Geoscientific
Model Development
Discussions

Interactive comment on "Evaluation of the Community Multiscale Air Quality (CMAQ) model v5.0 against size-resolved measurements of inorganic particle composition across sites in North America" *by* C. G. Nolte et al.

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Anonymous Referee 1

We thank the referee for the constructive comments on our manuscript. The referee's comments are given point-by-point below, followed by our responses.

This manuscript presents an evaluation of the Community Multiscale Air Quality Model (CMAQ) v5.0 against a unique set of size resolved measurements of inorganic aerosol mass.

Similar CMAQ evaluation studies have been published before (as referenced properly), but the present study is the most comprehensive analysis using, as the authors claim, the most extensive data set of size resolved inorganic particle mass available in North America. This data set consists of Micro-orifice Uniform Deposit Impactor (MOUDI) measurements from a rather large number of campaigns conducted across the United States and Canada between the years 2001-2005. This paper is an excellent example that the best observation data available for model evaluation are not necessarily the most recent ones and that it may be very useful to revisit some of the more ancient data sets.

The publication is very well written, clearly structured, and to the point. The analysis is highly relevant as the inorganic fraction makes up a significant fraction of the aerosol, and is fairly unique as model evaluation studies of size-resolved inorganic particle composition are still very scarce. I thus strongly recommend this manuscript for publication in GMD once the following points (mostly minor) have been addressed.

Main point:

Model-observation differences are only discussed in terms of possible model deficiencies implicitly assuming that the measurements are correct. Since I don't know the MOUDI instrument, I cannot really judge the quality of the measurements, but offline aerosol composition measurements may easily be susceptible to sampling biases for some compounds, most notably nitrate. Possible biases of the measurements should be discussed and, if relevant, better emphasized in the manuscript. As explained by the authors, the gas-particle partitioning of nitrate is thermodynamically driven and is a function of temperature and humidity. At what temperatures and humidity are the MOUDI instruments operated? How are the samples treated after collection? PM10 filter samples taken in winter, for example, are known to lose some of the nitrate mass once taken to the lab where they are analyzed at higher temperatures (references xxx). Potential biases in nitrate would also affect the chloride measurements.

In any case, some discussion of measurement uncertainty is needed.

MOUDI instruments are operated at ambient conditions. Particles are collected on filters used as impaction substrates, which are brought back to the laboratory, where they are extracted with deionized water and analyzed by ion chromatography. The referee is correct that nitrate (and to a lesser extent chloride) can be lost by volatilization from filters during sampling.

In the case of the MOUDI measurements made by Colorado State University, parallel measurements of $PM_{2.5}$ nitrate were made using denuder/filter pack sampling trains designed to account for ammonium nitrate volatilization. These measurements show some MOUDI loss of nitrate at most sites, but typically less than 20-30%. This loss is mentioned briefly in the Lee et al. (2008a) paper, but is quantified only in Taehyoung Lee's Ph.D. dissertation. We expect that the degree of volatilization would be similar in the other data sets.

We have changed the last sentence of Section 3.2 to read "The PILS data further demonstrate that aerosol concentrations varied substantially on much shorter timescales than could be captured by the integrated MOUDI measurements, which are subject to volatilization losses during sampling, particularly in summer (Lee, 2007; Lee et al., 2008a)." In addition, we added two sentences in Section 3.4: "NO_3^- is also subject to measurement artifacts, including the loss of semivolatile ammonium nitrate from the MOUDI. Parallel measurements made using denuder/filter-pack sampling trains designed to account for ammonium nitrate volatilization showed some loss of nitrate at most sites, but typically less than 20-30% (Lee, 2007)."

Minor points: - Page 3864, line 5: These are "numerical" rather than "mathematical" models

The suggested modification has been made.

- P3866, L13: Since this manuscript evaluates aerosol size distributions and compo-

sition, it would be useful to add 2 or 3 sentences here briefly explaining the aerosol module AERO6 (Modal or sectional, number of modes, etc.). This is described later under "Data pairing and analysis" but I feel that section 2.1 would be the better location.

To address this comment, as well as a similar comment by Referee #2, we have revised the text to describe in section 2.1 the version of the CMAQ aerosol model used in the present study:

> The CMAQ model configuration was the same for all simulations, with the only differences being in the year-specific emission and meteorological input data. Aerosols in CMAQ are represented using three lognormal modes—Aitken, accumulation, and coarse (Binkowski and Roselle, 2003). Inorganic species in the Aitken and accumulation modes are assumed to be in thermodynamic equilibrium with the gas phase, while gas-particle partitioning between the gas phase and the coarse mode is treated dynamically (Kelly et al., 2010). The secondary organic aerosol formulation in CMAQ has been described by Carlton et al. (2010). The simulations in this study used CMAQ version 5.0.1 with the AERO6 aerosol module, which includes speciation of trace metals (Reff et al., 2009; Appel et al., 2013) and source-specific ratios of organic mass to organic carbon (Simon and Bhave, 2012), and incorporates version II of the ISORROPIA thermodynamic equilibrium module (Fountoukis and Nenes, 2007).

- P3866, L18: Is this exactly the same 35 layers as in CMAQ? Does CMAQ have a model top at 50 hPa, too?

Yes, these are exactly the same 35 layers. In our runs, WRF and CMAQ had a model top at 50 hPa, but this is configurable. To clarify this is the case, we have reorganized section 2.1 to describe the modeling chain more clearly, first discussing the WRF simulations, including the vertical layering, then MCIP, and finally CMAQ:

The Weather Research and Forecasting (WRF; Skamarock and Klemp, 2008) model version 3.3 simulated meteorology over the contiguous United States and southern Canada with 12 km by 12 km horizontal grid spacing. A terrain-following sigma vertical coordinate was used, with 35 vertical layers extending up to 50 hPa, and the top of the lowest model layer at approximately 20 m. *[another sentence on WRF configuration]* Version 4.0 of the Meteorology-Chemistry Interface Processor (MCIPv4.0; Otte and Pleim 2010) was used to prepare WRF outputs for CMAQ using the same 35-layer vertical structure as in WRF.

- P3872, L20: How is the model evaluated at mountain sites? At the lowest model level or at the true elevation of the site (which may be well above model ground)? It would be good to add the altitude of the stations in table 1.

WRF uses a terrain-following sigma vertical coordinate, and since here CMAQ is using meteorology fields from WRF, CMAQ inherits this vertical coordinate. Accordingly, the lowest model level is always at the surface, and all sampling locations were in layer 1 of the model. Rather than give the elevation of the stations in Table 1, we have a "Comment" column which we use to describe the terrain (e.g., "clean coastal" or "mountainous". Further details on the sampling locations (including the site elevations) are available in the references given in the right-hand column of Table 1.

- P3874, L7: I assume you are suspecting that the missing Ca^{2+} source is sea spray. Why not mention this explicitly?

We do model Ca^{2+} emissions from sea spray. The higher proportion of Ca^{2+} near the coast is either due to a non-sea-spray origin of Ca^{2+}, or perhaps inaccurate speciation of sea spray (though the latter seems unlikely, given that the chemical composition of seawater is well characterized). We have revised the text to read: "Unlike the situation for Mg^{2+}, the ratio of Ca^{2+} to Na^+ in the measurements at coastal sites is substantially greater than can be explained by their relative abundances in seawater (Fig. 6 and

Supplement Fig. S7). This suggests that there is a source (most likely not originating from seawater) of Ca^{2+} at those sites that is either absent or is underrepresented by the model."

- P3874, L17ff: Do you know which source of K^+ is more important: Natural biomass burning or anthropogenic biofuel burning?

The answer to this question depends on the specific location and time period of interest, and which class of biomass burning is predominant in that vicinity. While the sources of K^+ emissions are outside the scope of the present manuscript, we can convey on this Discussion page some information from Reff et al. (2009) who summarized U.S. total emissions for fine-particulate K and other trace elements. During 2002, an estimated 101,000 metric tons of K were emitted to the atmosphere (see Figure S4e of Reff et al.) of which wildfires contributed approximately 14,000 tons. Anthropogenic biofuel burning contributed over 42,000 tons of K, including 33,000 from agricultural burning, 5900 from wood- fired boilers, and 3300 from residential wood combustion. Other large sources of K in the U.S. inventory are agricultural soil (12,000 tons), unpaved road dust (11,000 tons), construction dust (2700 tons), and paved road dust (2300 tons). The U.S. inventory does not include wind-blown dust or sea spray, nor does it separately distinguish K^+ from total K.

- P3875, L4: As mentioned earlier, NO3 might not only be a challenge for the model but also for the measurements.

We have added a sentence noting that semivolatile ammonium nitrate can be lost from MOUDI impaction substrates during sampling, particularly in summer, and that parallel URG denuder/filter-pack measurements at CSU sites quantified the nitrate losses in the MOUDI as typically not more than about 20%.

- P3877, L5: Could the summer low bias be due to SOA?

Yes, CMAQ has a negative bias for SOA, which is worst in summer. The text has been

modified to insert this point, citing Carlton et al. (2010).

- P3878: Use past tense as done in section 2.1. Thus, change "are" to "were" on line 2, "is" to "was" on line 9, and "are" to "were" on lines 10 and 12.

The suggested edits have been made.

- P3878, L16: "non-carbonaceous organic matter" sounds like a contradiction in itself. Is this supposed to be all molecules other than C?"

The text has been modified to read "noncarbon organic mass (NCOM)" and to cite Simon and Bhave (2012), which describes the use of source-specific organic mass-to-carbon ratios (OM/OC). NCOM is defined as the difference between organic mass (OM) and organic carbon (OC).

- P3880, L6: PMEMIS should probably be replaced by BASE here.

No, the CONSIG sensitivity was built on top of PMEMIS. We have deleted "Similar to the PMEMIS sensitivity" from the sentence to clarify.

- P3881,L27: Again, the obvious reason for the underestimation of Ca^{2+} at coastal sites is not mentioned explicitly.

As noted above, the fact that the model does a reasonable job at capturing Na^+ and Mg^{2+} at those sites, but a poor job of capturing Ca^{2+}, suggests that the extra Ca^{2+} is not due to sea spray but rather has some other source, likely windblown dust. We have modified the text to make this point clearer: "By contrast, the model substantially underpredicts Ca^{2+} at many coastal sites while having better performance than for Mg^{2+} at some inland sites, which may be attributable to errors in windblown dust emissions as well as speciation profiles for windblown and anthropogenic fugitive dust."

- P3882, L9: Maybe a good place to mention that some of the nitrate biases are related to biases in other ions.

The fact that nitrate gas-particle partitioning is sensitive to other ions, as well as temper-

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ature and humidity, is discussed in Section 3.4. We feel it is not necessary to reiterate that discussion here in the conclusion.