Seasonal Variations of Aerosols in Pakistan: Contributions of Domestic Anthropogenic Emissions and Transboundary Transport

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ABSTRACT

Air pollution has become a serious challenge for developing countries like Pakistan. Very scarce information is available regarding pollution levels in this geographic region. This study presents the first modelling work to simulate the spatial distribution and temporal variation of aerosol concentrations over Pakistan by using the Weather Research and Forecasting Model coupled with chemistry (WRF-Chem). Simulated aerosols species include sulfate, nitrate, ammonium, organic carbon, black carbon, and PM2.5 (particles with a diameter of 2.5 μm or less), which are evaluated against ground-based observations and satellite measurements. In year 2006, simulated PM2.5 concentrations averaged over northeastern Pakistan (71–74.5°E, 28–34°N) are 55, 48.5, 31.5, and 98 µg/m3 in January, April, July, and October, respectively. The simulated highest PM2.5 concentration in October results from the relatively low temperatures that favor nitrate formation as well as the lowest precipitation that leads to the smallest wet deposition of all aerosol species. The simulated lowest concentration of PM2.5 in July can be attributed to the largest precipitation associated with the South Asian summer monsoon. Sensitivity studies show that transboundary transport contributes to PM2.5 aerosol levels in northeastern Pakistan by 10–20% in January and April and by 10–40% in July and October of year 2006. Wind over India and Pakistan is found to be the major meteorological parameter that determines the transboundary aerosol transport.

Keywords: WRF-Chem; Aerosols in Pakistan; Seasonal variations.

INTRODUCTION

Aerosols are important air pollutants that have adverse health impacts, lead to reductions in visibility and changes in climate (Intergovernmental Panel on Climate Change (IPCC), 2013). Over the past two decades, South Asian countries have undergone rapid urbanization and industrialization which dramatically increase emissions of air pollutants (Gurjar et al., 2008). The health impacts from regional phenomena such as the Asian Brown Cloud (ABC) and intense winter fog episodes have made the South Asian region very important. Concentrations of major atmospheric aerosol species, including sulfate (SO42–), nitrate (NO3–), ammonium (NH4+), black carbon (BC), and organic carbon (OC), are especially high in eastern Pakistan. Furthermore, lack of efficient monitoring and control measures of air pollution has made Pakistani cities more vulnerable as compared to the developed world and even neighboring countries. Towards filling these gaps, air quality modeling is essential and can be used, for example, to understand the emission sources, concentrations, and seasonal variations of aerosols in Pakistan.

Pakistan is located in South Asia, sharing borders with Afghanistan and Iran in the west, China in the north, the Arabian Sea in the south, and India in the east. There exist several studies about the observed aerosols in Pakistan. Husain et al. (2007) reported that in Lahore, the second largest city in Pakistan, the seasonal mean concentration of BC was 21.7 μg/m3 in winter of 2005 to early 2006. Dutkiewicz et al. (2009) reported that the average concentration of BC in Karachi, the largest city in Pakistan, was about 10 μg/m3 in winter and 2 μg/m3 in summer in the years of 2006–2007. Lodhi et al. (2009) reported that PM2.5 concentrations at Lahore were in the range of 53–
476 µg/m³ from November 2005 to December 2007. Biswas et al. (2008) reported average PM$_{2.5}$ concentration of 209 µg/m³ at Lahore from December 2005 to February 2006. Measurements by the Environmental Protection Agency (EPA) of Pakistan reported that the average PM$_{2.5}$ concentrations over 2005–2010 in cities of Islamabad, Lahore, Karachi, Peshawar, Quetta were 73.0, 121.8, 70.2, and 47.1 µg/m³, respectively (Economic Survey, 2009–10). Measurements showed that nitrate, sulfate, and ammonium were the largest components that contributed to PM$_{2.5}$ at Lahore (Biswas et al., 2008; Lodhi et al., 2009; Stone et al., 2010) and sulfate was the dominant species in PM$_{2.5}$ in Karachi (Ghauri et al., 1994; Mansha et al., 2012). These observational studies, however, were quite limited in terms of chemical species and spatial coverage of aerosols.

Another issue that is associated with the aerosol levels in Pakistan is the transboundary aerosol transport. Some observational analyses have demonstrated the importance of transport of aerosols from North India (Begum et al., 2011). Indian coal based power plants are major sources of transboundary air pollution that influence northeastern Pakistan (Ghauri, 2010). Despite of the importance of transboundary transport, none of the previous studies has quantified the contributions to aerosol concentrations in Pakistan by domestic anthropogenic emissions and transboundary transport.

Seasonal variations of aerosols are driven by seasonal variations in both emissions and meteorological conditions. Pakistan has four seasons: cool and dry winter from December through February, hot and dry spring from March through May, the summer rainy season (or monsoon period) from June through September, and the retreating monsoon period of October and November. Adhikary et al. (2007) reported that aerosol concentrations in South Asia showed minimum values in the monsoon period (June–September) and maximum levels in the post monsoon season (October–November).

The aim of this study is to understand the seasonal variations of aerosols and the impacts of transboundary transport on aerosol levels in Pakistan. The Weather Research and Forecasting Model coupled with Chemistry (WRF-Chem) (Grell et al., 2005) is employed to simulate aerosol concentrations over Pakistan during the months of January, April, July, and October of year 2006. The paper is organized as follows. The WRF-Chem model setup, emissions, numerical experiments as well as model evaluation on meteorological parameters, aerosol concentrations, and aerosol optical depth are described in the following sections. Simulated seasonal variations of aerosols over Pakistan and evaluations of simulated aerosol concentrations are then presented. Finally, simulated impacts of transboundary transport on aerosol levels in Pakistan are presented.

#### Model Description and Numerical Simulations

**The WRF-Chem Model**

This study uses the version 3.2.1 of the WRF-Chem, developed by National Oceanic and Atmospheric Administration (NOAA) and National Center for Atmospheric Research (NCAR) (http://ruc.noaa.gov/wrf/WG11/). The model domain is defined by a Lambert projection centered at 30°N and 70°E and covers Pakistan at 30 km spatial resolution as shown in Fig. 1.
model has fully coupled meteorology-aerosols-radiation-clouds (Grell et al., 2005; Fast et al., 2006; Gustafson et al., 2007; Chapman et al., 2009). The gas-phase chemistry scheme used in this work is the CBM-Z mechanism (Zaveri and Peters, 1999) with photolysis rates calculated using the Fast-J scheme (Wild et al., 2000). The aerosol module is the Model for Simulating Aerosol Interactions and Chemistry (MOSAIC) (Zaveri et al., 2008) with eight size bins (0.039–0.078, 0.078–0.156, 0.156–0.3125, 0.3125–0.625, 0.625–1.25, 1.25–2.5, 2.5–5.0, 5.0–10 μm). Aerosol particles in each size bin are considered to be internally mixed. Simulated aerosol species in MOSAIC include SO4 \(^{2-}\), NO3 \(^{-}\), NH4 \(^{+}\), OC, and BC. The WRF-Chem model considers the interactions of the aerosol radiative effects with meteorological fields. The Goddard shortwave radiative transfer model (Chou et al., 1998) and the Rapid Radiative Transfer Model Longwave Radiation scheme (Mlawer et al., 1997) are used to calculate the aerosol direct radiative effects. The modified Purdue Lin microphysics module by Lin et al. (1983) is used for cloud microphysics.

Emissions Inventories

For simulation of aerosol precursors and all aerosol species in the WRF-Chem model, anthropogenic emissions for NOx, CO, non-methane volatile organic compounds (NMVOCs), SO2, BC, and OC are taken from the Intergovernmental Panel on Climate Change (IPCC) inventory (http://mic.greenresource.cn/intex-b2006) for year 2006. The INTEX-B inventory has a horizontal resolution of 0.5 degree. Emissions of NH3 are taken from Streets et al. (2003). Table 1 summarizes anthropogenic emissions from different sectors (power, industry, residential, and transportation) in Pakistan. Summed over Pakistan (20–40°N, 60–80°E), anthropogenic emissions of NOx, CO, NMVOCs, SO2, NH3, BC, and OC are 2.4 Tg N/yr, 28.8 Tg CO/yr, 5.2 Tg C/yr, 4.8 Tg S/yr, 3.4 Tg N/yr, 0.2 Tg C/yr, and 0.7 Tg C/yr, respectively, in year 2006. Industry and transportation are the two major emission sources of NOx, accounting for 39.6% and 43.2% of total NOx emission in Pakistan, respectively. Residential activities are the largest sources of emissions of CO, NMVOCs, BC, and OC, which contribute, respectively, 62.9%, 43.3%, 58.7%, and 96.3% to the annual total emissions of these species. Industry has the largest contribution to SO2 emissions (accounting for 75.6% of the total). Emissions of NH3 in Pakistan are mainly from agricultural sector. Fig. 2 shows the horizontal distributions of annual anthropogenic emissions of SO2, NOx, NH3, BC, and OC over the simulation domain. Emissions of all species have the same spatial pattern, with highest emissions over northeastern, central, and southeastern Pakistan. Note that because of the lack of information about seasonal variations in emissions, monthly emissions are the same in our simulations for January, April, July, and October of 2006.

Numerical Experiments

The following WRF-Chem simulations are performed in order to examine the seasonal variations in aerosols and to quantify the impacts of transboundary transport on aerosol concentrations in Pakistan:

1. Ctrl: The control simulation of SO4 \(^{2-}\), NO3 \(^{-}\), NH4 \(^{+}\), OC, BC, and PM2.5 for 4 months (i.e., January, April, July, and October) of year 2006.
2. TransB: Sensitivity simulation to examine the impacts of transboundary transport on aerosol concentrations in Pakistan in different seasons. This simulation is the same as the CTRL simulation except that anthropogenic emissions over Pakistan are turned off.

For simulation of each of the four months in year 2006, the model is spun up for 7 days in simulation CTRL or TransB. Initial and lateral boundary conditions for meteorological parameters are taken from the NCEP FNL data with horizontal resolution of 1 degree and temporal resolution of 6 h. (http://rda.ucar.edu/datasets/ds083.2/). Initial conditions and boundary conditions for chemical species are taken from the Model for Ozone and Related Chemical Tracers-version 4 (MOZART-4) (Emmons et al., 2010).

MODEL EVALUATION

Evaluation of Meteorological Parameters

The simulated meteorological fields are evaluated

| Species | Power (Gg) | Industry (Gg) | Residential (Gg) | Transportation (Gg) | Total (Gg) |
|---------|------------|--------------|------------------|--------------------|------------|
| NOx     | 96.3       | 270.5        | 20.4             | 293.6              | 680.7      |
|         | (13.5%)    | (39.6%)      | (3.0%)           | (43.2%)            |            |
| CO      | 0.0        | 1009.5       | 4637.9           | 1730.5             | 7377.9     |
|         | (0%)       | (13.7%)      | (62.9%)          | (23.5%)            |            |
| NMVOCs  | 1.6        | 232.9        | 609.9            | 560.8              | 1405.3     |
|         | (0.1%)     | (16.5%)      | (43.3%)          | (39.9%)            |            |
| SO2     | 421.3      | 2179.8       | 70.1             | 210.7              | 2881.9     |
|         | (14.6%)    | (75.6%)      | (2.4%)           | (7.3%)             |            |
| BC      | 0.7        | 36.3         | 67.4             | 10.4               | 114.8      |
|         | (0.6%)     | (31.6%)      | (58.7%)          | (8.7%)             |            |
| OC      | 06         | 2.8          | 336.8            | 9.3                | 349.4      |
|         | (1.7%)     | (0.8%)       | (96.3%)          | (2.6%)             |            |
against the reanalysis data. We compare modeled monthly mean surface-air temperature, relative humidity (RH), and wind components with NCEP FNL datasets, which are available at the horizontal resolution of 1 degree and the temporal resolution of 6 h. Simulated precipitation is also compared with datasets from the Tropical Rainfall Measuring Mission (TRMM). We use TRMM Level-3 monthly products available at http://gdata1.sci.gsfc.nasa.gov/daac-bin/G3/gui.cgi?instance_id=TRMM_Monthly. We also quantify the model performance using statistical parameters of mean bias (MB), normalized mean bias (NMB), and correlation coefficient ($R$) (Table 2). These statistics are calculated using the simulated and reanalyzed meteorological parameters that are averaged over the model domain and are sampled every 6 hours (to be consistent with the temporal resolution of NCEP FNL datasets).

Fig. 3 compares simulated and reanalyzed monthly mean surface-air temperature for January, April, July, and October.
of 2006. Surface-air temperatures are higher in central and southern Pakistan than in northern regions in all months, with the maximum temperatures exceeding 35°C in July. The model captures well the magnitudes and distributions of temperatures, with monthly MBs of 0.6°C, 2.2°C, 0.8°C, and −0.01°C and NMBs of 9.4%, 12.4%, 3.2%, and −0.05% in January, April, July, and October, respectively.

Fig. 4 shows simulated and reanalyzed monthly mean surface-layer RH for January, April, July, and October of 2006. The simulated RH is generally high (> 40%) throughout the year in northern and southern parts of Pakistan. The high RH in northern Pakistan is associated with precipitation in that region, and the high RH in southern Pakistan is caused by the low latitudes and moist air from the nearby ocean. RH is well simulated with monthly MBs of 0.8%, −4.6%, −4.1%, and −2.5% and NMBs of 1.6%, −10.5%, −7.7% and −5.4% for January, April, July, and October (Table 2), respectively. The bias is relatively large in April because the absolute value of RH averaged over the model domain is the smallest among the four months.

Fig. 5 shows the simulated wind vectors over the model domain. Winds in northeastern and northern Pakistan are generally smaller than those over the Arabian Sea. In the month of July, strong southerlies prevail in southern and central Pakistan, which are associated with the South Asian summer monsoon. The comparisons of simulated and reanalyzed monthly mean zonal and meridional wind components at surface level are shown in Fig. 6. Against the NCEP datasets for January, April, July and October, the zonal wind is simulated with monthly MBs of −0.01, 0.2, 0.1, and −0.01 m/s while the meridional wind has monthly MBs of −0.2, 0.2, −0.05, and 0.1 m/s (Table 2), respectively. Because of the offsets of positive and negative winds, the absolute values of wind speed are small, leading to large NMBs shown in Table 2. The simulated winds correlate well with reanalyzed winds, with correlation coefficients in the range of 0.84–0.95 (Table 2).

Fig. 7 shows spatial distributions of monthly accumulated

![Fig. 3. The monthly mean surface air temperature (°C) from the CTRL simulation (left column) and the NCEP FNL datasets (right column) over the model domain in January, April, July, and October of year 2006.](image-url)
precipitation from simulation as well as the NCEP and TRMM datasets. The largest precipitation of exceeding 300 mm occurs over the northeastern Pakistan in the month of July. The total rainfall in January also exceeds 200 mm over northern Pakistan because of westerlies over the high mountains. The model captures very well the magnitude and seasonal variation of precipitation over the model domain.

Evaluation of Chemical Parameters

In Pakistan, measurements of aerosols are very scarce for the entire country. Limited ground-based observations are available from the two largest cities in Pakistan: Lahore (Lodhi et al., 2009) and Karachi (Mansha et al., 2012). The geographical locations of these sites are shown in Fig. 1 and Table 3 summarizes the ground-based measurements we collected from the literature.

As shown in Table 3, measured aerosol concentrations vary significantly with season and year. Observed concentrations at Lahore and Karachi, exhibited maximum in winter and minimum in summer (Harrison et al., 1997; Hameed et al., 2000; Rattigan et al., 2002; Biswas et al., 2008; Lodhi et al., 2009; Economic Survey 2009–2010; Alam et al., 2011a; Stone et al., 2012; Mansha et al., 2012).

We evaluate first the simulated aerosol concentrations at Lahore. Due to the unavailability of measurements for April, July, and October of 2006, the model results are compared with observations at Lahore for January 2006 (Fig. 8), with measurements taken from Lodhi et al. (2009). Observed $\text{SO}_4^{2-}$ concentrations from years 1999 and 2000 and observed $\text{NO}_3^-$ from year 1999, which were reported in Rattigan et al. (2002) and Hameed et al. (2000), are also shown in Fig. 8 to demonstrate the magnitudes of observed concentrations. The comparison shows that simulated $\text{SO}_4^{2-}$ concentrations agree closely with observed values for January of 2006. The model generally underestimates concentrations of $\text{NO}_3^-$, $\text{NH}_4^+$, OC, and PM$_{2.5}$ in January of 2006. Averaged over hours with measurements available, concentrations of $\text{NO}_3^-$, $\text{NH}_4^+$, OC, and PM$_{2.5}$ are simulated to be 14.0, 5.5,
Table 2. Mean bias (MB) and normalized mean bias (NMB) of the simulated surface-layer meteorological parameters against the NCEP reanalyzed datasets for January, April, July, and October of 2006. The correlation coefficient ($R$) between the simulated and reanalyzed datasets is also shown. These statistics are calculated using the simulated and reanalyzed meteorological parameters that are averaged over the model domain and are sampled every 6 hours (to be consistent with the temporal resolution of NCEP FNL datasets).

| Variable     | Mean Bias (MB) | Normalized Mean Bias (NMB, %) | $R$ |
|--------------|----------------|-------------------------------|-----|
| Temperature  |                |                               |     |
| January      | 0.6°C          | 9.4%                          | 0.98|
| April        | 2.2°C          | 12.4%                         | 0.99|
| July         | 0.8°C          | 3.2%                          | 0.99|
| October      | –0.01°C        | –0.05%                        | 0.98|
| Relative Humidity |          |                               |     |
| January      | 0.8%           | 1.6%                          | 0.98|
| April        | –4.6%          | –10.5%                        | 0.98|
| July         | –4.1%          | –7.7%                         | 0.99|
| October      | –2.5%          | –5.4%                         | 0.99|
| U–wind       |                |                               |     |
| January      | –0.01 m/s      | –26.0%                        | 0.94|
| April        | 0.2 m/s        | 12.6%                         | 0.95|
| July         | 0.1 m/s        | 8.2%                          | 0.94|
| October      | –0.01 m/s      | –1.4%                         | 0.91|
| V-wind       |                |                               |     |
| January      | –0.2 m/s       | 58.5%                         | 0.94|
| April        | 0.2 m/s        | –42.9%                        | 0.89|
| July         | –0.05 m/s      | –19.6%                        | 0.84|
| October      | 0.1 m/s        | –35.3%                        | 0.87|

Fig. 5. Simulated monthly mean wind vectors over the model domain during (a) January, (b) April, (c) July, and (d) October of year 2006. Wind speed and wind direction are represented by arrows. The length of arrow of wind speed of 10 m/s is indicated below the bottom right panel.

15.4, and 48.0 µg/m³, while observed concentrations are 25.2, 12.6, 57.1, and 142.2 µg/m³, respectively. These model biases suggest that there might be some uncertainties in anthropogenic emissions.

We then evaluate simulated aerosol concentrations at Karachi. Measured concentrations of SO$_4^{2-}$, NO$_3^-$, and PM$_{2.5}$ at Karachi during January, April, July, and October of 2006 are taken from Mansha et al. (2012). Fig. 9 compares simulated and observed concentrations for dates with measurements available. Simulated SO$_4^{2-}$ concentrations peak in July, but the observed SO$_4^{2-}$ concentrations show maximum in October. Simulated NO$_3^-$ concentrations agree with measurements in January and April, and the model results show large low biases in July and October.
Simulated concentrations of NO$_3^-$ over Karachi during the months of July and October are very low, which can be attributed to several reasons. First, emissions of all chemical species over Karachi are lower than emissions over northeastern Pakistan (Fig. 2). Second, strong southerlies from Arabian Sea in July (Fig. 5) transport NO$_3^-$ from Karachi to downwind areas. Third, high temperatures during July and October in southern Pakistan are not favorable for NO$_3^-$ formation. While the simulated NO$_3^-$ concentrations are practically zero in July and October, measured nitrate concentrations are in the range of 5–50 µg/m$^3$ in these two months. With respect to PM$_{2.5}$, simulated concentrations are about 20 µg/m$^3$ in all seasons. It should be noted that observed PM$_{2.5}$ concentrations are the highest in January (100–120 µg/m$^3$), followed by April (50–80 µg/m$^3$), July (40–50 µg/m$^3$), and October (about 40 µg/m$^3$).

**Evaluation of Aerosol Optical Depth (AOD)**

Satellite measurements provide large spatial and temporal coverage and can be used to evaluate simulated aerosols by examining aerosol optical depth. We use retrieved AOD from the Moderate-resolution Imaging Spectroradiometer (MODIS) Terra satellite at the wavelength of 550 nm for months of January, April, July, and October in 2006. The datasets are level 3 monthly products downloaded from NASA Giovanni website (http://disc.sci.gesfc.nasa.gov/giovanni). We also use retrieved AOD from the Aerosol Robotic NETwork (AERONET) (Holben et al., 1998). Currently
there are 2 AERONET sites in Pakistan and their levels 1.0, 1.5 and 2.0 products of AOD are available. Retrieved level 2.0 AOD values at Lahore during January 2007–October 2012 and at Karachi, October 2006–October 2012 are used in model evaluation. The optical properties of aerosols simulated in the WRF-Chem model are at the wavelengths of 300, 400, 600, and 999 nm. Since AOD from AERONET and satellite are at the wavelengths of 500 nm and 550 nm, respectively, simulated AOD values are interpolated to 500 nm and 550 nm following the Angström power law (http://disc.sci.gsfc.nasa.gov/data-holdings/PIP/aerosol_angstrom_exponent.shtml).

Fig. 10 shows the simulated monthly mean AOD in the CTRL simulation and MODIS retrieved AOD for 2006. Simulated AOD values are the averages over hours 10 and 11 AM, since the Terra local equatorial crossing time is approximately 10:30 AM (http://nsidc.org/data/modis/terra_aqua_differences/). Simulated monthly mean AOD values are in the range of 0.3–0.5 in January, and are 0.5–0.7 in northern Pakistan and 0.7–0.9 in southern Pakistan in April. Simulated AOD exceeds 0.9 over eastern Pakistan in July as a result of the high RH of 40–60% in this month (Fig. 4). In October, simulated monthly mean AOD values are 0.5–0.7 over eastern Pakistan. The simulated seasonal variations and magnitudes of AOD agree closely with the MODIS measurements. Both simulated and observed AOD values peak in July although simulated PM$_{2.5}$ concentrations are the lowest in this month (Fig. 12). However, the model slightly overestimates AOD in April as compared to the MODIS measurements. Note that mineral dust aerosol contributes largely to AOD in the months of April and July. Kaskaoutis et al. (2011) reported that dust load is high over northwestern India and Pakistan in April to July due to the long range transport of dust from the Arabian Peninsula and the Middle East. Dey et al. (2004) also reported that high AOD values were observed over Indian
Table 3. Ground-based measurements of aerosols in Pakistan reported in the literature.

| Location | Period | Concentration (µg/m³) | Reference |
|----------|--------|------------------------|-----------|
| Lahore (74°22'E, 31°32'N) | October, 1992–October, 1993 | 18.4 | Harrison et al. (1997) |
| | December, 1998–January, 1999 | 17–99 | Hameed et al. (2000) |
| | December, 1999–January, 2000 | 4–141 | Rattigan et al. (2002) |
| | June, 2007 | 0.5–7.2 | Stone et al. (2012) |
| | December, 2007 | 0.5–10.6 | Stone et al. (2012) |
| | November, 2005–March, 2006 | 3.3–59 | Lodhi et al. (2009) |
| | December, 2005–February, 2006 | 19.2 | Lodhi et al. (2009) |
| Karachi (67°E, 24°53'N) | January–March, 2006–2008 | 0.9–7.5 | Mansha et al. (2012) |
| | April–June, 2006–2008 | 1.0–7.6 | Mansha et al. (2012) |
| | July–September, 2006–2008 | 1.8–8.8 | Mansha et al. (2012) |
| | October–December, 2006–2008 | 3.6–10.5 | Mansha et al. (2012) |
| | 2005–2010 | 53.2 | Economic Survey (2009–2010) |
| Lahore (74°22'E, 31°32'N) | October, 1992–October, 1993 | 12.8 | Harrison et al. (1997) |
| | December, 1998–January, 1999 | 22.8–56.5 | Hameed et al. (2000) |
| | December, 1999–January, 2000 | 3–74.5 | Rattigan et al. (2002) |
| | June, 2007 | 0.3–2.9 | Stone et al. (2012) |
| | December, 2007 | 0.8–16.0 | Stone et al. (2012) |
| | November, 2005–March, 2006 | 2.10–73 | Lodhi et al. (2009) |
| Karachi (67°E, 24°53'N) | January–March, 2006–2008 | 0.6–6.28 | Mansha et al. (2012) |
| | April–June, 2006–2008 | 1.8–4.7 | Mansha et al. (2012) |
| | July–September, 2006–2008 | 12.4–14.3 | Mansha et al. (2012) |
| | October–December, 2006–2008 | 13.1–15.4 | Mansha et al. (2012) |
| Lahore (74°22'E, 31°32'N) | November, 2005–January, 2006 | 21.7 | Hussain et al. (2007) |
| | November, 2005 | 17.3 | Dutkiewicz et al. (2009) |
| | January, 2006 | 21.7 | Dutkiewicz et al. (2009) |
| Karachi (67°E, 24°53'N) | November 2006–February 2007 | 10 | Dutkiewicz et al. (2009) |
| | June–September, 2007 | 2 | Dutkiewicz et al. (2009) |
| Pakistan | April, 2002–2005 | 10 | Hopke et al. (2008) |

subcontinent during June to August, as a result of the strong southwesterlies that transported dust from the Thar and the Arabian deserts.

Fig. 11 compares simulated and AERONET AOD values at 500 nm for Lahore and Karachi. The AERONET datasets are only available for October 2006 for Karachi; therefore we also compare the simulated AOD values with measurements from years 2007–2012. Modeled AOD values over Lahore
Fig. 8. Simulated and observed daily variations in surface-layer concentrations (µg/m³) of (a) SO₄²⁻, (b) NO₃⁻, (c) NH₄⁺, (d) OC, and (e) PM₂.₅ at Lahore in January of 2006.
Fig. 9. Simulated and observed surface-layer concentrations (µg/m³) of (a) SO$_4^{2-}$, (b) NO$_3^-$, and (c) PM$_{2.5}$ at Karachi in January, April, July, and October of 2006.
Fig. 10. Comparisons of simulated monthly mean AOD (left column) with the MODIS AOD (right column) for year 2006. Regions with white color indicate places with no MODIS AOD datasets available.

are within the range of AERONET retrievals in January, April, July, and October. In Karachi, simulated AOD values agree with AERONET observations in January and October, but the model overestimates AOD values by about 0.4–0.5 in April and July. Alam et al. (2010b) reported that AOD values were high in the southern coastal areas of Pakistan during the humid summer season due to hygroscopic aerosols as well as the presence of mineral dust.

SEASONAL VARIATION OF AEROSOLS IN PAKISTAN

The simulated horizontal distributions of monthly mean concentrations of aerosols are shown in Fig. 12 for January, April, July, and October to represent aerosol concentrations in four seasons in Pakistan. Over eastern Pakistan, $\text{SO}_4^{2-}$ aerosol exhibits maximum concentrations of 5–10 µg/m$^3$ in July and October and of 3–5 µg/m$^3$ in January and April. Strong photochemistry facilitates maximum $\text{SO}_4^{2-}$ formation in July almost all over Pakistan. High sulfate concentrations in summer are attributed to more rapid oxidation of SO$_2$ to sulfate in warmer months because of higher rate constants and higher oxidant concentrations (Aw and Kleeman, 2003; Dawson et al., 2007; Kleeman, 2007). Simulated concentrations of NO$_3^-$ are generally higher than those of SO$_4^{2-}$ in northeastern Pakistan. The highest NO$_3^-$
Fig. 11. Comparison of simulated AOD and AERONET retrieved AOD at 500 nm for (a) Lahore and (b) Karachi.

Concentrations of 30–50 µg/m³ are simulated in April and October, as a result of the relatively low temperatures and precipitation. In contrast, high temperatures and large rainfall lead to maximum NO₃⁻ concentrations of about 25–30 µg/m³ in July. The simulated high nitrate concentrations are likely caused by the overestimate of NOₓ emissions. Ghude et al. (2013) reported the overestimation of NOₓ emissions in the INTEX-B inventory for the western and eastern Indo-Gangetic region using the WRF-Chem model with an iterative inverse technique. Simulated highest BC (or OC) concentrations in northeastern Pakistan are 5–10 µg/m³ (or 10–20 µg/m³) in January and October. Simulated PM<sub>2.5</sub> concentrations averaged over northeastern Pakistan (71–74.5°E, 28–34°N) are 55, 48.5, 31.5, and 98 µg/m³ in January, April, July, and October, respectively.

In general, simulated aerosol concentrations are high over eastern Pakistan and aerosol concentrations show strong seasonal variations. Compared to the concentrations in January, aerosol levels in April show reductions but high concentration levels remain over the northeastern Pakistan. In July, the summer monsoon cleans out northeastern part of the Pakistan but pollutants start to build up over the central and southern Pakistan where precipitation is not significant (Fig. 7). During the post monsoon period (October), aerosol concentrations become significant again, with concentrations in October higher than those in January.

Fig. 13 shows the percentages of SO₄²⁻, NO₃⁻, NH₄⁺, BC, and OC in the total PM<sub>2.5</sub> concentration over Pakistan for the four months. In January and April, NO₃⁻ and OC are simulated to have the largest contributions to PM<sub>2.5</sub> over northeastern and central Pakistan, with NO₃⁻ accounting for about 35–60% of PM<sub>2.5</sub> in eastern Pakistan and OC accounting for 25–45% in central Pakistan. In July, SO₄²⁻ is simulated to be the most dominant chemical component of PM<sub>2.5</sub> all over Pakistan, which contributes to PM<sub>2.5</sub> by about 30–40% in northern Pakistan and by about 50–90% in southern Pakistan. In October, NO₃⁻ is simulated to have the largest contribution of 40–50% to PM<sub>2.5</sub> over eastern Pakistan, and SO₄²⁻ is still the most dominant aerosol species in southern Pakistan.

The large contributions of NO₃⁻, OC, and SO₄²⁻ to PM<sub>2.5</sub> can also be seen in Fig. 14, in which we show the percentages of each anthropogenic aerosol species in the total PM<sub>2.5</sub> concentration in the two largest cities of Lahore and Karachi. Over Lahore, the most dominant aerosol species are OC (27–32%) and NO₃⁻ (24–28%) in January and April, SO₄²⁻...
Fig. 12. Simulated monthly mean surface-layer concentrations (µg/m³) of SO$_4^{2-}$, NO$_3^-$, NH$_4^+$, BC, OC, and PM$_{2.5}$ in the CTRL simulation for (a) January, (b) April, (c) July, and (d) October of 2006.

(31%) and OC (30%) in July, and NO$_3^-$ (38%) in October. Over Karachi, SO$_4^{2-}$ has a dominant contribution to PM$_{2.5}$ by 47%, 66%, and 58% in April, July, and October, respectively.

IMPACTS OF TRANSBOUNDARY TRANSPORT ON AEROSOL LEVELS OVER PAKISTAN

As described in the section of “Numerical Experiments”, we performed a simulation experiment TransB (with anthropogenic emissions from Pakistan turned off) in order to examine the impacts of transboundary transport on aerosol concentrations in Pakistan in different seasons. Simulated monthly mean surface-layer concentrations of SO$_4^{2-}$, NO$_3^-$, NH$_4^+$, BC, OC, and PM$_{2.5}$ from TransB are shown in Fig. 15. The contributions of transboundary transport to aerosol levels in Pakistan can also be quantified.
Fig. 13. Simulated percentages (%) of SO$_4^{2-}$, NO$_3^-$, NH$_4^+$, BC, and OC in the total PM$_{2.5}$ concentration for (a) January, (b) April, (c) July, and (d) October of year 2006.

by the ratios of aerosol concentrations in TransB to those simulated in the CTRL simulation (Fig. 16). Simulated aerosol concentrations in TransB (Fig. 15) show that the transboundary pollution plays an important role in aerosol levels over northeastern Pakistan in all months. In January, easterlies in northeastern Pakistan (Fig. 6) lead to high concentrations of NO$_3^-$, NH$_4^+$, and OC transported from India (Fig. 15). As a result, 5–10 µg/m$^3$ (or 10–20% as shown in Fig. 16) of PM$_{2.5}$ concentration in northeastern Pakistan in January can be attributed to transboundary transport. During April, transboundary transport contributes 5–10 µg/m$^3$ (or 10–20%) of PM$_{2.5}$ over the border of northeastern Pakistan.

During the month of July, strong southeasterlies associated with the summer monsoon favor the transport of aerosols from India to northeastern Pakistan, but aerosols are washed out by heavy precipitation. Transboundary transport contributes 10–40% of PM$_{2.5}$ over the whole northern Pakistan in July, although the overall PM$_{2.5}$ levels in Pakistan are the lowest in this month (Fig. 12). In October, with prevailing easterlies and low precipitation in northeastern Pakistan and India, 10–35 µg/m$^3$ (or 10–40%) of PM$_{2.5}$ in northeastern Pakistan are transported from India (Figs. 15 and 16).
CONCLUSIONS

We present here a first regional modeling study on the spatial distribution and temporal variation of aerosol concentrations over Pakistan using the WRF-Chem Model. Concentrations of sulfate, nitrate, ammonium, black carbon, organic carbon, and PM$_{2.5}$ are simulated for year 2006 by using anthropogenic emissions from the INTEX-B emissions inventory. Because of the lack of information about seasonal variations in emissions, annual mean emissions are used in our simulations. We examine seasonal variations of aerosols and the impacts of transboundary transport on aerosol levels in Pakistan.

Concentrations of aerosols are simulated for January, April, July, and October of 2006 to represent aerosol concentrations in four seasons in Pakistan. Model simulation shows that concentrations of nitrate, ammonium, black carbon, organic carbon, and PM$_{2.5}$ are the highest in October, followed by those in January, April, and July. The highest concentrations of these aerosol species in October result from the relatively low temperatures that favor nitrate formation as well as the lowest precipitation that leads to the smallest wet deposition of aerosols. The simulated lowest concentrations of nitrate, ammonium, black carbon, organic carbon, and PM$_{2.5}$ in July are attributed to the largest precipitation associated with the South Asian summer monsoon. Note that simulated sulfate aerosol shows different seasonal variations from other aerosol species; simulated sulfate concentrations are the highest in July. In year 2006, simulated PM$_{2.5}$ concentrations averaged over northeastern Pakistan (71–74.5°E, 28–34°N) are 55, 48.5, 31.5, and 98 µg/m$^3$ in January, April, July, and October, respectively. Over Lahore, the most dominant aerosol species are simulated to be OC (account for 27–32% of PM$_{2.5}$) and NO$_3^-$ (24–28%) in January and April, SO$_4^{2-}$ (31%) and OC (30%) in July, and NO$_3^-$ (38%) in October. Over Karachi, SO$_4^{2-}$ has a dominant contribution to PM$_{2.5}$ by 47%, 66%, and 58% in April, July, and October, respectively.

We also perform a sensitivity simulation with anthropogenic emissions in Pakistan turned off to examine the impacts of transboundary transport on aerosol concentrations in Pakistan in different seasons. Transboundary pollution is simulated to be important over northeastern Pakistan in all months; transboundary transport contributes to PM$_{2.5}$ aerosol levels in northeastern Pakistan by 10–20% in January and April and by 10–40% in July and October. Wind over...
India and Pakistan is found to be the major meteorological parameter that determines the transboundary aerosol transport. Comparisons our simulated aerosols with ground-based measurements of concentrations and satellite measurements of aerosol optical depth suggest further improvements in studies of aerosols in Pakistan. First, emission inventories of aerosol precursors and aerosols need continuing improvement in terms of both total amount and seasonal variations. With limited observational datasets available, the comparisons with observations at Lahore and Karachi show that the model can reproduce the magnitude of sulfate aerosol concentrations but tends to underestimate concentrations of NO$_3^-$, NH$_4^+$, OC, and PM$_{2.5}$. Second, nationwide long-term ground-based measurements of both aerosol precursors and aerosols are needed for evaluation of emission inventories and for improving the representations of chemical species in models. Third, natural aerosol species, such as mineral dust and sea salt, should be examined in

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**Fig. 15.** Simulated monthly mean surface-layer concentrations (µg/m$^3$) of SO$_4^{2-}$, NO$_3^-$, NH$_4^+$, BC, OC, and PM$_{2.5}$ in the TransB simulation for (a) January, (b) April, (c) July, and (d) October of 2006.
our future work since these two species contribute largely to simulated and observed aerosol optical depth in April and July.

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REFERENCES

Adhikary, B., Carmichael, G.R., Tang, Y., Leung, L.R.,
Qian, Y., Schauer, J.J., Stone, E.A., Ramanathan, V. and Ramana, M.V. (2007). Characterization of the Seasonal Cycle of South Asian Aerosols: A Regional-scale Modeling Analysis. J. Geophys. Res. 112: D22S22.

Alam, K., Thomas, B., Pierre, M., Azam, M., Majid, H., Thomas, T. and Said, R. (2011a). Aerosol Size Distribution and Mass Concentration Measurements in Various Cities of Pakistan. J. Environ. Monit. 13: 1944–1952.

Alam, K., Iqbal, M.J., Blaschke, T., Qureshi, S. and Khan, G. (2010b). Monitoring Spatio-temporal Variations in Aerosols and Aerosol–cloud Interactions over Pakistan Using MODIS Data. Adv. Space Res. 46: 1162–1176.

Aw, J. and Kleeman, M.J. (2003). Evaluating the First-order Effect of Intra-annual Temperature Variability on Urban Air Pollution. J. Geophys. Res. 108: 4365.

Begum, A.B., Biswas, K.S., Gauri, G. Pandit, G.G., Saradhi, V.I., Waheed, S., Siddique, N., Seneviratne, M.C.S., Cohen, D.D., Andreas, M. and Hopke, P.K. (2011). Long–range Transport of Soil Dust and Smoke pollution in the South Asian Region. Atmos. Pollut. Res. 2: 151–157.

Biswas, K.F., Ghauri, B.M. and Husain, L. (2008). Gaseous and Aerosol Pollutants during Fog and Clear Episodes in South Asian Urban Atmosphere. Atmos. Environ. 42: 7775–7785.

Chapman, E.G., Gustafson Jr., W.I., Easter, R.C., Barnard, J.C., Ghan, S.J., Pekour, M.S. and Fast, J.D. (2009). Coupling Aerosol-Cloud-Radiative Processes in the Wrf-Chem Model: Investigating the Radiative Impact of Elevated Point Sources. Atmos. Chem. Phys. 9: 945–964.

Chou, M.D., Suarez, M.J., Ho, C.H., Yan, M.M.H. and Lee, K.T. (1998). Parameterizations for Cloud Overlapping and Shortwave Single-Scattering Properties for Use in General Circulation and Cloud Ensemble Models. J. Clim. 11: 202–214.

Dawson, J.P., Adams, P.I. and Pandis, S.N. (2007). Sensitivity of PM_{2.5} to Climate in the Eastern US: A Modeling Case Study. Atmos. Chem. Phys. 7: 4295–4309.

Dey, S., Sarkar, S. and Singh, R.P. (2004). Comparison of Aerosol Radiative Forcing over the Arabian Sea and the Bay of Bengal. Adv. Space Res. 33: 1104–1108.

Dutkiewicz, V.A., Alvi, S., Ghauri, B.M., Choudhary, M.I. and Husain, L. (2009). Black Carbon Aerosols in Urban Air in South Asia. Atmos. Environ. 43: 1737–1744.

Economic Survey 2009–2010. http://Economic.gov.pk/survev/chapter_10/15_Environment.pdf.

Emmons, L.K., Walters, S., Hess, P.G., Lamarque, J.F., Pfister, G.G., Fillmore, D., Granier, C., Guenther, A., Kinnison, D., Laepple, T., Orlando, J., Tie, X.X., Tyndall, G., Wiedinmyer, C., Buhcgham, S.L. and Kloster, S. (2010). Description and Evaluation of the Model for Ozone and Related Chemical Tracers, Version 4 (MOZART-4). Geosci. Model Dev. 3: 43–67.

Fast, J.D., Gustafson W.I., Easter, R.C., Zaveri, R.A., Barnard, J.C., Chapman, E.G., Grell, G.A. and Peckham, S.E. (2006). Evolution of Ozone, Particulates, and Aerosol Direct Radiative Forcing in the Vicinity of Houston Using a Fully Coupled Meteorology-Chemistry-Aerosol Model. J. Geophys. Res. 111: D21305.
Kleeman, M.J. (2007). A Preliminary Assessment of the Sensitivity of Air Quality in California to Global Change. Clim. Change 87: S273–S292.

Lin, Y.L., Farley, R.D. and Orville, H.D. (1983). Bulk Parameterization of the Snow Field in a Cloud Model. J. Clim. Appl. Meteorol. 22: 1065–1092.

Lodhi, A., Ghauri, B., Khan, R. M., Rahman, S. and Shafique, S. (2009). Particulate Matter (PM$_{2.5}$) Concentration and Source Apportionment in Lahore. J. Braz. Chem Soc. 20: 1811–1820.

Mansha, M., Ghauri, B., Rahman, S. and Amman, A. (2012). Characterization and Sources Apportionment of ambient Air Particulate matter (PM$_{2.5}$) in Karachi. Sci. Total Environ. 425: 176–183.

Mlawer, E.J., Taubman, S.J., Brown, P.D., Iacono, M.J. and Clough, S.A. (1997). Radiative Transfer for Inhomogeneous Atmospheres: RRTM, a Validated Correlated-K Model for the Longwave. J. Geophys. Res. 102: 16663–16682.

Rattigan, O.V., Mirza, M.I., Ghauri, B.M., Khan, A.R., Swami, K., Yang, K. and Husain, L. (2002). Aerosol Sulfate and Trace Elements in Urban Fog. Energy Fuels 16: 640–646.

Stone, E., Schauer, J., Quraishi, T.A. and Mahmood, A. (2010). Chemical Characterization and Source Apportionment of Fine and Coarse Particulate Matter in Lahore, Pakistan. Atmos. Environ. 44: 1062–1070.

Streets, D.G., Bond, T.C., Carmichael, G.R., Fernandes, S.D., Fu, Q., He, D., Klimont, Z., Nelson, S.M., Tsai, N.Y., Wang, M.Q., Woo, J.H. and Yarber, K.F. (2003). An Inventory of Gaseous and Primary Aerosol Emissions in Asia in the Year 2000. J. Geophys. Res. 108: 8809–8832.

Wild, O., Zhu, X. and Prather, M.J. (2000). Fast-J: Accurate Simulation of in- and Below-Cloud Photolysis in Tropospheric Chemical Models. J. Atmos. Chem. 37: 245–282.

Zaveri, R.A. and Peters, L.K. (1999). A New Lumped Structure Photochemical Mechanism for Large Scale Applications. J. Geophys. Res. 104: 30387–30415.

Zaveri, R.A., Easter, R.C., Fast, J.D. and Peters, L.K. (2008). Model for Simulating Aerosol Interactions and Chemistry (Mosaic). J. Geophys. Res. 113: D13.

Zhang, Q., Streets, D.G., Carmichael, G.R., He, K.B., Huo, H., Kannari, A., Klimont, Z., Park, I.S., Reddy, S., Fu, J.S., Chen, D., Duan, L., Lei, Y., Wang, L.T. and Yao, Z.L. (2009). Asian Emissions in 2006 for the NASA INTEX-B Mission. Atmos. Chem. Phys. 9: 5131–5153.

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