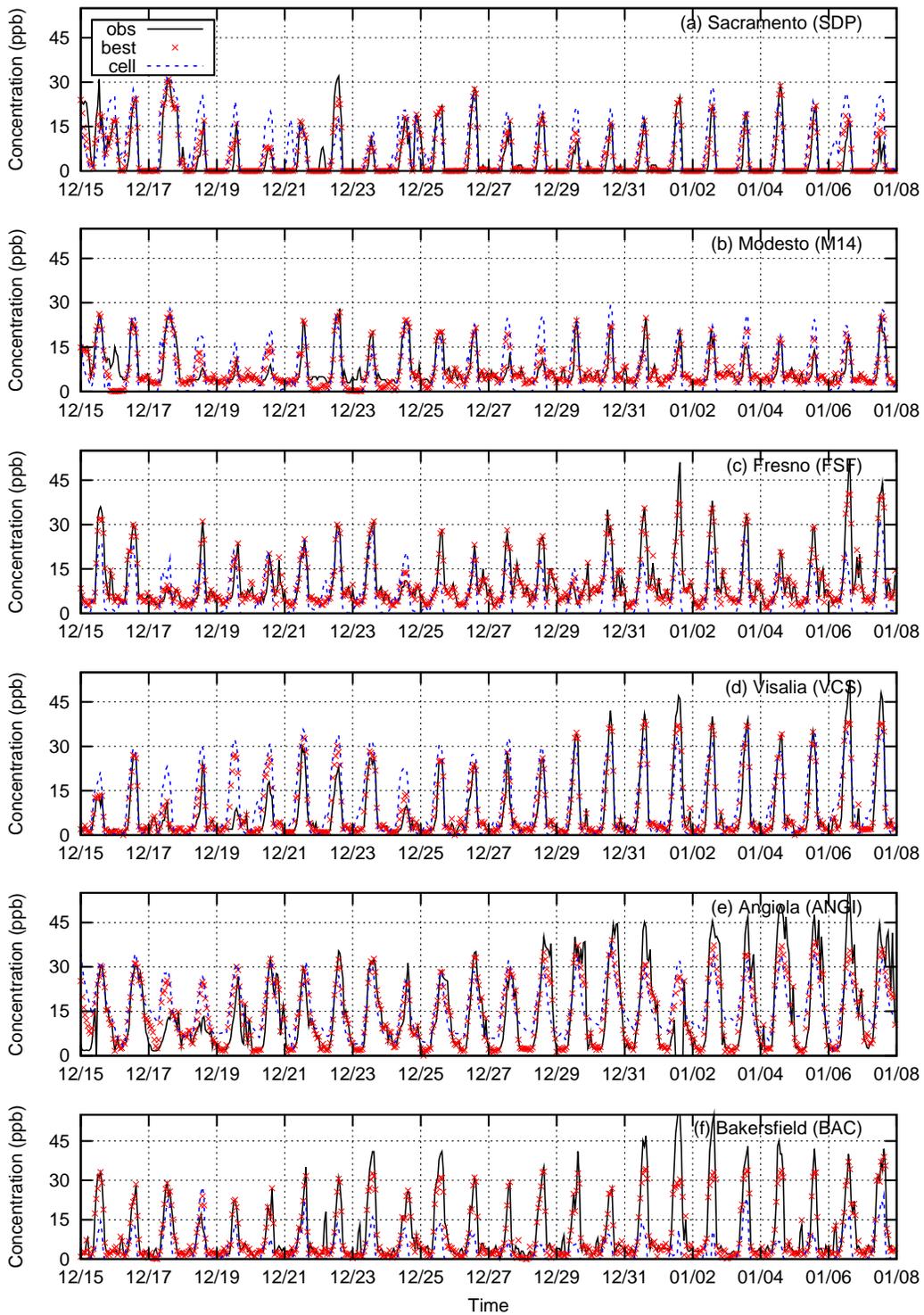


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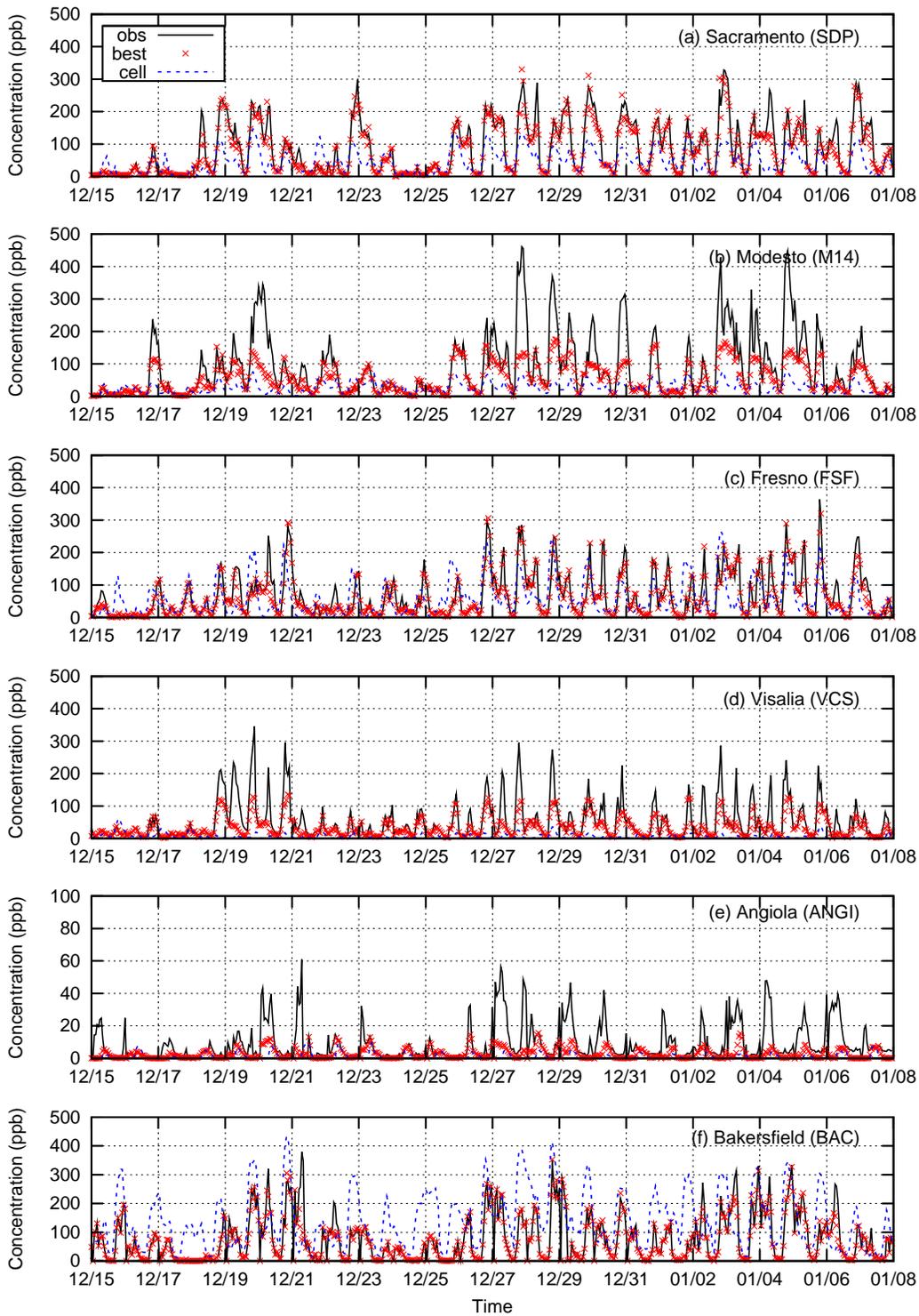


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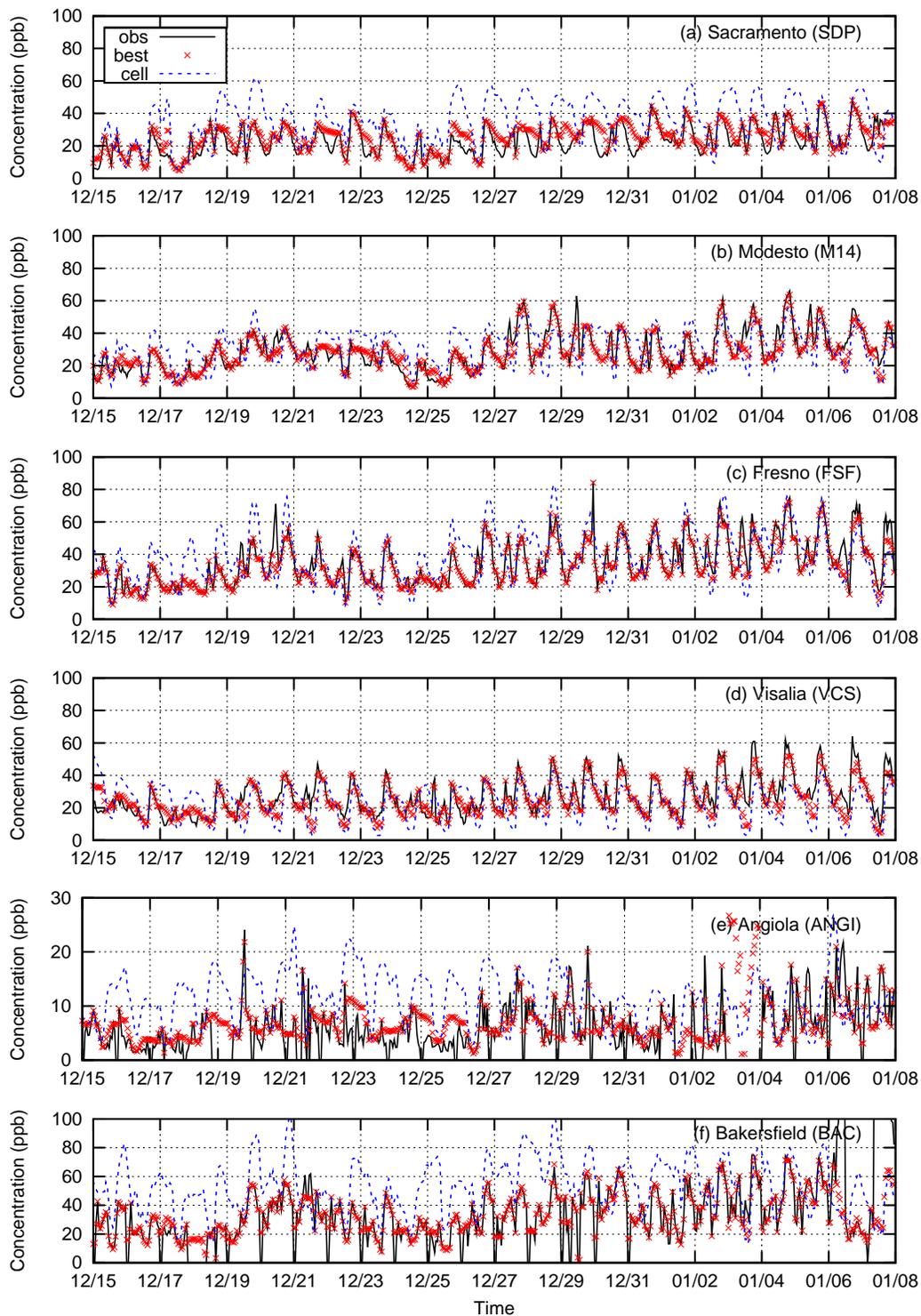


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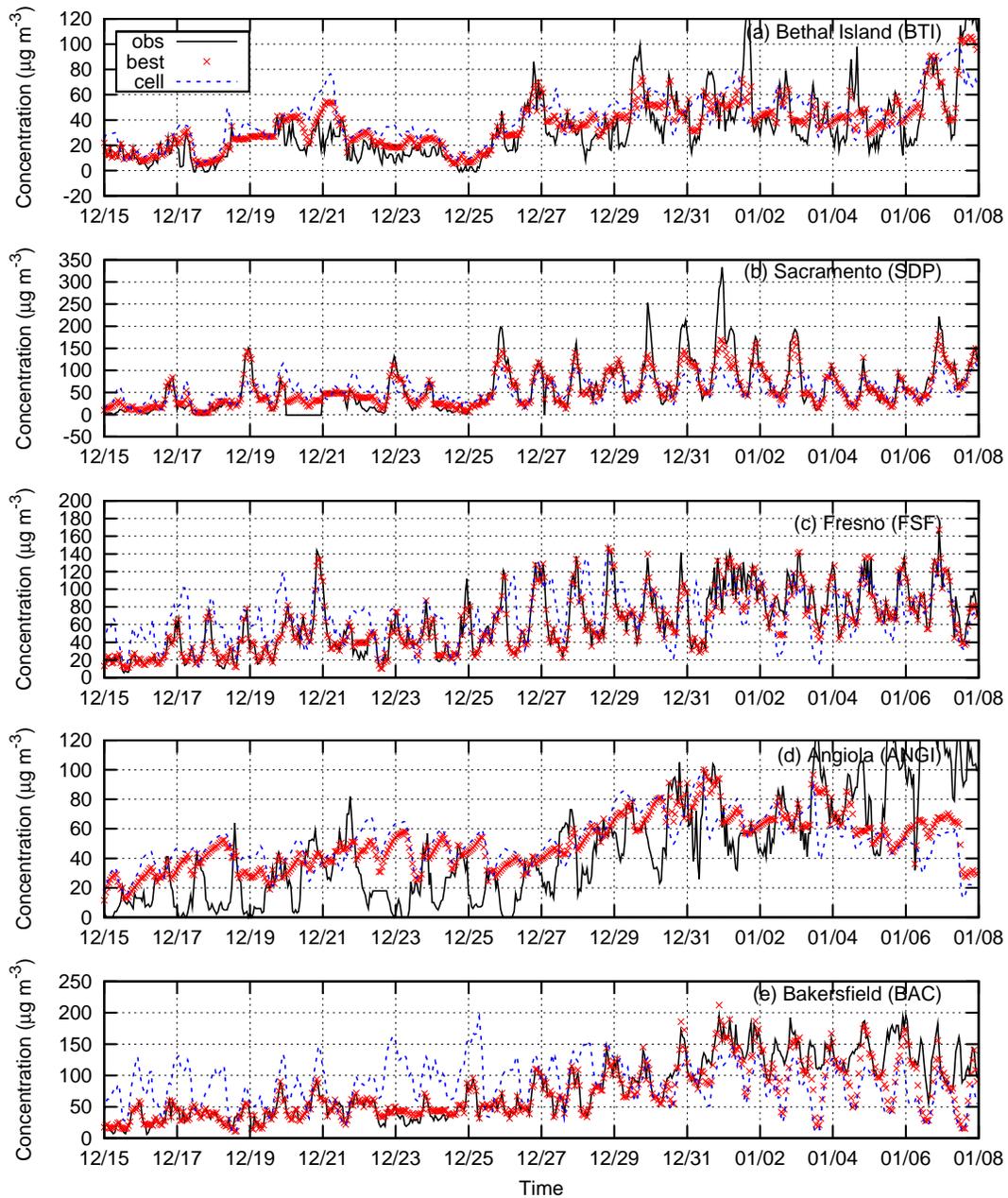


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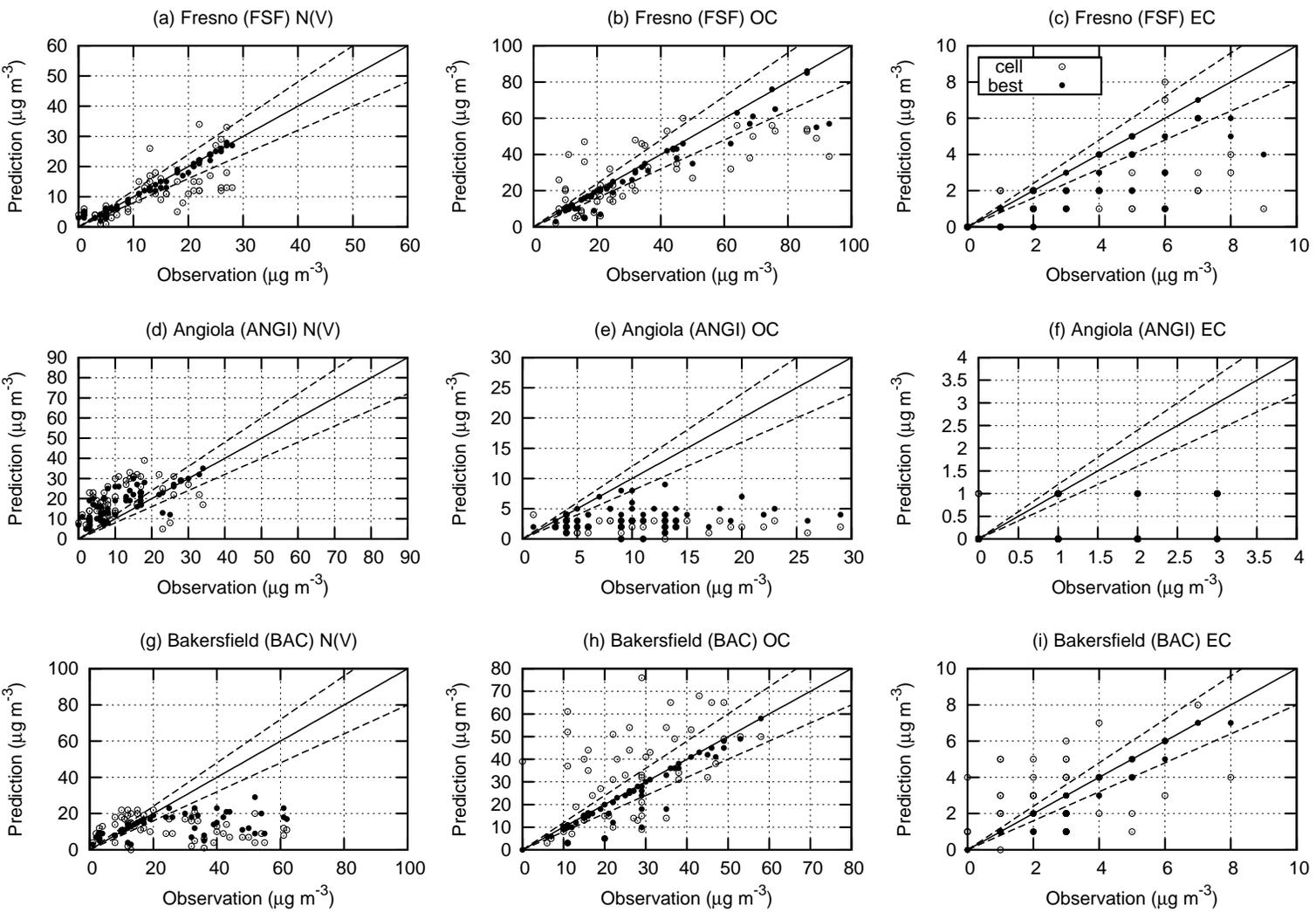


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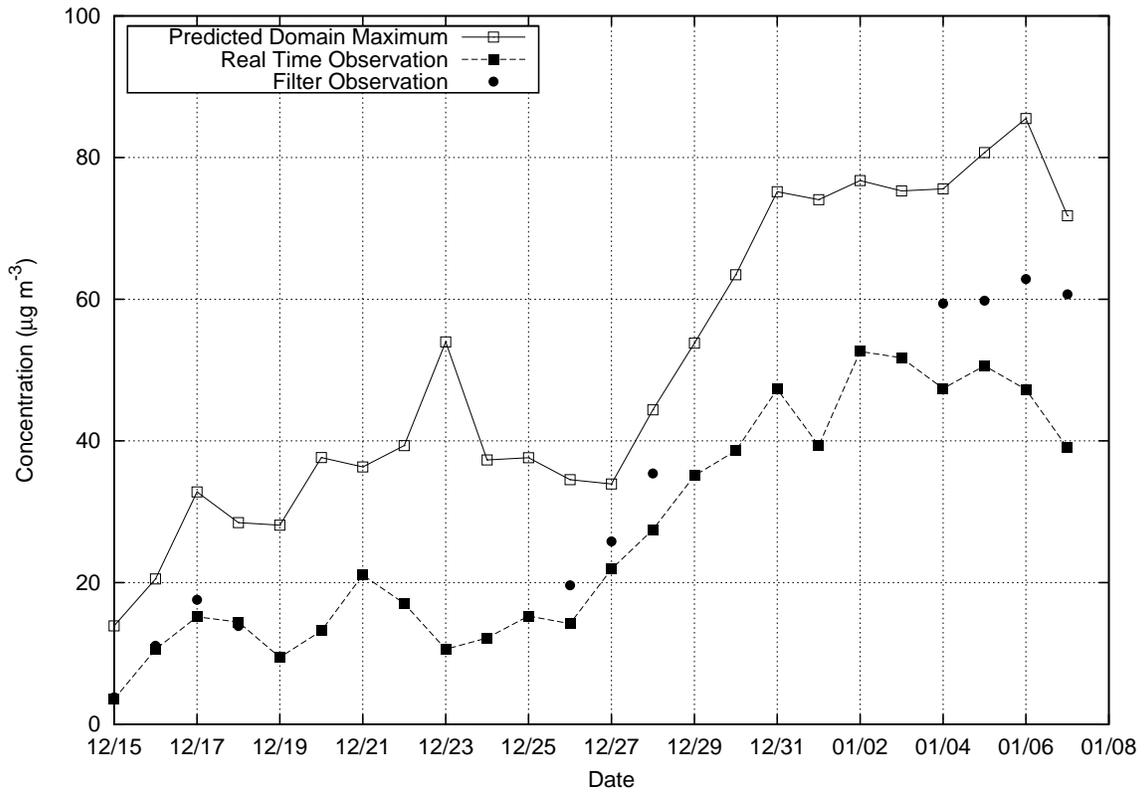


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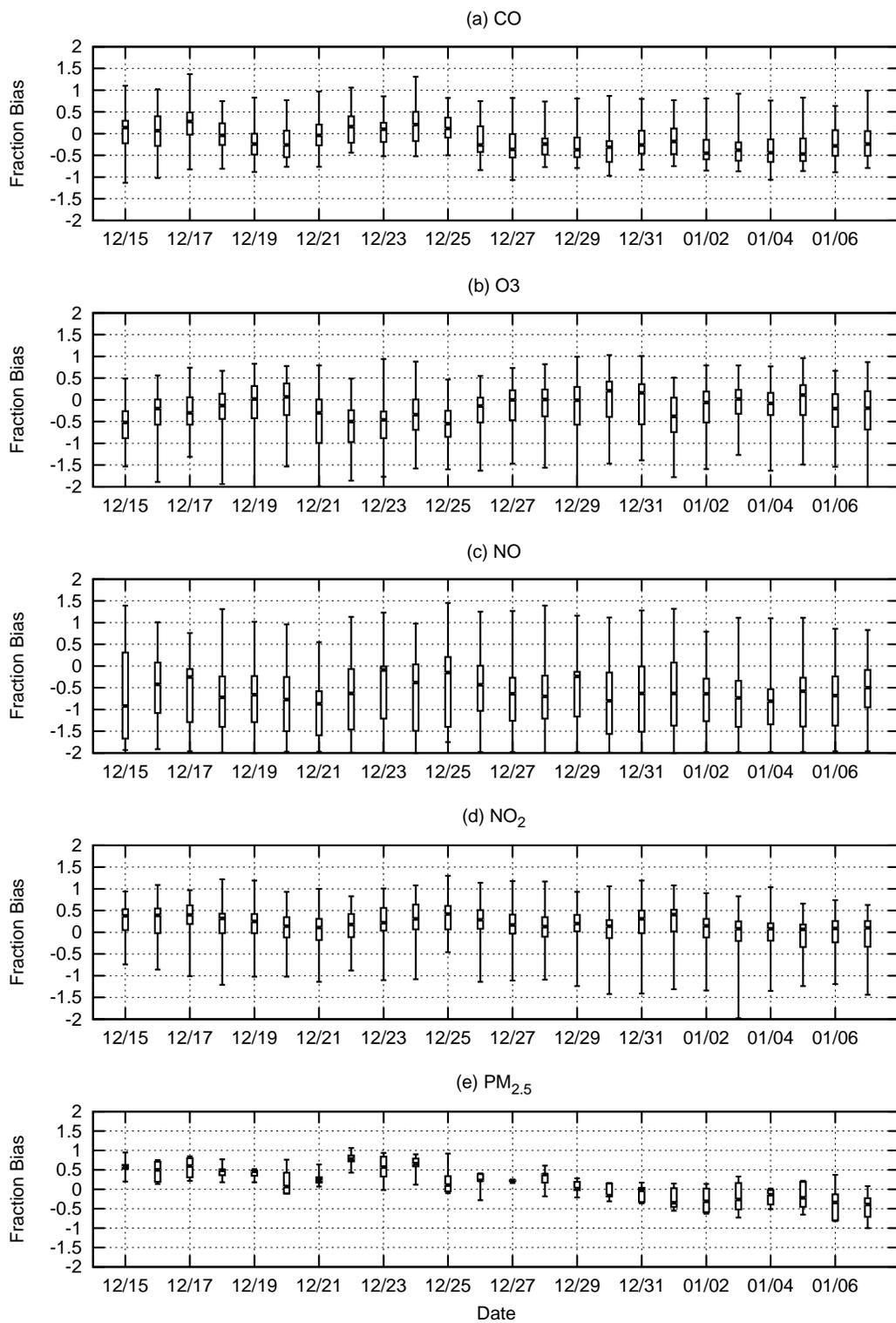


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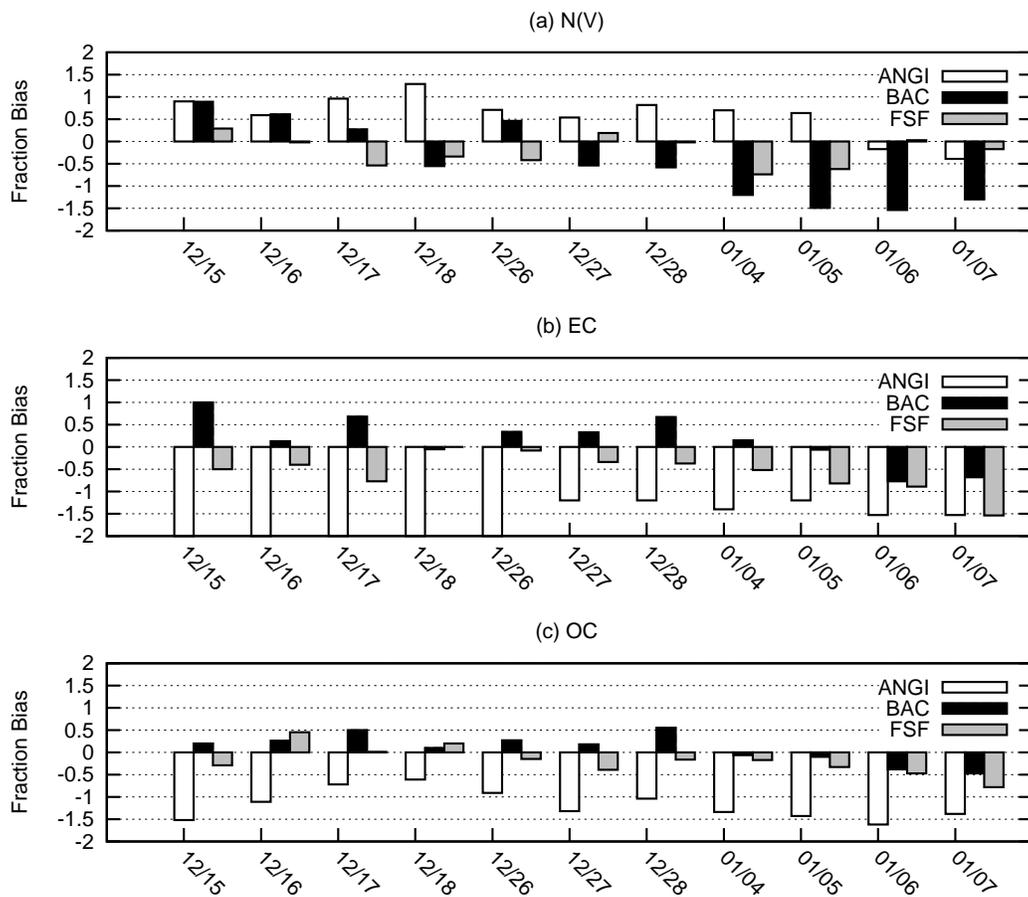


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