

available at www.sciencedirect.comwww.elsevier.com/locate/scitotenv

Fate and transport of emissions for several trace metals over the United States

William T. Hutzell*, Deborah J. Luecken

Atmospheric Modeling Division, National Exposure Research Laboratory, U.S. Environmental, Protection Agency, Research Triangle Park, North Carolina, 27711, USA

ARTICLE INFO

Article history:

Received 27 July 2007

Received in revised form

30 January 2008

Accepted 5 February 2008

Keywords:

Toxic metals

Particulate matter

Model

Air pollution

ABSTRACT

A regional model for atmospheric photochemistry and particulate matter is used to predict the fate and transport of five trace metals: lead, manganese, total chromium, nickel, and cadmium over the continental United States during January and July 2001. Predicted concentrations of the metals are compared to observations. Lead predictions have the lowest mean differences with observations and the highest correlation coefficients. They best agree with observations made in January over residential and commercial areas in the eastern United States and worst with observations over remote forests and deserts located in the western United States during July. Manganese predictions show similar abilities to reproduce observations but had larger changes between months. Chromium and nickel predictions show diminishing ability to reproduce observations over both urban and rural areas. Cadmium predictions show the least ability to reproduce observations. Potential causes are examined for the errors in predictions. For errors in lead, manganese and perhaps chromium predictions, aerial suspension and biomass burning are suspected because simulations did not include emissions from these sources. Nickel, cadmium and, to a lower extent, chromium predictions suffer from errors in the emissions that represent current anthropogenic activities. Predicted concentrations of all metals show errors from not including sub-grid processes in meteorological and emission rates. Examples include sea breeze circulation along coastal areas and individual sources in urban areas. These errors reduce the ability to reproduce the time dependence of observations.

Published by Elsevier B.V.

1. Introduction

Trace metals in particulate matter can have serious health and environmental effects. Although mercury has received great amounts of attention recently, lead, a criteria as well as a Hazardous Air Pollutant (HAP), continues to adversely affect human health despite decades of control efforts (U.S. EPA, 2006a). Several other metals are classified by the United States Clean Air Act as HAPs based on known or suspected environmental and ecological effects. For example, studies link exposure to chromium, manganese, nickel, and cadmium to chronic health effects such as cancer, asthma and cardio-

pulmonary disease (Schlesinger et al., 2006). Exposure pathways include inhaling ambient air concentrations and consuming contaminated water, soil and food. Based on inhalation risks to human health posed by these elements, the United States Environmental Protection Agency (US EPA) lists these five trace metals and three others as among the worst urban air toxics (www.epa.gov/ttn/atw/nata/34poll.html).

These potential health risks motivate research on how air concentrations of trace metals vary with location and time as well as what atmospheric processes determine the concentrations. Monitoring sites can be used only to a limited extent. They measure concentrations at select locations and times but

* Corresponding author. Tel.: +1 919 541 3425.

E-mail address: hutzell.bill@epa.gov (W.T. Hutzell).

cannot be deployed in sufficient number to characterize the concentrations over large and diverse geographic areas, such as the United States. Also, monitors only measure current concentrations and cannot readily predict how concentrations change for different emissions and meteorological scenarios, such as in emission control strategies or climate variability. For these reasons, atmospheric models are important tools for understanding the fate and transport of trace metals as well as predicting air concentrations and atmospheric deposition.

The US EPA has used an atmospheric model to assess concentrations of trace metals and their health risks, as reported in the National Air Toxics Assessment (U.S. EPA, 2006b). Previous assessments used ambient air concentrations estimated by the Assessment System for Population Exposure Nationwide (ASPEN) model (Rosenbaum et al., 1999). ASPEN calculates the concentrations by dispersing emissions in a Gaussian plume such as in the Industrial Source Complex Long Term (U.S. EPA, 1995) model. ASPEN has several shortcomings. Emissions affect concentrations only up to 50 km away from the source thereby underestimating concentrations because trace metals exist in Particulate Matter with diameters less than 2.5 μm ($\text{PM}_{2.5}$). Such aerosols undergo long-range transport based on their low dry deposition velocities and sporadic scavenging by precipitation. ASPEN also assumes a constant sedimentation velocity because it does not use an aerosol distribution that depends on time and location. The assumption fails over regional distances and seasonal periods over which the predicted concentrations are needed. In future assessments, the EPA will attempt to remove these problems, but not all of them, by using an improved Gaussian plume model called the American Meteorology Society-Environmental Protection Agency Regulatory Model (Cimorelli et al., 2005).

The above problems may be overcome by using Eulerian models that simulate atmospheric photochemistry and particulate matter. Such models determine spatial and temporal changes in particulate matter with size distributions by solving mass continuity equations that include emissions, advection, diffusion, photochemical production, wet, and dry depositions. Previous studies have used Eulerian models to simulate trace metals in $\text{PM}_{2.5}$ from global to urban scales.

The Meteorological Synthesizing Centre — East model simulated fate and transport of mercury, lead, and cadmium emissions over Europe (Ilyin et al., 2005, 2006). Results were used to examine the roles of trans-boundary transport versus emissions and have concluded that simulations need to include natural emissions such as aerial suspension of dust and sea salt. Over North America, the Global and Regional Atmospheric Heavy Model (Dastoor and Larocque, 2004) simulated atmospheric mercury to provide boundary conditions for nested simulations by several air quality models including a version of Community Multi-scale Air Quality (CMAQ) modeling system for atmospheric mercury (Bullock and Brehme, 2002). Their predictions were used for an inter-comparison between regional mercury models (Bullock et al., 2006). The Comprehensive Air Quality Model with extensions (CAMx) was used to estimate the amounts of hexavalent chromium, total chromium and diesel emissions found in $\text{PM}_{2.5}$ over southern California (Marshall et al., 2006) in order to assess exposure from ambient and indoor concentrations.

We have adapted the CMAQ modeling system (Byun and Ching, 1999; Byun and Schere, 2006) to simulate air concentrations and deposition of HAPs, including several trace metals. The adapted model is part of version 4.6 of the modeling system and is available from the Community Modeling and Analysis System (<http://www.cmascenter.org>). To test the model, we completed simulations over the continental United States and compared predicted concentrations to observations of five trace metals: lead, manganese, chromium, nickel and cadmium. We also attempt to demonstrate the model and to explore problems in simulating trace metals over the modeling domain. The following sections describe the model, simulations and comparison to observations. The final sections discuss potential reasons why predictions differ from observations and suggest how simulations could be improved.

2. Modeling

Our study uses version 4.6 of the CMAQ modeling system that simulates urban and regional air quality. The Chemical Transport Model in CMAQ (CCTM) uses one of two mechanisms for the photochemistry for HAPs: either the Carbon Bond Mechanism version 05 (Luecken et al., in press; Yarwood et al., 2005) or the SAPRC99 mechanism (Carter, 2000) modified to include additional species. The additional species represent HAPs as solely gas or aerosol phase compounds. Our study uses the supplemented version of SAPRC99 called SAPRC99TX3 in CMAQ version 4.6. Luecken et al. (2006) described how the mechanism was supplemented with gas phase HAPs and evaluated predictions for some of these pollutants. To simulate aerosol phase HAPs, we adapted the aerosol module within the CCTM that uses three lognormal modes to simulate aerosol microphysics and chemistry (Binkowski and Roselle, 2003). Aerosol phase HAPs track components within particulate matter and are treated as chemically inert but undergo the same microphysical processes and deposition rates determined within the aerosol module. This paper considers five trace metals: cadmium, chromium (trivalent and hexavalent), lead, manganese, and nickel. Each metal is treated as aerosol phase HAP within the CCTM. Trivalent and hexavalent chromium likely violate the assumption about being chemically inert because research (Kotas and Stasicka, 2000; Zhang, 2000; Seigneur and Constantinou, 1995) indicates that reversible changes occur between valence states of chromium via chemistry within cloud droplets. However, the kinetics are not well understood so the CCTM does not simulate the chemical process. Neglecting it should not affect predictions for total chromium because valence changes do not alter the volatility of chromium. Hence, this paper presents observations and predictions for total chromium. Total concentrations were calculated after model simulations.

Simulations were performed for two periods covering January and July 2001. The computational grid used 147 by 112 grid cells with horizontal dimensions equal to $36 \times 36 \text{ km}^2$ covering the continental United States. Vertically, the model domain spanned from the surface to 10^4 Pa ($\approx 12 \text{ km}$) and divided the distance into 14 layers based on sigma pressure coordinates. Simulations used meteorological data produced by the Penn State/NCAR Mesoscale Model (MM5) (<http://box.mmm.ucar.edu/mm5/>), version 3.6.1. McNally (2003) and

Gilliam et al. (2006) describe the configuration used in MM5. To create meteorological inputs for the CCTM, MM5 results were processed through the Meteorology-Chemical Interface Processor (MCIP), version 3.2, part of the CMAQ modeling system. The horizontal and vertical advection used an advection method based on Yamartino (1993). Horizontal diffusion used the multi-scale method while vertical diffusion was based on the Atmospheric Convection Mechanism (Pleim, 2007).

Initial and boundary concentrations used represent clean air concentrations (Gipson, 1999) and did not have values for the trace metals simulated. Observations of trace metals have been collected over the remote marine boundary layer (Witt et al., 2006; Spokes et al., 2001). For the metals that are being studied, the total observed concentrations varied from 0.010 to 0.200 ng/m³ and concentrations in PM_{2.5} were less than 0.050 ng/m³. As shown in Table 1, PM_{2.5} concentrations in the marine boundary layer are generally below the lowest concentrations observed over rural locations in the United States that include the agricultural areas, forests and deserts. Predicted concentrations should not significantly alter if observations in the marine boundary layer were used as boundary conditions.

Simulations used hourly emissions of the trace metals, other HAPs, Volatile Organic Compounds and inorganic compounds based on annual emissions in the 1999 National Emission

Inventory (NEI) version 3 (<http://www.epa.gov/ttn/chief/net/1999inventory.html#final3haps>). The NEI provided the best inventory available. We expect small differences between 1999 and 2001 emissions. Biogenic emissions were calculated with the Biogenic Emissions Inventory System (BEIS) version 3.12 (<http://www.epa.gov/asmdnerl/biogen.html>). The Sparse Matrix Operator Kernel Emissions (SMOKE) version 2.0 (<http://cf.unc.edu/cep/emppd/products/smoke/index.cfm>) was used to produce emission files for the CCTM simulations.

3. Observations

To evaluate predictions, we obtained observations of metals in PM_{2.5} from the US EPA's Air Quality System database (AQS) (U. S. EPA, 2006c). Observations come from local, state and federal agencies. They cover a national scale (Fig. 1) and have an averaging period equal to 24 h. Sampling frequencies range from several days to a week. Measurements of metals come from several types of monitors that have detection limits around 0.005 ng/m³. Measurements equal to zero are actually below this limit. Such observations happen frequently and make difficult the comparison between predictions and observations because the predictions are always nonzero.

Table 1 – Comparison statistics based on all observations

Metal	Month	Location	# Observations	Observed average ^a (observed S.D.)	Mean bias ^b (mean relative bias)	Model S.D. (normalized model S.D. ^c)	r ² (95% confidence limits)
Cd	Jan	Rural	3	0.000 (0.000)	0.134 (#N/A)	0.113 (#N/A)	#N/A (#N/A, #N/A)
Cd	Jul	Rural	140	0.972 (1.953)	-0.894 (-91.98%)	0.112 (5.71%)	0.011 (-0.155, 0.176)
Cr	Jan	Rural	922	0.488 (0.945)	-0.298 (-60.91%)	0.368 (38.90%)	0.142 (0.078, 0.204)
Cr	Jul	Rural	1219	0.630 (2.052)	-0.383 (-60.78%)	0.487 (23.74%)	0.172 (0.117, 0.226)
Mn	Jan	Rural	922	0.827 (1.847)	0.034 (4.09%)	1.516 (82.08%)	0.117 (0.053, 0.180)
Mn	Jul	Rural	1219	1.252 (1.949)	-0.489 (-39.08%)	1.595 (81.84%)	0.253 (0.200, 0.305)
Ni	Jan	Rural	922	0.251 (0.873)	0.057 (22.69%)	0.665 (76.13%)	0.319 (0.260, 0.376)
Ni	Jul	Rural	1219	0.492 (1.101)	-0.215 (-43.69%)	0.490 (44.51%)	0.361 (0.311, 0.409)
Pb	Jan	Rural	922	0.999 (1.564)	-0.008 (-0.82%)	2.534 (162.02%)	0.408 (0.352, 0.460)
Pb	Jul	Rural	1219	1.247 (1.971)	-0.438 (-35.12%)	1.331 (67.53%)	0.372 (0.323, 0.420)
Cd	Jan	Suburban	99	1.124 (1.759)	-0.890 (-79.14%)	0.345 (19.58%)	0.227 (0.031, 0.406)
Cd	Jul	Suburban	467	1.188 (2.087)	-1.028 (-86.53%)	0.348 (16.69%)	-0.003 (-0.093, 0.088)
Cr	Jan	Suburban	99	1.266 (1.474)	0.505 (39.86%)	1.995 (135.35%)	0.264 (0.070, 0.438)
Cr	Jul	Suburban	467	1.325 (2.312)	0.509 (38.42%)	2.151 (93.04%)	0.154 (0.064, 0.242)
Mn	Jan	Suburban	99	3.524 (5.199)	0.178 (5.04%)	5.172 (99.48%)	0.079 (-0.120, 0.272)
Mn	Jul	Suburban	467	3.780 (3.638)	-1.709 (-45.21%)	2.777 (76.33%)	0.183 (0.094, 0.269)
Ni	Jan	Suburban	99	3.043 (5.651)	-1.933 (-63.52%)	1.186 (20.99%)	0.056 (-0.143, 0.250)
Ni	Jul	Suburban	467	2.930 (4.720)	-1.852 (-63.21%)	0.809 (17.15%)	0.205 (0.116, 0.290)
Pb	Jan	Suburban	99	7.233 (6.837)	-3.479 (-48.10%)	3.666 (53.62%)	0.321 (0.132, 0.487)
Pb	Jul	Suburban	467	5.475 (10.740)	-1.728 (-31.56%)	6.921 (64.44%)	0.405 (0.326, 0.478)
Cd	Jan	Urban	133	1.291 (2.309)	-1.077 (-83.42%)	0.242 (10.49%)	0.061 (-0.111, 0.229)
Cd	Jul	Urban	342	1.249 (2.244)	-1.096 (-87.75%)	0.160 (7.11%)	0.044 (-0.062, 0.149)
Cr	Jan	Urban	133	1.467 (2.048)	-0.285 (-19.43%)	1.563 (76.32%)	0.114 (-0.057, 0.279)
Cr	Jul	Urban	360	1.528 (2.290)	-0.680 (-44.52%)	0.851 (37.17%)	0.022 (-0.081, 0.125)
Mn	Jan	Urban	133	3.629 (9.565)	-0.777 (-21.42%)	3.025 (31.63%)	0.116 (-0.055, 0.281)
Mn	Jul	Urban	360	4.512 (10.310)	-2.391 (-52.99%)	2.053 (19.91%)	0.236 (0.136, 0.331)
Ni	Jan	Urban	133	12.970 (66.830)	-11.590 (-89.36%)	1.602 (2.40%)	0.140 (-0.031, 0.303)
Ni	Jul	Urban	360	2.863 (3.467)	-1.771 (-61.86%)	1.466 (42.28%)	0.060 (-0.044, 0.162)
Pb	Jan	Urban	133	9.033 (10.000)	-0.691 (-7.65%)	14.350 (143.50%)	0.422 (0.271, 0.552)
Pb	Jul	Urban	360	4.501 (7.759)	-0.146 (-3.23%)	6.928 (89.29%)	0.407 (0.317, 0.490)

^a Observed average and standard deviation (S.D.) are in ng/m³.

^b Mean bias equals $(1/N) \sum_{i=1}^N (\text{predicted}_i - \text{observed}_i)$ and relative mean bias equals the mean bias divided by the observed average.

^c Normalized model S.D. uses the observed S.D. as the normalization constant.

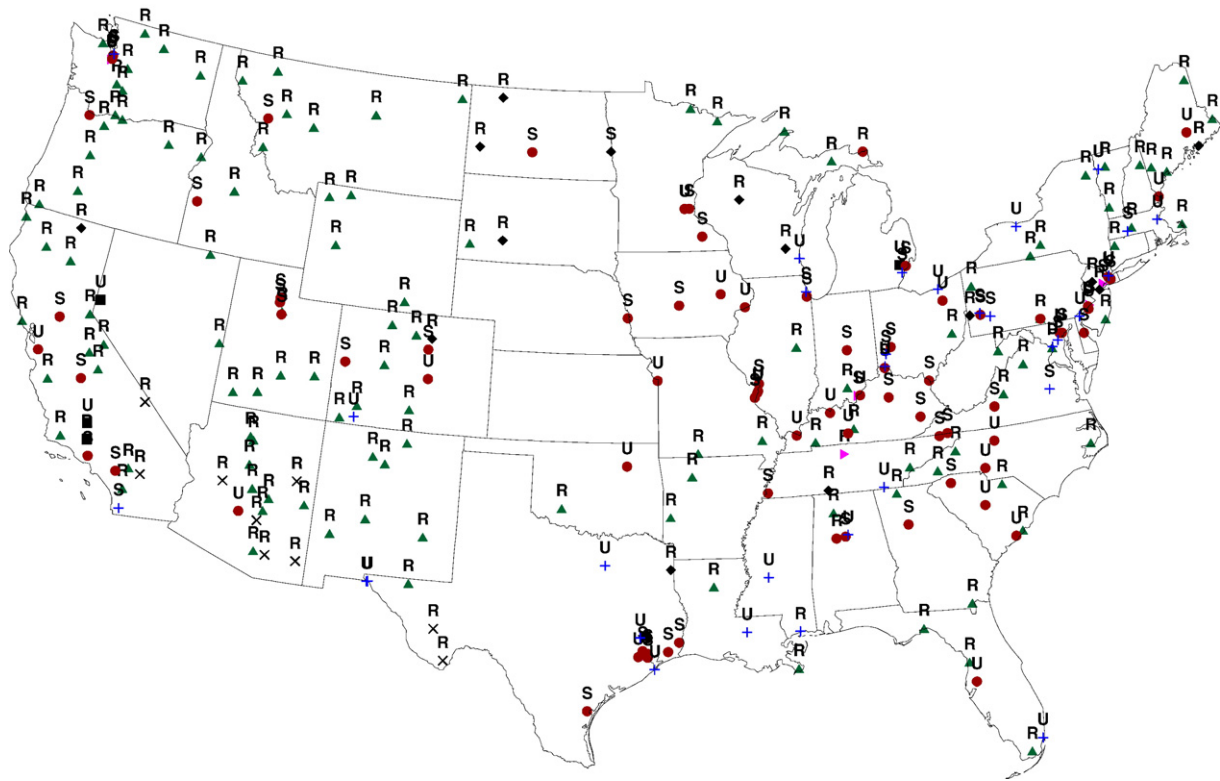


Fig. 1– The points show locations of monitors for cadmium, chromium, lead, manganese and nickel in $PM_{2.5}$ during 2001. Sites are plotted based on their surroundings or land use: forest (\blacktriangle), desert (\times), agriculture (\blacklozenge), residential (\bullet), commercial ($+$), mobile (\blacksquare) and industrial (\blacktriangleright). A letter above each site states whether the location is rural (R), suburban (S), and urban (U).

Under these circumstances, the comparisons give inaccurate positive values for the model biases because the actual observation lies below the detection limit by an uncertain amount. As shown later, such errors occur at rural locations such as desert, forests and agricultural areas. We assess how the zero concentrations affect the comparison to observations by presenting two sets of statistical summaries. One set which this paper predominantly uses is computed based on all observed concentrations. The second set is computed based on observed and predicted concentrations that both exceed 0.005 ng/m^3 . A separate problem creates uncertainties on how the comparison changes between months because many sites in forests reported observations only during July. We address the last problem by comparing predictions to observations based on month, land use and geographic location after giving statistical summaries for each metal.

4. Results

Table 1 summarizes the comparison between observations and predictions. For both months, the predictions underestimate observed concentrations (negative biases) and have a weak ability to match the time dependency of observations (low correlation coefficients). Lead predictions match observations within 50% at all locations. Manganese and chromium predictions have similar skills only at urban and suburban locations while nickel predictions match observations within

50% only at rural locations. Predictions for cadmium are completely unable to match observed concentrations within a factor of two. Regarding how the comparison changes between months, all predictions have lower errors at rural locations during January but only manganese predictions have lower errors at all locations during the month. The opposite or weak trends exist in the change of monthly errors in the predictions for lead, nickel and chromium predictions at suburban and urban locations. While all the metals predicted have problems matching how observations change over time, lead predictions best match the range of observed concentrations and have the highest correlation coefficients.

Table 2 shows the number of nonzero concentrations and demonstrates how excluding zero concentrations changes the comparison. At rural locations, zero concentrations occur in more than 50% of the collected concentrations except for lead. If the comparison between observations and predictions excludes zero concentrations at rural locations, the mean relative biases show larger underestimates because overestimating zero concentrations compensate for underestimating nonzero values. **Table 2** also shows that the normalized standard deviations increase at rural locations because predictions cannot reproduce the range of observed concentrations if the comparison includes zero concentrations (**Table 1**). At urban and suburban locations, zero concentrations occur in less than 20% of the comparisons except for cadmium. The mean biases and squared errors are more independent from zero concentrations at these locations. Excluding zero concentrations has little effect on the correlation

Table 2 – Comparison statistics based on nonzero concentrations

Metal	Month	Location	# Observations	Observed average ^a (observed S.D.)	Mean bias ^b (mean relative bias)	Model S.D. (normalized model S.D. ^c)	r ² (95% confidence limits)
Cd	Jan	Rural	0	#N/A	#N/A	#N/A	#N/A (#N/A, #N/A)
Cd	Jul	Rural	51	2.476 (2.517)	-2.415 (-97.54%)	0.080 (3.16%)	0.319 (0.048, 0.547)
Cr	Jan	Rural	251	1.653 (1.087)	-1.447 (-87.54%)	0.365 (33.57%)	0.459 (0.355, 0.551)
Cr	Jul	Rural	376	1.998 (3.298)	-1.598 (-79.98%)	0.686 (20.81%)	0.117 (0.016, 0.215)
Mn	Jan	Rural	343	2.199 (2.478)	-1.222 (-55.57%)	1.592 (64.25%)	0.163 (0.058, 0.264)
Mn	Jul	Rural	566	2.688 (2.076)	-1.788 (-66.52%)	2.015 (97.06%)	0.319 (0.243, 0.391)
Ni	Jan	Rural	298	0.750 (1.406)	-0.260 (-34.68%)	0.687 (48.88%)	0.462 (0.367, 0.547)
Ni	Jul	Rural	680	0.877 (1.355)	-0.496 (-56.55%)	0.555 (40.92%)	0.346 (0.278, 0.410)
Pb	Jan	Rural	781	1.176 (1.638)	-0.035 (-2.97%)	2.724 (166.30%)	0.389 (0.328, 0.447)
Pb	Jul	Rural	1188	1.276 (1.988)	-0.469 (-36.72%)	1.337 (67.25%)	0.379 (0.329, 0.426)
Cd	Jan	Suburban	50	2.226 (1.920)	-1.994 (-89.58%)	0.353 (18.38%)	0.413 (0.153, 0.620)
Cd	Jul	Suburban	203	2.724 (2.416)	-2.563 (-94.09%)	0.324 (13.39%)	-0.007 (-0.145, 0.131)
Cr	Jan	Suburban	94	1.333 (1.483)	0.497 (37.30%)	2.022 (136.35%)	0.246 (0.045, 0.427)
Cr	Jul	Suburban	411	1.504 (2.410)	0.329 (21.89%)	2.113 (87.68%)	0.172 (0.077, 0.264)
Mn	Jan	Suburban	89	3.920 (5.342)	-0.118 (-3.01%)	5.374 (100.60%)	0.069 (-0.142, 0.273)
Mn	Jul	Suburban	457	3.863 (3.634)	-1.761 (-45.59%)	2.797 (76.97%)	0.174 (0.083, 0.261)
Ni	Jan	Suburban	95	3.171 (5.734)	-2.033 (-64.11%)	1.203 (20.98%)	0.043 (-0.160, 0.243)
Ni	Jul	Suburban	450	3.041 (4.774)	-1.951 (-64.16%)	0.811 (16.99%)	0.200 (0.110, 0.287)
Pb	Jan	Suburban	95	7.537 (6.812)	-3.742 (-49.65%)	3.712 (54.49%)	0.319 (0.125, 0.489)
Pb	Jul	Suburban	413	6.191 (11.230)	-2.252 (-36.38%)	7.269 (64.73%)	0.403 (0.319, 0.481)
Cd	Jan	Urban	66	2.601 (2.713)	-2.355 (-90.54%)	0.261 (9.63%)	-0.024 (-0.264, 0.220)
Cd	Jul	Urban	153	2.710 (2.645)	-2.537 (-93.62%)	0.180 (6.79%)	-0.022 (-0.180, 0.137)
Cr	Jan	Urban	120	1.626 (2.096)	-0.405 (-24.89%)	1.606 (76.62%)	0.101 (-0.079, 0.275)
Cr	Jul	Urban	323	1.675 (2.356)	-0.814 (-48.60%)	0.789 (33.49%)	0.026 (-0.083, 0.135)
Mn	Jan	Urban	119	4.056 (10.030)	-1.070 (-26.38%)	3.127 (31.18%)	0.102 (-0.079, 0.277)
Mn	Jul	Urban	336	4.563 (9.513)	-2.374 (-52.03%)	2.063 (21.69%)	0.286 (0.185, 0.381)
Ni	Jan	Urban	123	14.030 (69.400)	-12.610 (-89.88%)	1.577 (2.27%)	0.143 (-0.035, 0.312)
Ni	Jul	Urban	342	3.000 (3.495)	-1.912 (-63.73%)	1.412 (40.40%)	0.071 (-0.036, 0.175)
Pb	Jan	Urban	128	9.386 (10.030)	-0.801 (-8.53%)	14.570 (145.26%)	0.414 (0.260, 0.549)
Pb	Jul	Urban	311	5.210 (8.124)	-0.581 (-11.15%)	7.381 (90.85%)	0.399 (0.301, 0.488)

^a Observed average and standard deviation (S.D.) are in ng/m³.

^b Mean bias equals $(1/N) \sum_{i=1}^N (\text{predicted}_i - \text{observed}_i)$ and relative mean bias equals the mean bias divided by the observed average.

^c Normalized model S.D. uses the observed S.D. as the normalization constant.

coefficients except for chromium and nickel at rural locations during January. The uncertainties in correlation coefficients support the conclusion because the coefficients in Tables 1 and 2 have ranges that overlap within the 95% confidence limits.

Fig. 2 further examines the biases in Table 1 by calculating the mean relative biases based on the land use over which the observation took place. For lead predictions, rural concentrations have a larger negative bias during July because the forests – where most rural observations occurred (Fig. 1) – have larger under estimates. Lead predictions improve at suburban and urban location during July mostly because they better match observations over commercial and residential categories where most suburban and urban observations occurred. Chromium and nickel predictions have similar characteristics over these land use categories. In contrast, manganese predictions are better over forest, urban and suburban locations during January than July. Cadmium predictions have poor overall quality because they underestimate observed concentrations over all categories by more than 70%. Because the cadmium predictions have biases that almost completely miss observations over all land use categories, cadmium predictions are less discussed in the remaining comparison to observations.

We next examine how biases change with geographic location between the months. Predictions of lead (Fig. 3) and

manganese (Fig. 4) show similar trends. Most predictions under estimate observations approximately within 50% over the Atlantic and Gulf coast during January. During July, errors roughly double and predictions under estimate observations in some urban areas by 100%. Over the Tennessee valley, predictions tend to over estimate observed concentrations during January but over estimates decrease in number during July and disappear for lead. In these eastern regions, most monitors exist in residential and commercial areas where anthropogenic sources dominate. Though several sites exist in forests, they are probably not located in remote areas because the average concentration (1.5 to 8 ng/m³) are two to three time averages over forests in more pristine locations such the Rocky Mountains and Pacific Northwest (0.5 to 4 ng/m³). This western region provides a contrast because most average concentrations are low and show weak influences from anthropogenic emissions. A zone around Salt Lake City is an exception because observed averages have values similar to over the eastern United States (1.5 to 8 ng/m³). The zone exists because it contains larger population and anthropogenic emissions. Over this western region, predictions mostly miss observations by 75% to 100% from January to July, respectively. Nickel the western region differs from lead and manganese because many predictions over estimate observations

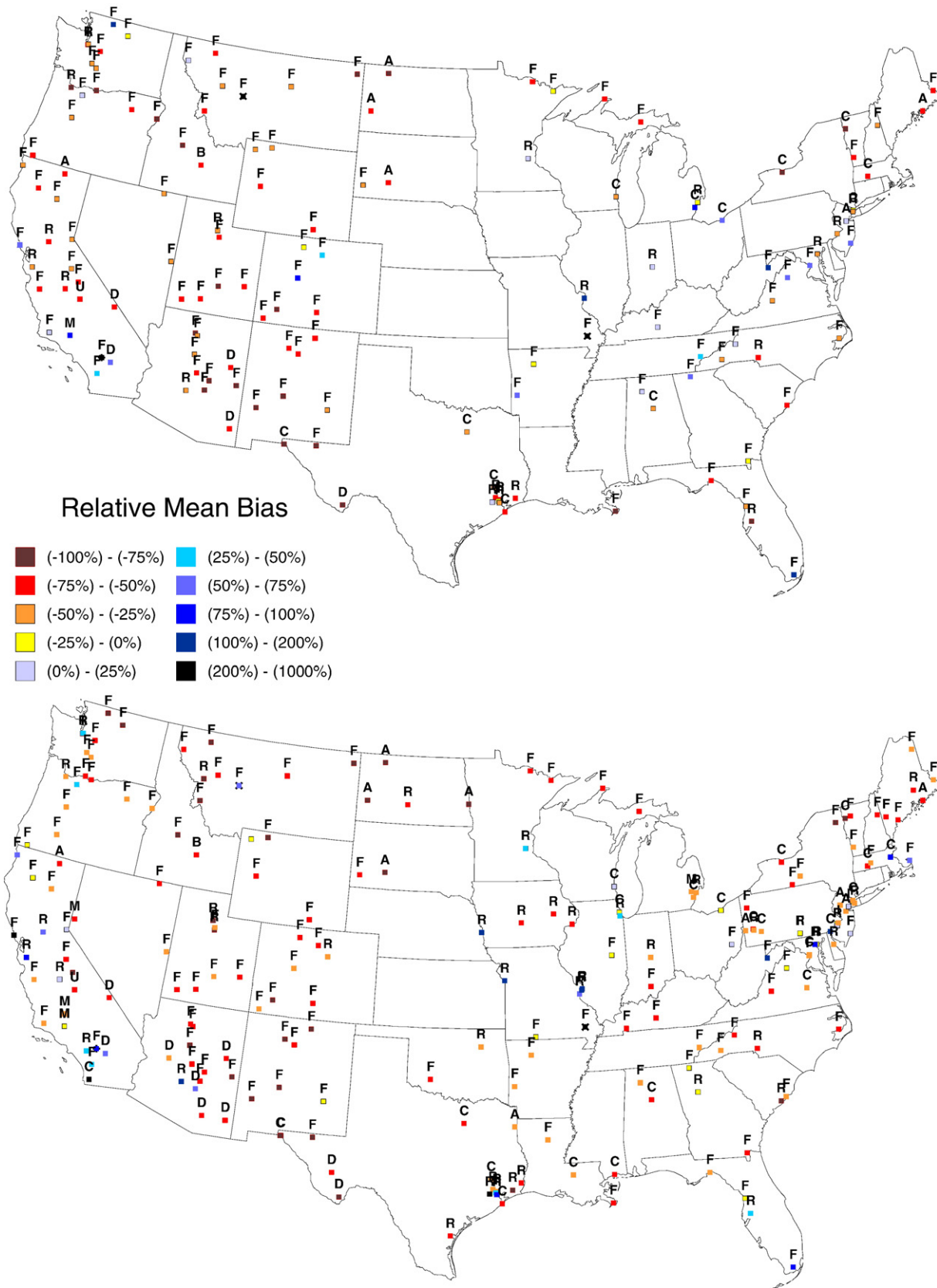


Fig. 3–The plots give relative mean bias from comparing predictions to observed lead concentrations during January (top) and July (bottom). The letter above a point gives the land use category of the monitoring site.

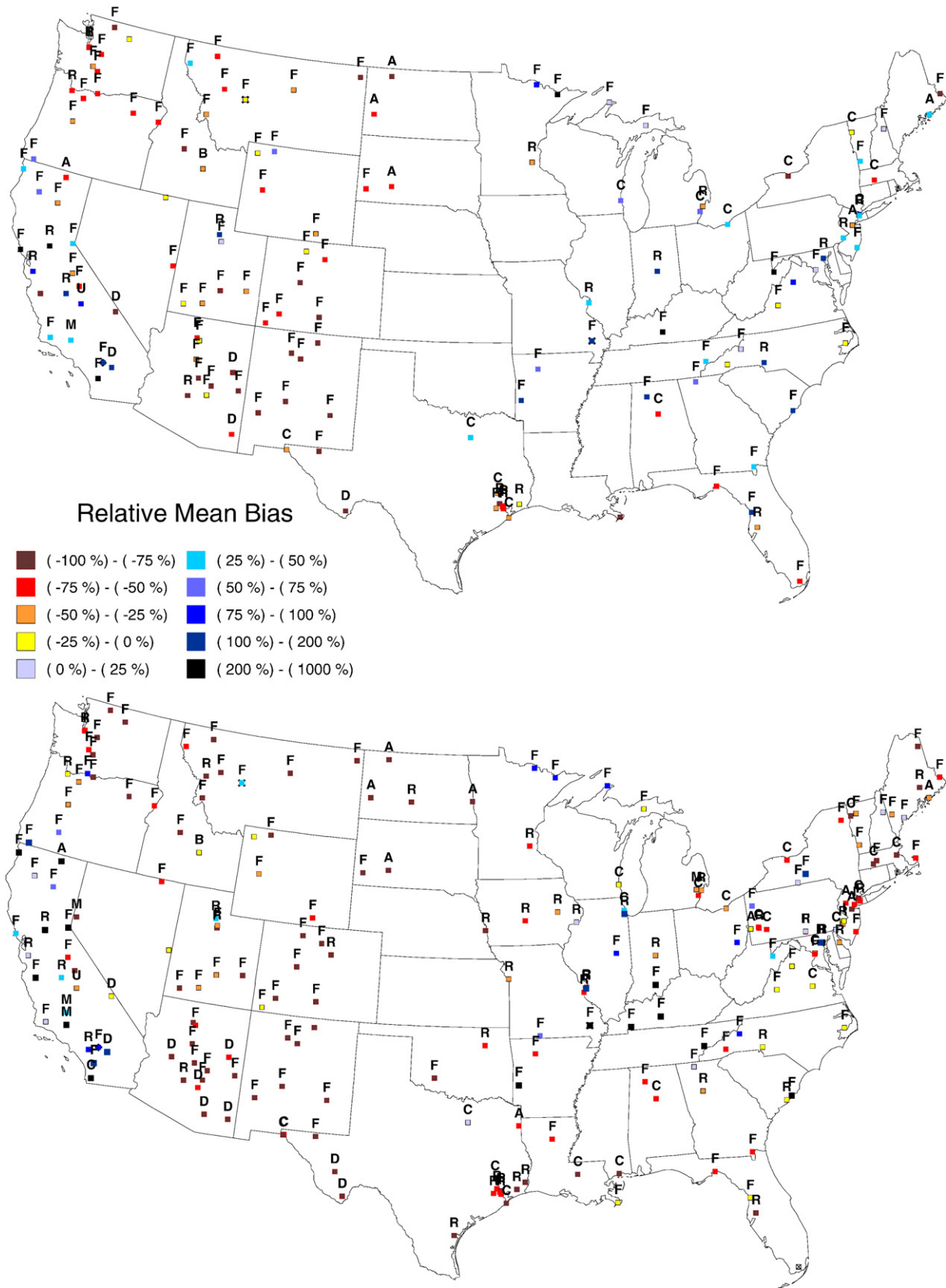


Fig. 4– The plots give relative mean bias from comparing predictions to observations for manganese concentrations during January (top) and July (bottom). The letter above a point gives the land use category of the monitoring site.

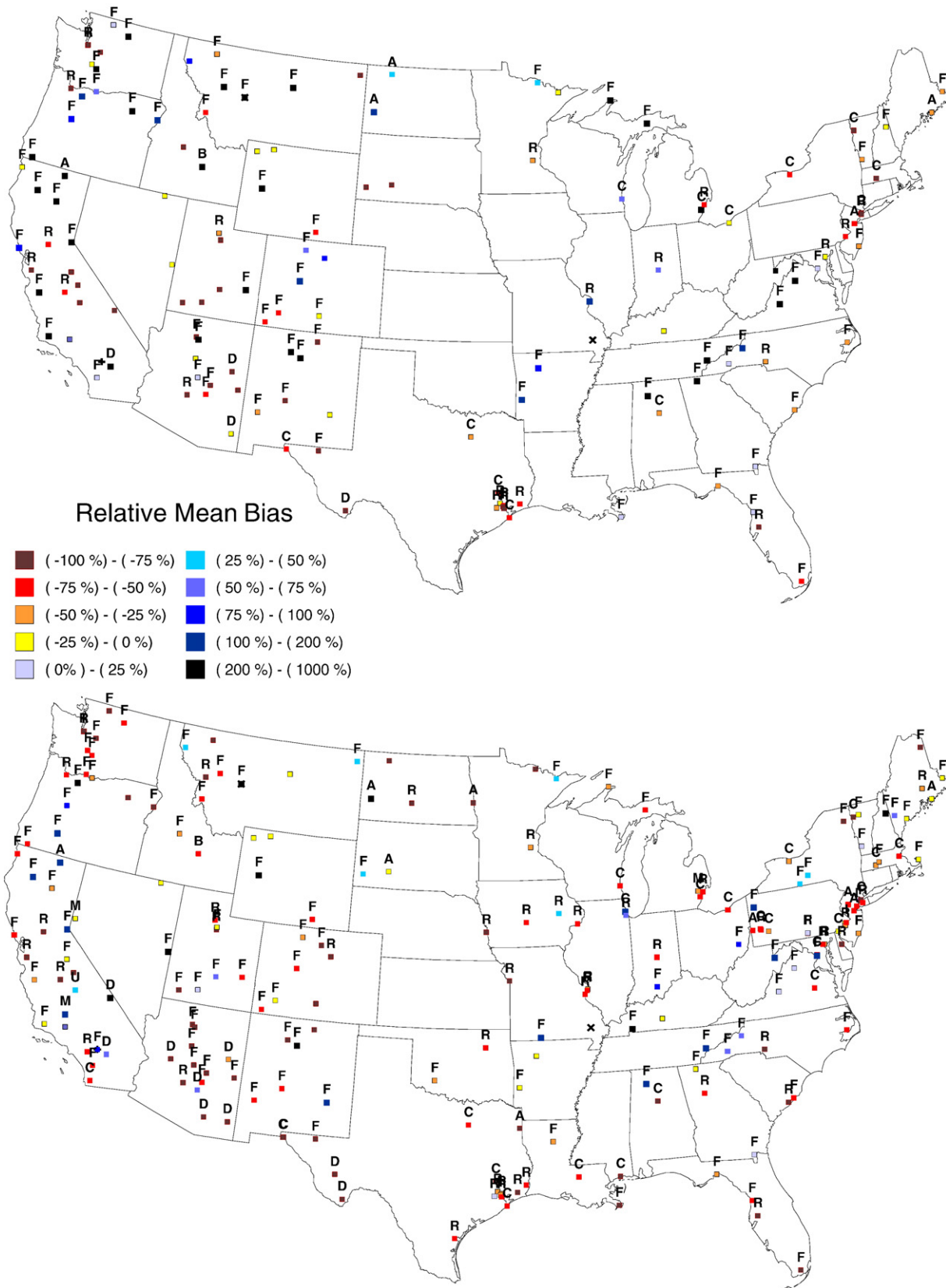


Fig. 5 – The plots give relative mean bias from comparing predictions to observed concentrations for nickel during January (top) and July (bottom). The letter above a point gives the land use category of the monitoring site.

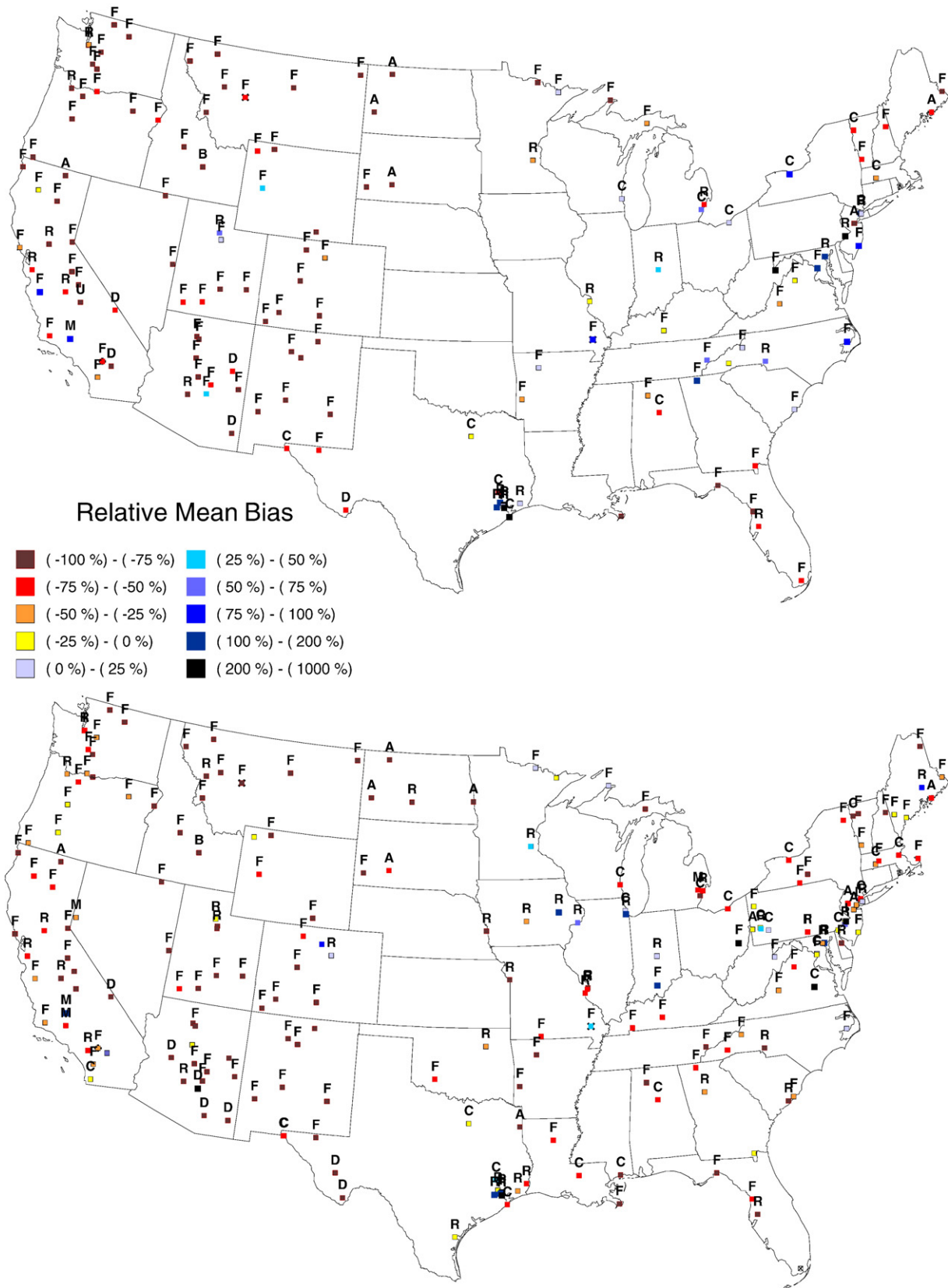


Fig. 6– The plots give relative mean bias from comparing predictions to observed concentrations for chromium during January (top) and July (bottom). The letter above a point gives the land use category of the monitoring site.

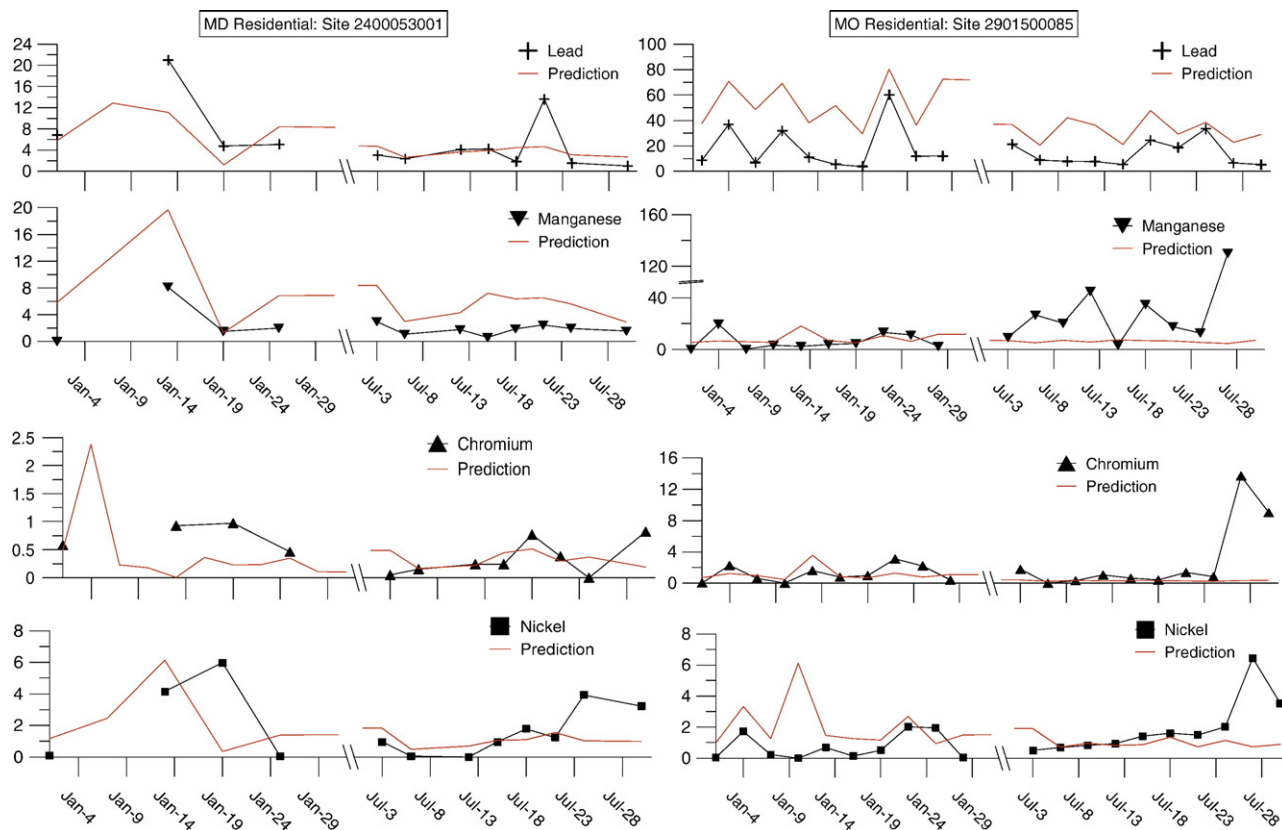


Fig. 7 – The time series show the predicted and observed concentrations over residential sites located in the eastern and central portions of the United States. The Maryland site is a suburban location two miles east of Baltimore, MD. The Missouri site is located in urban St. Louis, MO.

appear to be based on whether a site exists in a populated area and perhaps where it is geographically located. Populated areas such as residential areas show periods when the observations and predictions agree regarding the phase in concentration changes (Figs. 7 and 8) but may not agree in the amplitude of change or mean concentration. Agreement breaks down when observations suddenly change by a large amount. These problems appear larger over the central and western states. Less populated areas such as forests also show that predictions have less ability to match observations moving from western to central states. They fail to reproduce observed changes that suddenly increase from near zero concentrations (Figs. 9 and 10). Overall, lead predictions appear to have the best skill at producing changes in observed concentrations. Chromium predictions have the worst skill. Over the eastern states, manganese predictions have more skill reproducing the observed changes during January. Nickel predictions often fail to match observation regarding timing of observed changes.

5. Discussion

Predictions better match observations that smoothly vary over time and they often fail to match observations that have large and rapid increases. The latter conclusion is apparent over forests located in the western states and the former over residential areas in the eastern states. A possible cause is that

meteorological inputs omit processes such as a sea breeze fronts, valley winds, and urban canopies because the grid cells are too large to resolve such processes. Predicted concentrations will not show how these sub-grid processes disperse pollutants around the monitoring site. Besides affecting the range of predicted concentrations, sub-grid processes produce differences between when predicted and observed concentrations change. The residential site in Texas illustrates this error. The site resides near the coastline and shows influences from the propagation of sea breeze fronts during July. The front affects observations of each metal differently because each has emission sources at different locations relative to the front.

Poor resolution further affects emission processes because grid cells use hourly rates that are composites of many sources. The simplification removes how individual sources affect concentrations based on its time dependent emissions and location relative to monitoring site. Composite sources produce larger errors in grid cells where individual sources have large and chaotic changes in emissions such as densely populated residential areas in urban locations. For example, the Missouri residential site is located in the urban center of St. Louis. Observed concentrations reflect unpredictable activity in adjacent automotive traffic, construction and businesses.

Other errors omit anthropogenic emissions over Canada and Mexico and may explain why predictions have large biases over the north eastern and south western United States. The errors are difficult to quantify but a global inventory of lead emissions,

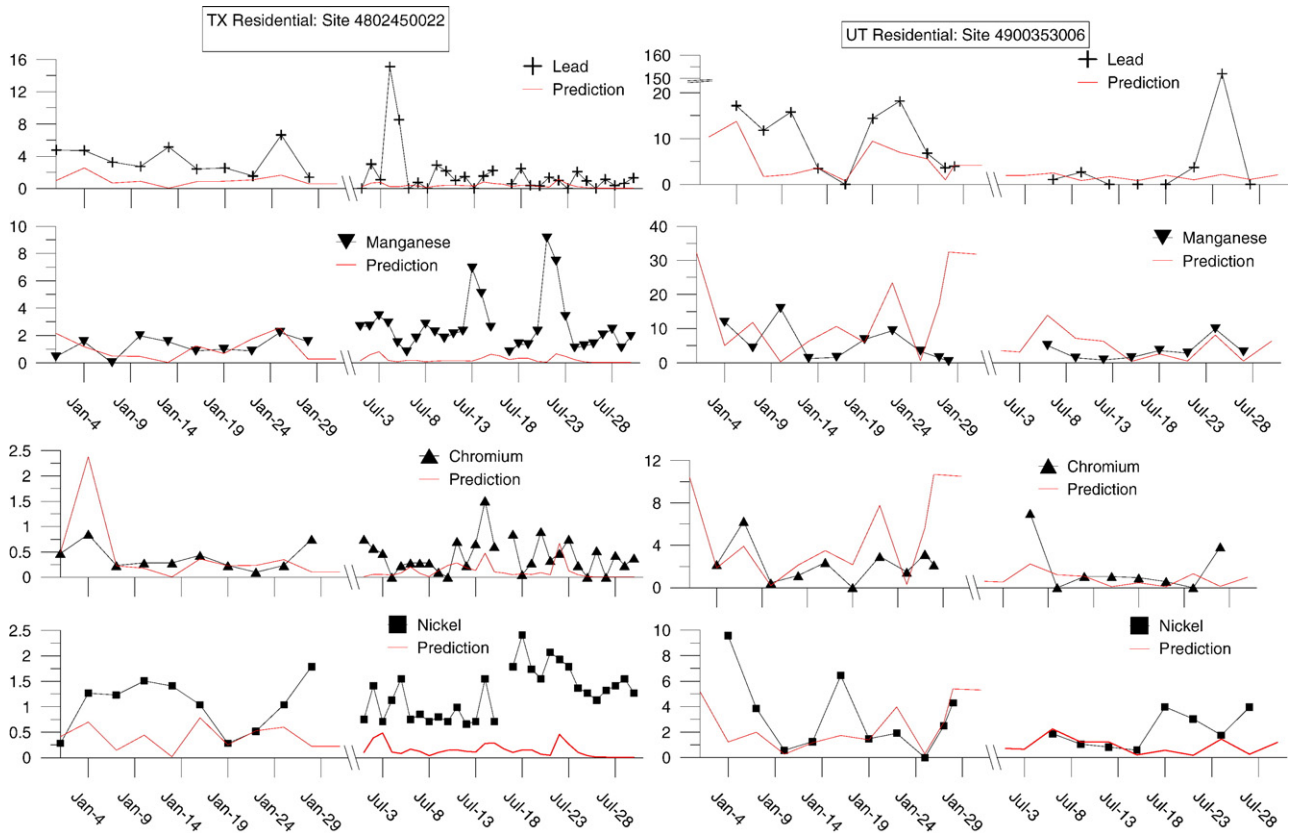


Fig. 8 – The time series show the predicted and observed concentrations over residential sites located in the central and western portions of the United States. The Texas site is located in a suburb west of Port Arthur, TX and several miles inland. The Utah site is a suburban location in Salt Lake City, UT.

collected for the Global Emissions Inventory Activity (Pacyna et al., 1995, <http://www.ortech.ca/cgeic/>), provides clues. In Canada, territories adjacent to the international border contain areas where lead emissions are greater than 10^4 kg/yr. In Mexico, states south of the border are carpeted with areas where lead emissions are greater than 10^4 kg/yr. The omitted emissions are comparable to rates over the United States and imply that the two nations also emit significant amounts of manganese, chromium, nickel and cadmium.

The NEI, itself, likely contains errors in HAP emissions that are larger than for the criteria pollutants. Except for the mobile source, the HAP emissions depend on the Toxics Release Inventory (TRI) compiled by the US EPA and state agencies. de Marchi and Hamilton (2006) found that the TRI underestimates lead emissions by as much as 50% and suspected that it underestimates emissions for most other HAPs. The conclusion was based on comparing observations to adjacent sources. Underestimates were proposed to exist due to a combination of several reasons. Reporting HAP emissions for the TRI is voluntary. Regulatory agencies do not audit or verify reports perhaps because HAPs, unlike criteria pollutants, do not have national air quality standards with regulatory penalties if violated. Lastly, businesses submitting reports wish to reduce the possibility of environmental lawsuits based on their reports. Koehler and Spengler (2007) indicated that the TRI has both positive and negative biases between reported to actual

emissions because how businesses estimate emissions and report them. Businesses often standardize the estimation method when they have multiple facilities. The methodology may ignore how an individual facility uniquely generates emissions. In reporting emissions, businesses can report their emissions as falling within a range if their emissions are below a given value. Subsequently, the TRI uses a single value to represent the range and does not accurately represent the population of emission rates within the range. Overall, Koehler and Spengler (2007) believed that the TRI tends to underestimate actual emissions based on their analysis of emissions for Polycyclic Aromatic Compounds from the aluminum production industry. Errors in lead emissions reported by de Marchi and Hamilton (2006) infer errors in the emissions for the other metals studied because these metals have similar sources from industrial processes that involve high temperature processes such as metal smelting and fuel combustion (Pacyna et al., 1995).

Emission errors include natural and anthropogenic sources over or near the United States not in the NEI. Manganese has sources from the aerial suspension of sea droplets and dust particles based on abundance in sea water and soil (Seinfeld and Pandis, 1998). Nriagu (1989) calculated that the same sources are important for chromium. Other metals have similar sources from the re-suspension from contaminated areas (Lough et al., 2005). Lead may have sources from re-suspending atmospheric deposition based on its historical

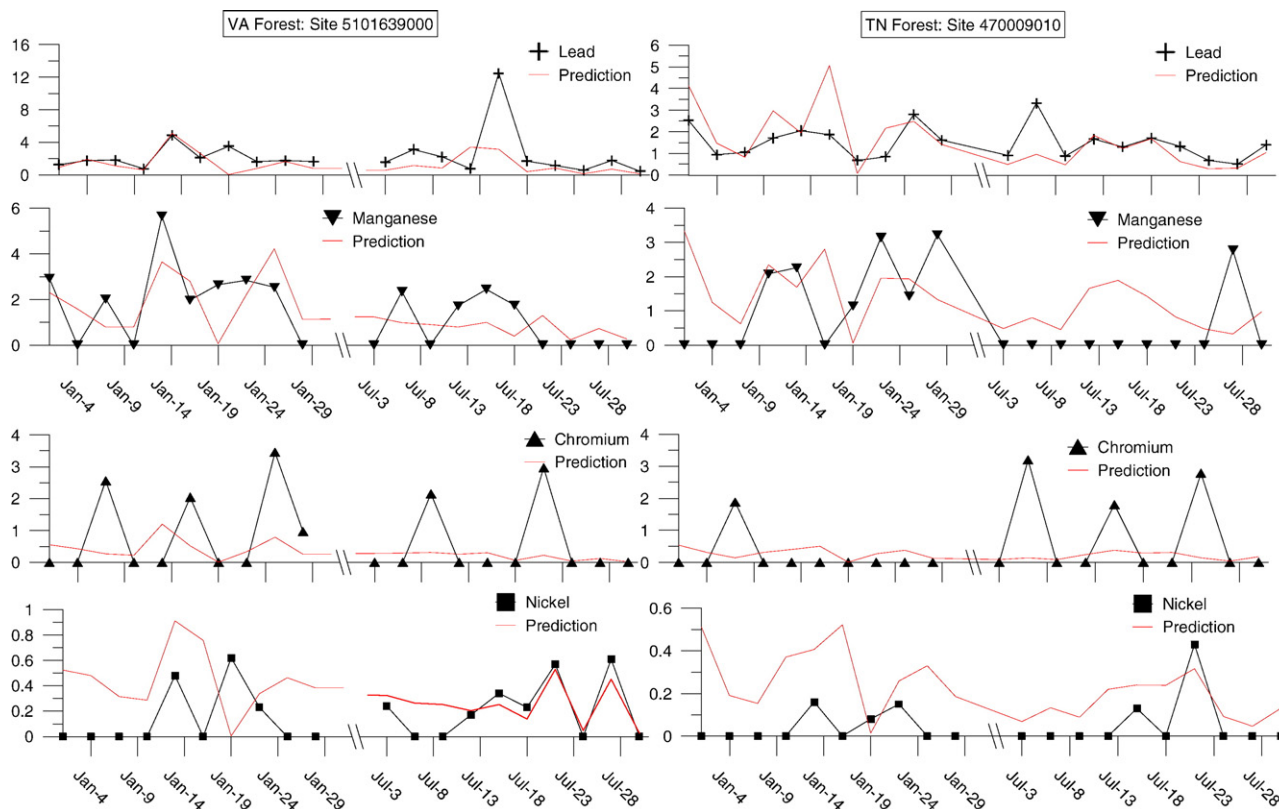


Fig. 9 – The time series show the predicted and observed concentrations over forested sites located in the eastern and central portions of the United States. The Virginia site is in a rural location approximately 40 miles north east of Roanoke, VA. The Tennessee site is located near the Great Smoky Mountains National Park.

emissions from mobile and industrial sources (U.S. EPA, 2006a; Harris and Davidson, 2005). Sources driven by wind speed will have significant effects over the remote locations such as forests and deserts located in the Rocky Mountains (Pace, 2005). They may explain the large increases in observed concentrations especially during summer months that have lower soil moistures, lower snow coverage, and higher wind speeds. Forest and brush fires, both wild and prescribed, also produce such episodes (Sillanpää et al., 2005; Breulmann et al., 2002; Yamasoe et al., 2000). Simulations did not include this type of biomass burning. Metallic emissions arise from both fuel combustion and aerosol suspension driven by fires.

Besides the problems in the meteorological and emissions inputs, the CCTM has a shortcoming because it does not include an aerosol mode that represents ultrafine particles (diameters <50 to 100 nm). The aerosol mode is emitted by combustion and industrial sources such as diesel engines, boilers, metal foundries and plating or is produced by gas to particle conversion near emission sources. Ultrafine particles have faster dispersion rates than the fine and coarse modes (Ketzel and Berkowicz, 2004) and possible unique microphysical processes (Gramotnev and Gramotnev, 2005). The shortcoming introduces larger prediction errors at urban and some suburban locations where sources of ultrafine particles are more numerous and coagulation is too slow to grow ultrafine particles into fine particles. This shortcoming of the CCTM involves not only the aerosol microphysics but also the relatively large horizontal dimensions of grid cells because the ultrafine aerosol processes would occur as sub-

scales process (Gramotnev and Gramotnev, 2005) within grid cells between which transport and deposition dominate. How much can ultrafine particles contribute to the observed $PM_{2.5}$ concentrations of trace metals? The ultrafine contributions for lead, manganese and cadmium were measured less than 5% if any nearby roadways were used by less than 15,000 vehicles while nickel had an ultrafine contribution between 15% and 20% (Pakkanen et al., 2001). For roadways with ten times more vehicle traffic, ultrafine contributions were measured around 50% for lead, manganese, and nickel (Ntziachristos et al., 2007).

Some of the errors discussed suggest why specific metals are better predicted. Predicted concentrations of lead best match observations where the emissions are evenly distributed over space and time. Locations best predicted include residential, commercial and perhaps agricultural areas that are located in the eastern United States and not adjacent to international borders. Aerial suspension and biomass burning that were excluded from simulations less likely determine observed concentrations over these areas. Neglecting these natural sources causes large errors over rural areas in the central to western United States during July. Lead predictions have problems matching the time dependence of observed concentrations when the grid cells do not resolve variations in local emissions and meteorology. Manganese predictions rank second in the comparison to observation because aerial suspension and biomass burning are more important sources for manganese than lead. Emission errors also affect chromium predictions but the cause is difficult to identify. Despite conclusions in

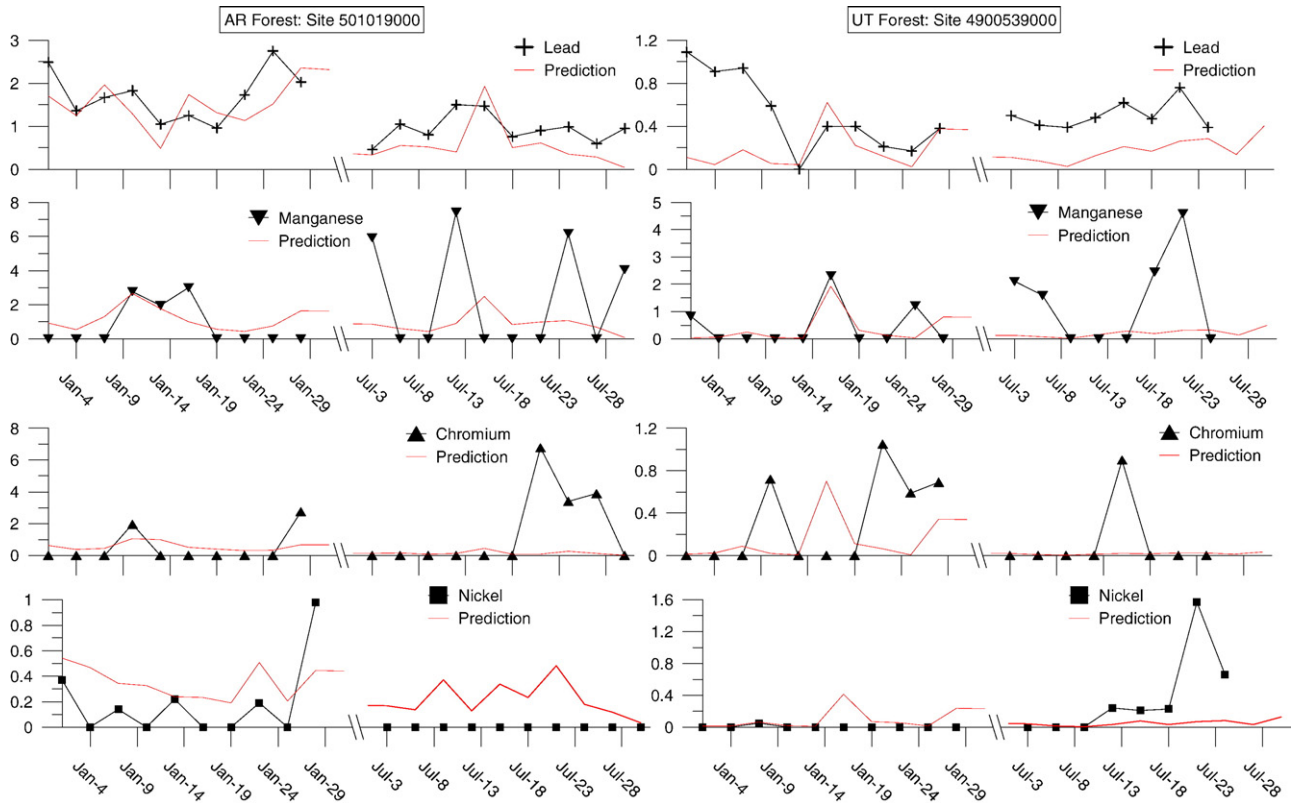


Fig. 10–The time series show the predicted and observed concentrations over forested sites located in the central and western portions of the United States. The Arkansas site is located in clearing near the town of Dear, AR. The Utah site is located between the Zion National Park and a mixture of housing development and farm land.

Nriagu (1989), comparison to observations does not identify aerial suspension as a major source because chromium biases do not show the same dependences as manganese and lead. We conclude that anthropogenic emissions cause errors in chromium predictions. Resolution of meteorology and emissions explain errors in chromium predictions where the sources are more confined such as urban areas. Based on their lower natural abundances, nickel and cadmium error predictions are more dependent on errors in anthropogenic emissions. Cadmium emissions appear to have especially large errors in these emissions.

6. Summary

We applied the CMAQ model for HAPs to predict concentrations of several trace metals in particulate matter. Comparison to observations showed that lead and manganese predictions have the most skill. They have lower errors over residential and commercial areas over the eastern United States. Nickel and chromium predictions also improve over these land use categories. Rural areas show larger errors because simulations did not include emissions from aerial suspension and biomass burning. Cadmium predictions show the highest amount of error. The exact cause is uncertain because the observed concentrations had the lowest number of values and locations. Errors appear to come from the NEI based on the size of error relative to other metals and similar treatment of cadmium within the model.

Our study recommends future research that may improve trace metals predicted by the CMAQ model. Recommendations would include emissions for aerial suspension and biomass burning. Including the sources requires models of aerial suspension and combustion as well as data about soil composition over location and composition of the fuel. Predicted concentrations of lead and manganese will benefit the most by including these emissions. Recommended research includes better quantifying the anthropogenic emissions of chromium, nickel and cadmium in the NEI. Cadmium predictions will benefit the most from such work. A large improvement will be gained by including anthropogenic emissions from Canada and Mexico. Improving nickel along with chromium predictions likely requires better resolving meteorology and emissions within grid cells by decreasing the size of the grid cells. This step will never capture all emission processes and local meteorology but model predictions should improve over coastal areas and in urban locations. To further resolve these sub-grid processes, research has to develop model algorithms that better represent them.

Disclaimer

The research presented here was performed under the Memorandum of Understanding between the U.S. Environmental Protection Agency (EPA) and the U.S. Department of Commerce's National Oceanic and Atmospheric Administration (NOAA) and under agreement number DW13921548. This

work constitutes a contribution to the NOAA Air Quality Program. Although it has been reviewed by EPA and NOAA and approved for publication, it does not necessarily reflect their policies or views.

REFERENCES

- Binkowski FS, Roselle SJ. Models-3 Community Multiscale Air Quality (CMAQ) model aerosol component, 1, model description. *J Geophys Res* 2003;108(D6):4183–200, doi:10.1029/2001JD001409.
- Breulmann G, Markert B, Weckert V, Herpin U, Yoneda R, Ogino K. Heavy metals in emergent trees and pioneers from tropical forest with special reference to forest fires and local pollution sources in Sarawak, Malaysia. *Sci Total Environ* 2002;285(1–3):107–15.
- Bullock RO, Brehme KA. Description and evaluation of atmospheric mercury simulation using the CMAQ model. *Atmos Environ* 2002;36:2135–46.
- Bullock R, Lohman K, Seigneur C, Vijayaraghavan D, Davignon Selin NE, Jacob DJ, et al. Results from the North American Mercury Model Inter-comparison Study (NAMMIS). Presented at 8th International Conference on Mercury, Madison, WI.; 2006.
- Science algorithms of the EPA Models-3 Community Multiscale Air Quality (CMAQ) Modeling System. In: Byun DW, Ching JKS, editors. EPA-600/R-99/030, US Environmental Protection Agency, Research Triangle Park, NC; 1999. <http://www.epa.gov/asmdnerl/models3/doc/science/science.html>.
- Byun DW, Schere KL. Review of the governing equations, computational algorithms, and other components of the Models-3 Community Multiscale Air Quality (CMAQ) Modeling System. *Appl Mech Rev* 2006;59(2):51–77.
- Carter WPL. Implementation of the SAPRC-99 chemical mechanism into the models-3 framework. Report to the United States Environmental Protection Agency, January 29; 2000. Available online at <http://pah.cert.ucr.edu/~carter/absts.htm>.
- Cimorelli AJ, Perry SG, Venkatram A, Weil JC, Paine RJ, Wilson RB, Lee RF, Peters WD, Brode RW. AERMOD: a dispersion model for industrial source applications. Part I: general model formulation and boundary layer characterization. *J Appl Meteorol* 2005;44:682–93.
- Dastoor AP, Larocque YL. Global circulation of atmospheric mercury: a modelling study. *Atmos Environ* 2004;38:147–61.
- de Marchi S, Hamilton JT. Assessing the accuracy of self reported data: an evaluation of the toxics release inventory. *J Risk Uncertain* 2006;32:57–76.
- Gipson GL. The initial concentration and boundary condition processors. In: Byun DW, Ching JKS, editors. Science Algorithms of the EPA Models-3 Community Multiscale Air Quality (CMAQ) Modeling System. EPA-600/R-99/030, US Environmental Protection Agency, Research Triangle Park, NC.; 1999.
- Gilliam RC, Hogrefe C, Rao ST. New methods for evaluating meteorological models used in air quality applications. *Atmos Environ* 2006;40(26):5073–86.
- Gramotnev DK, Gramotnev G. A new mechanism of aerosol evolution near a busy road: fragmentation of nanoparticles. *J of Aerosol Sci* 2005;36(3):323–40.
- Harris AR, Davidson CI. The role of resuspended soil in lead flows in the California South Coast Air Basin. *Environ Sci Technol* 2005;39(19):7410–5.
- Ilyin I, Travnikov O. Modelling of heavy metal airborne pollution in Europe: evaluation of the model performance. EMEP/MS-C-Technical Report 8/2005; 2005.
- Ilyin I, Travnikov O, Aas W, Uggerud HT. Heavy metals: trans-boundary pollution of the environment. EMEP Status Report 2/2006, Meteorological Synthesizing Centre — East, Moscow, Russia 1504-6109; 2006.
- Ketzel M, Berkowicz R. Modelling the fate of ultrafine particles from exhaust pipe to rural background: an analysis of time scales for dilution, coagulation and deposition. *Atmos Environ* 2004;38(7):2639–52.
- Koehler DA, Spengler JD. The toxics release inventory: fact or fiction? A case study of the primary aluminum industry. *J Environ Manag* 2007;85:296–307.
- Kotas J, Stasicka Z. Chromium occurrence in the environment and methods of its speciation. *Environ Pollut* 2000;107:263–83.
- Lough GC, Schauer JJ, Park JS, Shafer MM, DeMinter JT, Weinstein JP. Emissions of metals associated with motor vehicle roadways. *Environ Sci Technol* 2005;39(3):826–36.
- Luecken DJ, Phillips S, Sarwar G, and Jang C, in press. Effects of using the CB05 vs. SAPRC99 vs. CB4 chemical mechanism on model predictions: ozone and gas-phase photochemical precursor concentrations. *Atmospheric Environment*. <http://www.sciencedirect.com/science/article/B6VH3-4PNM4G5-1/2/74d41e50239345225a3c4cddc363861> f).
- Luecken DJ, Hutzell WT, Gipson GL. Development and analysis of air quality modeling simulations for hazardous air pollutants. *Atmos Environ* 2006;40(26):5087–96.
- Marshall JD, Granvold PW, Hoats AS, McKone TE, Deakine E, Nazaroff WW. Inhalation intake of ambient air pollution in California's South Coast Air Basin. *Atmos Environ* 2006;40:4381–92.
- Nriagu JO. A global assessment of natural sources of atmospheric trace metals. *Nature* 1989;338:47–9.
- McNally D. Annual application of MM5 for calendar year 2001. Report to US EPA by Alpine Geophysics, Arvada, CO, March 31, 2003; 2003.
- Ntziachristos L, Ning Z, Geller MD, Sheesley RJ, Schauer JJ, Sioutas C. Fine, ultrafine and nanoparticle trace element compositions near a major freeway with a high heavy-duty diesel fraction. *Atmos Environ* 2007;41(27):5684–96.
- Pace TG. Methodology to estimate the Transportable Fraction (TF) of fugitive dust emissions for regional and urban scale air quality analyses. U.S. EPA, Research Triangle Park NC, August 2005; 2005. http://www.epa.gov/ttn/chief/emch/invent/transportable_fraction_080305_rev.pdf.
- Pacyna JM, Scholtz MT, Li YF. Global budgets of trace metal sources. *Environ Rev* 1995;3:145–59.
- Pakkanen TA, Kerminen V, Korhonen CH, Hillamo RE, Aarnio P, Koskentalo T, Maenhaut W. Urban and rural ultrafine (PM_{0.1}) particles in the Helsinki area. *Atmos Environ* 2001;35(27):4593–607.
- Pleim JE. A combined local and nonlocal closure model for the atmospheric boundary layer. part I: model description and testing. *J Clim Appl Meteor* 2007;46:1383–95.
- Rosenbaum AS, Axelrad DA, Woodruff TJ, Wei YH, Ligocki MP, Cohen JP. National estimates of outdoor air toxics concentrations. *J Air Waste Manage Assoc* 1999;49:1138–52.
- Schlesinger RB, Kunzli N, Hidy GM, Gotschi T, Jerrett M. The health relevance of ambient particulate matter characteristics: coherence of toxicological and epidemiological inferences. *Toxicology* 2006;18(2):95–125, doi:10.1080/08958370500306016.
- Seigneur C, Constantinou E. Chemical kinetics mechanism for atmospheric chromium. *Environ Sci Technol* 1995;29:222–31.
- Seinfeld JH, Pandis SN. *Atmospheric Chemistry and Physics: from Properties of Atmospheric Aerosols*. New York: J. Wiley; 1998.
- Sillanpää M, Saarikoski S, Hillamo R, Pennanen A, Makkonen U, Spolnik Z, et al. Chemical composition, mass size distribution and source analysis of long-range transported wildfire smokes in Helsinki. *Sci Total Environ* 2005;350(1–3):119–35.
- Spokes L, Jickells T, Jarvis K. Atmospheric inputs of trace metals to the northeast Atlantic Ocean: the importance of southeasterly flow. *Mar Chem* 2001;76:1:319–30.
- U.S. EPA. User's guide for the ISC3 dispersion models. The Office of Air Quality Planning and Standards Emissions, and Analysis Division. North Carolina; 1995.

- U.S. EPA. Air Quality: Criteria for Lead: 2006; EPA/600/R-5/144aF. Washington, DC: U.S. Government Printing Office; 2006a. October, 2006.
- U.S. EPA. The National-Scale Air Toxics Assessment, Washington, DC; 2006b. <http://www.epa.gov/ttn/atw/nata1999/index.html>.
- U.S. EPA. Air Quality System; 2006c. <http://www.epa.gov/air/data/aqsdb.html>. Accessed August 2006.
- Witt M, Baker AR, Jickells TD. Atmospheric trace metals over the Atlantic and South Indian Oceans: investigation of metal concentrations and lead isotope ratios in coastal and remote marine aerosols. *Atmos Environ* 2006;40:5435–51.
- Yamartino RJ. Nonnegative, conserved scalar transport using grid-cell-centered, spectrally constrained blackman cubics for applications on a variable-thickness mesh. *Mon Weather Rev* 1993;121:753–63.
- Yamasoe MA, Artaxo P, Miguel AH, Allen AG. Chemical composition of aerosol particles from direct emissions of vegetation fires in the Amazon Basin: water-soluble species and trace elements. *Atmos Environ* 2000;34(10):1641–53.
- Yarwood G, Rao S, Yocke M, Whitten GZ. Updates to the carbon bond mechanism: CB05. Report to the U.S. Environmental Protection Agency, RT-04-00675; 2005. Available online at http://www.camx.com/publ/pdfs/CB05_Final_Report_120805.pdf.
- Zhang H. Light and iron(III)-induced oxidation of chromium(III) in the presence of organic acids and manganese(II) in simulated atmospheric water. *Atmos Environ* 2000;34:1633–40.