Dear Samuel,

Thank you very much for your comments. We have added discussions of the impact of updated wet scavenging parameterization on sulfate simulation over the US. Since this manuscript focuses on nitrate, nitric acid, and ammonium (please see title, abstract, and introduction) and to avoid disrupting the logic flow, we put the table and figure with regard to sulfate as supporting material.

Thanks,

Gan

We thank the referee for the detailed reviews and constructive comments that help to improve the manuscript. Below we respond to the comments in detail. (Referee's comments are in Italic). The manuscript has been revised accordingly.

The authors aim to improve wet deposition simulation of nitric acid, nitrate and ammonium over the United States using GEOS-Chem via updating both in cloud stratiform cloud scavenging and below cloud washout. For in cloud scavenging, they adopt the dynamic varied condensed water content provided by MERRA2 meteorological fields needed in wet scavenging parameterization, instead of the current assumption of a global flat value. For below cloud washout, they derive a new set of empirical washout scavenging coefficient and exponential coefficient for nitric acid based on the size-resolved coefficients summarizing from field measurement and theoretical derivation. This is an interesting and valuable study. The study would have a potential impact on the broad atmospheric composition study via improving tracers' wet scavenging if the authors could validate their work for other aerosols and their precursors. A minor revision is required before the paper is published in GMD.

We appreciate the referee's positive comments about the importance of this study.

Major Comments

The authors test the physical-based condensed cloud water for stratiform cloud rainout. Convective cloud removal is important and is necessary to be studied as well. Studying convective rainout is particularly important for using the current generation of NASA GEOS meteorological fields since its partitioning of large scale and convective clouds tilts more towards the latter. The convective cloud fraction and water content can be provided by the GEOS model.

This is a valid point. However, the convective cloud fraction and water content, while available in GEOS online simulation, is not available in GMAO reanalysis datasets (including MERRA2) used to drive GEOS-Chem. Therefore, as we have already pointed out in the last paragraph of Session 2.2, "the updated wet scavenging method discussed above for stratiform precipitation cannot be directly applied to convective precipitation rainout scavenging in GEOS-Chem". We agree with the referee that "Convective cloud removal is important and is necessary to be studied as well" and have pointed this out in the discussion session.

The authors are highly encouraged to evaluate and summarize the impact of their work on other aerosols and their precursors. Once the GEOS-Chem adopts the improvements in wet scavenging parameterization suggested by the authors, all aerosols and their precursors undergoing wet scavenging will be impacted. To have confidence in using their work, they should at least provide a brief description of the model performance for all important aerosol fields in supplementary material. In addition, the authors' work focuses on the United States only. What is the anticipated *influence of the improved wet scavenging on other regions?*

Yes, we are evaluating the impacts of updated scheme on other aerosols and other regions. Based on preliminary comparisons with relevant measurements we analyzed so far, the updated wet scavenging parameterization also improves the model performance over Europe and Asia. More in-depth analysis is being carried out and we are preparing another paper on the impacts of updated wet scavenging parameterization on global simulation of aerosols in GEOS-Chem. We have pointed this out in the discussion session.

To be more useful of the proposed work on wet deposition, more words are needed about the broader impact of the study on the whole atmospheric chemistry community. Can other global chemistry models adopt their improvement? Is there anything that other modelers should be cautioned of in adopting their work?

The updates of rainout can be adopted by any atmospheric chemistry models which assume constant cloud condensation water. The empirical washout can help to reduce the overestimation of nitric acid gas shown in the work of Bian et al. (2017) by most of atmospheric chemistry models. Corresponding discussions have been added in the Summary and Discussion section.

Specific comments
1. Page 3 line 26 equation 1: Should the k in exponential term differ with the k in the denominator of coefficient? For my understanding, the k in exponential term, which is the first-order rainout rate, is linked to specific tracer species. One the other hand, the k in denominator represents the generic conversion rate of cloud water to precipitation. Please double check this. Please also give units of these fields and parameters in equation 1.

We double-checked this. As shown in the work (session 1.1) of Jacob et al. (2000), the k in exponential term and the k in the denominator of coefficient are the same for soluble species. In GEOS-Chem, the model assumes the first-order rainout rate for water soluble aerosols and nitric acid gas equals the generic conversion rate of cloud water to precipitation. The units have been added.

2. Page 7 lines 4-19: How about aerosols? Should the washout scavenging coefficients of aerosols be adjusted accordingly?

We applied empirical washout rate from Laakso et al. (2003) for water soluble aerosols and washout rate from Feng (2007) for water insoluble aerosols. Corresponding information has been updated in the revised text.

3. Page 8 line 7: Please add one more case study. Similar to case study 4 but empirical washout rate of HNO3 is applied only to large scale precipitation. This case, *combined with case 4, will give us further information about the relative washout contribution from large scale and convective scale precipitations.*

As shown in Figure S1 below, the exclusion of wash out by convective precipitation in GEOS-Chem has negligible impacts on surface level HNO3, nitrate, and ammonium over the US. It is because convective precipitation is large over Tropics and small over middle and high latitude continent. Convective precipitation over the US is 10-100 times smaller than large-scale precipitation over there.

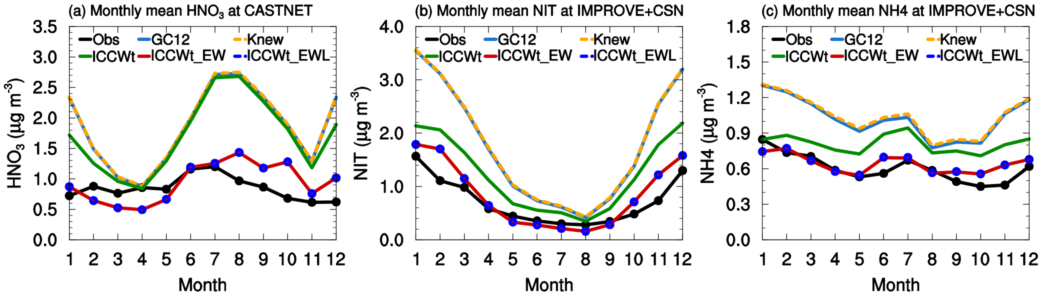

Figure S1. Monthly variations of mean for year 2011 showing the comparison between nitric acid (a), nitrate (b), and ammonium (c) mass concentrations observed at ground-based sites (black) and simulated by GC12 (blue), Knew (yellow dash), ICCW$_t$ (green), ICCW$_t$_EW, and ICCW$_t$_EWL (blue circular points) cases.

4. Page 8 line 7: Do the authors present the work of empirical washout rates for aerosols? Section 2.2 seems only give discuss for HNO3. What are the new empirical washout rates for aerosols?

In this study, empirical washout rate is from Laakso et al. (2003) for water soluble aerosols, while washout rate is from Feng (2007) for water insoluble aerosols. We modified corresponding sentences in the paper.

5. Page 9 lines 1-2: The change range shown here (from 150% to 24%) includes not only using empirical washout rate, but also changing cloud condensation water.

Corrected. We changed the value from 150 % to 125 %.

We thank the referee for the detailed reviews and constructive comments that help to improve the manuscript. Below we respond to the comments in detail. (Referee's comments are in Italic).

This paper presented a revised wet scavenging parameterization that considers the spatiotemporal variability of cloud liquid water content and an empirical washout(below-cloud scavenging) rate in the GEOS-Chem global chemical transport model. The authors showed that the updated parameterization significantly improves simulated annual mean (and seasonal) mass concentrations of nitric acid, nitrate, and am-monium as compared with surface observations over the U.S. This is an important contribution to the improvement of GEOS-Chem. Minor revision is recommended be-fore publication on GMD.

We appreciate the referee's positive comments about the importance of this study.

Major comments:

The impact of updated wet scavenging on model simulations was only assessed at the surface level and for nitric acid, nitrate, and ammonium over the U.S. It's not shown how the updated treatment of scavenging affects the global aerosol simulations, especially the vertical profiles and other aerosol species (e.g., sulfate). Consider discussing this in the Summary and Discussions section. Lead-210 aerosol tracer has been used to test wet deposition in GEOS-Chem (e.g., Liu et al., 2001), and this updated scavenging parameterization will need to be tested with (at least) lead-210 before it is incorporated into the standard version of the model.

Agree. We added additional discussions on these issues in the summary and discussions section. More in-depth analysis is being carried out and we are preparing another paper on the impacts of updated wet scavenging parameterization on all major aerosol species over the whole globe.

*Page 5, equation 4: 1). "CW is grid-box mean cloud water content". What's the corresponding variable name in MERRA-2? Does it include both cloud liquid (QL) and ice (QI), or QL only? 2). It's not clear why the rain water term "Pr*DeltaT" is needed. There is no prognostic precipitation (no raining condensate) in MERRA-2 or GEOS-5. Prognostic cloud liquid and ice are autoconverted to estimate precipitation. Are "CW" values for pre-conversion or post-conversion? More explanation as well as references are needed.*

CW is "QL" in MERRA2. It only includes cloud liquid. As shown in Equation 6 in MERRA2's file specification (Bosilovich et al., 2016), QL is the residual condensation water after precipitation. Due to large fraction of cloud water converted to rain water, cloud water in MERRA2 is low when precipitation is occurring. Because the fraction of soluble species rained out should equal to the fraction of total condensed water (or ICCW in our case) converted to rain water, we think that ICCW in Eq (3) should include rain water (i.e., Eq 4). The following reference is added to the reference list.

Bosilovich, M. G., R. Lucchesi, and M. Suarez, 2016: MERRA-2: File Specification. GMAO Office Note No. 9 (Version 1.1), 73 pp, available from http://gmao.gsfc.nasa.gov/pubs/office_notes.

Page 7, lines 20-23: The first-order rainout parameterization is not used for convective precipitation scavenging in GEOS-Chem driven by MERRA-2. Instead, scavenging in convective updrafts are coupled with convective transport (e.g., see section 2.3.1 of Liu et al., 2001).

We have modified the text to reflect this.

Minor comments:
Title: Suggest adding "surface" to the title since this study examined the impact of revised scavenging on surface aerosol concentrations only.

Accepted.

Page 1, line 21: typo "mentoring" ("monitoring")

Revised.

Page 3, lines 6-7: are there references for this statement?

We did the simulations with 4°×5° and 2°×2.5° horizontal resolutions in GEOS-Chem and found the switching of model resolution has small impact on simulated nitrate over the US.

Page 3, line 14: change "in-site observations" to "surface observations"

Accepted.

Page 3: A brief description of the GEOS-Chem model is needed here before discussing the wet scavenging scheme.

Accepted.

Page 3, section 2: See this webpage http://acmg.seas.harvard.edu/geos/geos_chem_narrative.html for "Narrative description (and how to cite GEOS-Chem)", which provides guidance on citing relevant model components. "The wet deposition scheme in GEOS-Chem is described by Liu et al. [2001] for water-soluble aerosols and by Amos et al. [2012] for gases. Scavenging of aerosol by snow and cold/mixed precipitation is described by Wang et *al. [2011, 2014]." Suggest citing Jacob et al. (2000) along with one of these publications, where appropriate, since it is an unpublished document. The first-order rainout parameterization (equations 1 and 2) is based on Giorgi and Chameides (1986), which also needs to be referenced.*

Added description and citation as suggested.

Specify the units for variables in all equations in the text.

Accepted.

Page 4, line 3: condensed water content includes liquid and ice phases. Do you revise warm cloud scavenging only here? Does "Pr" (rate of new precipitation formation) include snow? How about ice cloud scavenging?

We only revised rainout for warm cloud in this study. Pr, DQRLSAN in MERRA2, only includes rainwater. Ice cloud scavenging is applied to aerosols via washout by snow following the approach suggested by Wang et al. (2011).

Page 4, lines 23-25: Croft et al. (2016) previously used GEOS-5 cloud liquid and ice water content to replace the fixed value in their GEOS-Chem-TOMAS simulations. Consider citing that work here. (Croft, B., Martin, R. V., Leaitch, W. R., Tunved, P., Breider, T. J., D'Andrea, S. D., and Pierce, J. R.: Processes controlling the annual cycle of Arctic aerosol number and size distributions, Atmos. Chem. Phys., 16, 3665-3682, https://doi.org/10.5194/acp-16-3665-2016, 2016.)

Thanks for pointing us to this work. The major difference of rainout treatment between Croft et al. (2016) and our work is the assumption of ICCW. Croft et al. (2016) used cloud liquid and ice water content to replace the fixed ICCW, while we used the sum of cloud liquid water and rain water to replace the fixed ICCW which is critical for rainout calculation (Eqs. 2-3). Corresponding discussions have been added in the revised paper.

Page 8, line 4: these references are not for rainout and washout parameterizations, but for the standard GEOS-Chem model (or other model components).

Accepted. These references are cited at the brief description of the GEOS-Chem model in revised paper.

Page 9, line 13: CCW or ICCW?

It is ICCW. Revised.

Page 9, line 17: concentrations OF; line 20: showS

Revised.

Fig. 2 caption: indicate the year and number of sites over the U.S., and note the small differences between blue and green dashed lines.

Modified as suggested.

Fig.3 caption: annual mean surface

Modified as suggested.

Revised treatment of wet scavenging processes dramatically improves GEOS-Chem 12.0.0 simulations of surface nitric acid, nitrate, and ammonium over the United States

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Abstract

The widely used community model GEOS-Chem 12.0.0 and previous versions have been recognized to significantly overestimate the concentrations of gaseous nitric acid, aerosol nitrate, and aerosol ammonium over the United States. The concentrations of nitric acid are also significantly over-predicted in most global models participating a recent model inter-comparison study. In this study, we show that most or all of this overestimation issue appears to be associated with wet scavenging processes. Replacement of constant in-cloud condensation water (ICCW) assumed in GEOS-Chem standard versions with one varying with location and time from the assimilated meteorology significantly reduces mass loadings of nitrate and ammonium during the wintertime, while the employment of an empirical washout rate for nitric acid significantly decreases mass concentrations of nitric acid and ammonium during the summertime. Compared to the standard version, GEOS-Chem with updated ICCW and washout rate significantly reduces the simulated annual mean mass concentrations of nitric acid, nitrate, and ammonium at surface ~~mentoring~~monitoring network sites in US, from 2.04 to 1.03 µg m^{-3}, 1.89 to 0.88 µg m^{-3}, 1.09 to 0.68 µg m^{-3}, respectively, in much better agreement with corresponding observed values of 0.83, 0.70, and 0.60 µg m^{-3}, respectively. In addition, the agreement of model simulated seasonal variations of corresponding species with measurements is also improved. The updated wet scavenging scheme improves the skill of the model in predicting nitric acid, nitrate, and ammonium

concentrations which are important species for air quality and climate.

1. Introduction

Nitrate and ammonium are important secondary inorganic aerosols in the atmosphere, contributing significantly to total aerosol mass over most polluted regions (Bian et al., 2017) and to aerosol direct radiative forcing over urban and agriculture regions (Bauer et al., 2007; Myhre et al., 2013). The amount of nitrate and ammonium also regulates the concentration of gaseous ammonia which often plays an important role in the formation of new particles (Kirkby et al., 2011; Yu et al., 2018). In addition, nitrate and ammonium help newly formed particles grow to larger sizes suitable for cloud condensation nuclei (Yu and Luo, 2009) and thus can impact aerosol indirect radiative forcing (Twomey, 1977).

Nitric acid, nitrate, and ammonium concentrations are often overestimated by atmospheric models (Pye et al., 2009; Walker et al., 2012; Bian et al., 2017; Zakoura and Pandis, 2018), including the widely used community model GEOS-Chem (e.g., Zhang et al., 2012; Heald et al., 2012). Zhang et al. (2012) studied nitrogen deposition over the US with GEOS-Chem and found both nitric acid and nitrate concentrations are overestimated, especially in wintertime. They suggested that this is the result of excessive nitric acid formation via night time chemistry of heterogeneous N_2O_5 hydrolysis. However, Heald et al. (2012) found the overestimate of heterogeneous N_2O_5 hydrolysis does not fully account for the nitrate bias and suggested the positive nitrate bias is likely linked with an overestimate of nitric acid concentrations. Heald et al. (2012) investigated other possible causes for the overestimation of nitric acid concentrations arising from uncertainties in daytime formation and dry deposition, and concluded that none of these uncertainties could fully account for the reduction in nitric acid required to correct the nitrate bias. Based on comparisons of simulated nitrate and ammonium aerosol from nine AEROCOM models with ground station and aircraft measurements, Bian et al. (2017) concluded that most models overestimate surface nitric acid volume mixing ratio by a factor of up to 3.9 over North America and the overestimation cannot be simply attributed to model uncertainties. Backes et al. (2016) suggested that uncertainties in the temporal profiles of ammonia emissions could also contribute significantly to the bias of nitrate concentrations. However, the impact of ammonia mostly happened during summer time. Zakoura and Pandis (2018) found significant decrease in nitrate concentration when they enhanced their model resolution from 36 km × 36 km to 4 km × 4 km in the PMCAMx model. However, similar results are not found in global models with much coarser grids than regional models. All these studies indicate that the overestimation of nitric acid, nitrate, and ammonium mass concentrations in current atmospheric chemistry models remains to be resolved.

In this study, we proposed an improved treatment of wet scavenging in GEOS-Chem by considering cloud condensation water variability and empirical washout rate, which together significantly improve the estimates of nitric acid, nitrate, and ammonium over the US. ~~The improved wet scavenging in GEOS-Chem is described in section 2.~~ GEOS-Chem is a global 3-D model of atmospheric chemistry driven by meteorological input from the Goddard Earth Observing System (GEOS) of the NASA Global Modeling and Assimilation Office and includes state-of-the-art routines to deal with emissions, transport, and other key chemical and physical processes for atmospheric trace gases and aerosols (Keller et al., 2014; Fontoukis and Nenes, 2007; Martin et al., 2003; Bey et al., 2001). The improved wet scavenging in GEOS-Chem is described in section 2. The comparison of model results with ~~in-site~~surface observations and the changes of the three species over the US are presented in section 3. Section 4 is the summary and discussion.

2. Improved scheme for wet scavenging

Wet scavenging is the main removal pathway for many atmospheric air pollutants. Two mechanisms are involved in wet scavenging: rainout (in-cloud scavenging) and washout (below-cloud scavenging). GEOS-Chem treats wet scavenging associated with stratiform and convective precipitation separately. The wet deposition scheme in

GEOS-Chem is described by Jacob et al. (2000) and Liu et al. (2001) for water-soluble aerosols, and by Amos et al. (2012) for gases. Scavenging of aerosol by snow and cold/mixed precipitation is described by Wang et al. (2011, 2014). The first-order rainout parameterization is based on Giorgi and Chameides (1986).

2.1 Impact of in cloud condensed water (ICCW)

For stratiform precipitation, in the most recently released GEOS-Chem version 12.0.0 (GC12), rainout water soluble species is parameterized according to Jacob et al. (2000) and Liu at al. (2001) as

$$F = \frac{P_r}{k \cdot ICCW}\left(1 - e^{-k \cdot \Delta t}\right) \quad (1)$$

where F is the fraction of a water soluble tracer in the grid-box scavenged by rainout, Δt (s) is the model integration time step. k (s^{-1}) is the first-order rainout loss rate (Giorgi and Chameides, 1986) which represents the conversion of cloud water to precipitation water. $ICCW$ ($g\ m^{-3}$) represents the condensed water content (liquid) within the precipitating cloud (i.e., in cloud) and P_r ($g\ m^{-3}\ s^{-1}$) is the rate of new precipitation formation (rain only) in the corresponding grid-box.

The rainout loss rate (k) represents how fast cloud condensation water can be removed from the atmosphere and thus is critical for rainout scavenging. k is defined in Jacob et al. (2000) and coded in GC12 (called k_{GC12} thereafter) as

$$k_{GC12} = k_{min} + \frac{P_r}{ICCW} \quad (2)$$

where k_{min} (s^{-1}) is the minimum value of rainout loss rate derived from the stochastic collection equation which indicates that in one hour at least ~ 0.36 of cloud droplets are lost to autoconversion/accretion (Beheng and Doms 1986). In GC12, k_{min} is set to be 0.36 $hr^{-1} = 1 \times 10^{-4}\ s^{-1}$.

It should be noted that P_r in Eq. (2) is a grid-box mean value, while $ICCW$ is an in cloud value. To be physically consistent, we suggest a new expression of k (k_{new}) that replaces grid-box mean P_r with the corresponding in cloud value P_r/f_c.

$$k_{new} = k_{min} + \frac{P_r}{f_c \cdot ICCW} \quad (3)$$

where f_c is the grid-box mean cloud fraction. As we will show later, Eq. (3) gives k values in much better agreement with those derived from cloud model simulations and observations.

To calculate F, GC12 uses P_r from the Modern-Era Retrospective analysis for Research and Applications Version 2 (MERRA2) meteorological fields. For $ICCW$ in Eqs. 1-3, Jacob et al. (2000) used a constant value of 1.5 g m^{-3} and Wang et al. (2011) changed it to 1 g m^{-3}. In GC12, the default value of $ICCW$ is 1 g m^{-3}. However, $ICCW$ in the atmosphere varies with time and location. Here we suggest to use time and location dependent $ICCW$ (named $ICCW_t$) which can be derived from MERRA2 meteorological fields as

$$ICCW_t = \frac{CW + P_r \cdot \Delta t}{f_c} \quad (4)$$

where CW is grid-box mean cloud water content, while $P_r \cdot \Delta t$ represents rain water content produced during the time step Δt. In a previous study, Croft et al. (2016) used cloud liquid and ice water content to replace the fixed ICCW. However, as shown in Equation 6 in MERRA2's file specification (Bosilovich et al., 2016), cloud water is the residual condensation water after precipitation and is low when precipitation is occurring. Because the fraction of soluble species rained out should equal to the fraction of total condensed water (or ICCW in our case) converted to rain water, we think that ICCW in Eq (3) should include rain water (i.e., Eq 4).

Figure 1a shows seasonal variations of $ICCW_t$ (Eq. 4) averaged throughout the lower troposphere (0–3 km) of the whole globe ($ICCW_{t\_G}$), over all land surface ($ICCW_{t\_L}$), over the oceans ($ICCW_{t\_O}$), and over the continental US ($ICCW_{t\_US}$). For comparisons, the constant values of $ICCW$ assumed in Jacob et al. (2000) ($ICCW_{J2000}$) and GC12 ($ICCW_{GC12}$) are also shown. The monthly mean values of $ICCW_{t\_G}$, $ICCW_{t\_L}$, $ICCW_{t\_O}$, and $ICCW_{\mathrm{t\_US}}$ vary within the ranges of 0.90–1.03 g m^{-3}, 0.30–0.45 g m^{-3}, 1.15–1.26 g m^{-3}, and 0.21–0.53 g m^{-3}, respectively. This figure shows that $ICCW_{\mathrm{t\_G}}$ is close to the assumed $ICCW$ value of 1 g m^{-3} used in GC12. As can be seen from Fig.1a, $ICCW_{\mathrm{t\_O}}$ is greater than 1 g m^{-3}, but $ICCW_{\mathrm{t\_L}}$ is much less than the constant value of 1 g m^{-3} assumed in GC12. The mean $ICCW$ over the continental US (bright green line) is close to $ICCW_{\mathrm{t\_L}}$ (olive line), and is ~ 5 times less than the assumed value in GC12 during the wintertime and ~ 2 times less during the summertime. As we will show later, the constant $ICCW$ of 1 g m^{-3} assumed in GC12 leads to significant underestimation of rainout over the continental US, especially during the wintertime.

Figure 1b shows seasonal variations of mean k_{GC12}, k_{new}, and k_{new_ICCWt} in the lower troposphere (0-3 km) of the continental US. Referring to Eq. (2), the figure shows that k_{GC12} is dominated by $k_{\min}$ (which is physically unsound) and thus shows negligible seasonal variation. Conversely, k_{new} is low in the wintertime and high in the summertime. k_{new_ICCWt} is 2.3 times higher than k_{new} during January and 1.6 times higher than k_{new} during July. Both k_{new} and k_{new_ICCWt} are within the range of rainout loss rates (10^{-4}–10^{-3} s^{-1}) indicated by cloud model simulations and estimates based on observations (Giorgi and Chameides, 1986).

From Eqs. (1), (3), and (4), we can get the updated parameterization for rainout loss fraction at each location and time step

$$F = \frac{f_c \cdot P_r}{k_{new\_ICCW_t}\left(CW + P_r \cdot \Delta t\right)}\left(1 - e^{-k_{new\_ICCW_t} \cdot \Delta t}\right) \quad (5)$$

2.2 Impact of empirical washout rate on nitric acid wet scavenging

Still considering the case of stratiform precipitation in GOES-Chem, the fraction of aerosols and HNO_3 within a grid-box that is scavenged by washout over a time step is parameterized as (Wang et al., 2011; Liu et al., 2001; Jacob et al., 2000)

$$F_{wash} = f_r(1 - exp(-k_{wash}\Delta t) \quad (6)$$

$$f_r = \max(\frac{P_r}{k \cdot ICCW}, f_{top}) \quad (7)$$

$$k_{wash} = \Lambda\left(\frac{P_r}{f_r}\right)^b \quad (8)$$

where f_r is the horizontal areal fraction of the grid-box experiencing precipitation and f_{top} is the value of f_r in the layer overhead (f_{top} = 0 at the top of the precipitating column). k_{wash} is washout rate, Λ is washout scavenging coefficient, and b is an exponential coefficient. In the original GEOS-Chem, $\Lambda = 1$ cm^{-1} and $b = 1$ for both aerosols and nitric acid (Liu et al., 2001; Jacob et al., 2000).

It has been well recognized that, for aerosols, Λ and b depend on particle size (Wang et al., 2010; Feng, 2007; Andronache et al., 2006; Henzing et al., 2006; Laakso et al., 2003). Feng (2007) suggested values of b = 0.62, 0.61, and 0.8 for particles in nucleation (diameter 1 nm – 40 nm), accumulation (40 nm – 2.5 μm), and coarse mode (>2.5 μm), respectively. Many studies indicate that there are large difference between existing theoretical and observed size-resolved washout rates (Wang et al., 2010; Andronache et al., 2006; Henzing et al., 2006; Laakso et al., 2003). For particles within the diameter range of 0.01–2 μm, size-resolved washout rates derived from analytical formulas are one to two orders of magnitude smaller than those derived from field measurements (e.g., Wang et al., 2010). This large difference could result from turbulent flow fluctuations (Andronache et al. 2006; Khain and Pinsky, 1997), vertical diffusion process (Zhang et al., 2004), and droplet-particle collection mechanisms (Park et al., 2005).

In GC12, Λ and b for aerosols are parameterized as a function of particle size modes (Wang et al., 2011), following Feng (2007). For nitric acid, GC12 keeps $\Lambda = 1$ cm^{-1} and $b = 1$, unchanged from the original CEOS-Chem parameters. In this study, we employ the size-dependent aerosol washout parameterization derived from six years of field measurements over forests in southern Finland (Laakso et al., 2003; Wang et al., 2010). We further estimate nitric acid washout scavenging coefficients by referring to field measurements for particles of 10 nm (Laakso et al., 2003) and the theoretical dependence of scavenging coefficients on particle sizes for particles < 10 nm (Henzing et al., 2006). The collection efficiency of particles smaller than 10 nm by rain droplets is dominated by Brownian diffusion, and in this regard we can treat nitric acid as a single molecule (or particle) with diameter of 0.5 nm. Through this approach, we derive ~~an empirical Λ value for nitric acid of 2 cm^{-1}. In addition~~empirical K_{wash} value for nitric acid to be 3×10^{-3} s^{-1} when rain rate is 1 mm h^{-1}. This empirical value is about two orders of magnitude larger than the corresponding K_{wash} value in GC12 (0.1 hr^{-1} = 2.8×10^{-5} s^{-1}). For the dependence of K_{wash} on rain rate, we adopt the b value of 0.62 for nucleation mode particles (diameter 1 nm – 40 nm) (Feng, 2007) for nitric acid.~~ When in cloud precipitation intensity is 1 mm h^{-1},~~ With this empirical b value of 0.62 and empirical K_{wash} of 3×10^{-3} s^{-1}, we derive an empirical Λ value for nitric acid of 2. It should be noted that the unit of empirical Λ is not cm^{-1} when b is not unity. In our parameterization (Eq. 8), Λ=2 and P_r should be in the unit of cm s^{-1}. Washout rates for water soluble aerosols are using the empirical values from Laakso et al. (2003), while washout ~~loss rate equals 3×10^{-3} s^{-1}~~rates for water insoluble aerosols are still using the values from Feng (2007). No change is made to washout by snow, which is ~~about two orders of magnitude larger than the corresponding washout loss rate (0.1 hr^{-1} = 2.8×10^{-5} s^{-1}) currently in GC12.~~based on the approach described in Wang et al. (2011).

For convective precipitation, scavenging in convective updrafts are coupled with convective transport (e.g., Liu et al., 2001). Furthermore, MERRA2 meteorological fields do not provide convective cloud fraction and cloud water content. Therefore, the updated wet scavenging method discussed above for stratiform precipitation cannot be directly applied to convective precipitation rainout scavenging in GEOS-Chem. However, the empirical ~~value~~values for water soluble aerosol and nitric acid washout ~~is~~are also applied to convective washout in the present study as Case 4.

3. Model simulations and results

To study the impacts of various updates to the wet scavenging as described in Section 2 on model simulated nitric acid, nitrate, and ammonium mass concentrations, we run GEOS-Chem for 4 cases: (1) standard GC12 parameterizations for rainout and washout ~~(Keller et al., 2014; Fontoukis and Nenes, 2007; Martin et al., 2003; Bey et al., 2001),~~, called GC12; (2) same as the Case GC12 except k_{new} in Eq. 3 is used, called Knew; (3) same as the Case Knew except $\mathrm{ICCW_t}$ from MERRA2 (Eq. 4) is used, called $\mathrm{ICCW_t}$; (4) same as the Case $\mathrm{ICCW_t}$ except empirical washout rates for nitric acid and water soluble aerosols are used, called $\mathrm{ICCW_t}$_EW. For each case, we carry out simulations from December 2010 to December 2011, with the first month as spin-up. The model horizontal resolution is $2^{o}\times2.5^{o}$ and vertically there are 47 layers. The present analysis focuses on the continental United States. We compared simulated nitric acid with in-situ observations at Clean Air Status and Trends Network (CASTNET) sites, simulated nitrate and ammonium with in-situ observations at Interagency Monitoring of Protected Visual Environments (IMPROVE) and Chemical Speciation Network (CSN) sites. For 2011, there were 74 sites with available nitric acid observations from CASTNET. For the same year, IMPROVE had 120 sites with available nitrate and ammonium observations, while CSN had 94 sites with available nitrate observations and 63 sites with available ammonium observations.

The effects of different modifications to the GC12 wet scavenging parameterization on model simulated nitric acid, nitrate, and ammonium mass concentrations are shown in Figures 2-3 and Table 1. Most of the changes of mass concentrations of the 3 species over the US are caused by the changes of cloud condensation variability and/or empirical washout rate. The impact of new rainout loss rate (k_{new}) is relatively small because of the cancelling effect of k in the denominator and also in the exponent in Eq. 1. As shown in Figs. 2a-2b and Table 1, all cases except $\mathrm{ICCW_t}$_EW overestimate nitric acid at CASTNET sites by a factor 2–3 in both wintertime and summertime. Consideration of cloud condensation water variability slightly reduces nitric acid in January and December but has negligible effect during other months. The inclusion of the empirical washout rate reduces the normalized mean bias (NMB) of nitric acid from ~~~150~~125 % to 24 % (Table 1). Figures 2c and 2d show the impacts of improved wet scavenging on nitrate. It is clear that GC12 significantly overestimates nitrate concentration at most sites especially during the wintertime, in agreement with previous studies (Heald et al., 2012; Walker et al., 2012). Replacing constant ICCW with variable $ICCW_t$ reduces the NMB of nitrate from 170 % to 84 %. ICCW has significant impact on reducing nitrate mass concentration during the wintertime and a smaller impact during the summertime. Wintertime bias of nitrate was reduced from 2 µg m^{-3} to 0.7 µg m^{-3}. The change of washout rate from theoretical value to empirical formula results in an additional 59 % reduction of NMB for nitrate and impacts nitrate mass concentration significantly both in the winter and in the summer. For ammonium, NMB is reduced from 85 % to 43 % after considering rainout with variable cloud condensation water. Similar to nitrate, the impact of ~~CCW~~ICCW is large during the wintertime and smaller during the summer time. After considering empirical washout, the NMB of ammonium is reduced to 13 %. While the update in the wet scavenging parameterization significantly improves agreement of the model simulated mass concentrations of nitric acid, nitrate, and ammonium over the US with those observed, it does not affect the correlation coefficients of annual mean values (Table 1) which are dominated by spatial distributions (Fig. 3).

Figure 3 ~~shown~~shows the horizontal distributions of surface layer nitric acid, nitrate, and ammonium mass concentrations over the US for case GC12 (a-c) and case $ICCW_t$_EW (d-f). For comparison, annual mean mass concentrations observed at CASTNET, IMPROVE, and CSN sites are shown in filled cycles. The spatial pattern of the simulated concentrations of the three species for the ICCW_EW case is close to those for the GC12 case. High concentrations of nitric acid are mainly located at northeastern, southern, and western US with the values up to 2–4 µg m^{-3} based on GC12 (Fig. 3a) and

1-2 μg m^{-3} based on $ICCW_t$_EW (Fig. 3d). Horizontal distribution of nitrate is different from that of nitric acid. Nitrate is mainly located at the Ohio valley region and the Northeastern US with values up to 4–5 μg m^{-3} based on GC12 (Fig. 3b) and 1-3 μg m^{-3} based on $ICCW_t$_EW (Fig. 3e). Ammonium shows a similar horizontal distribution to that of nitrate, but its value is ~50 % lower than nitrate concentration. For the whole continental US domain, the annual mean nitric acid, nitrate, and ammonium concentration in the model surface layer are reduced from 1.48 μg m^{-3} to 0.78 μg m^{-3}, 1.03 μg m^{-3} to 0.46 μg m^{-3}, 0.76 μg m^{-3} to 0.47 μg m^{-3}, respectively. The percentage changes for nitric acid, nitrate, and ammonium concentrations averaged within the domain are -47%, -55%, and -38%, respectively. The improved wet scavenging treatment had significant impacts on nitric acid, nitrate, and ammonium modeling over the US. As can be seen from Figs. 3a-3f (and also Fig. 2 and Table 2), simulated nitric acid, nitrate, and ammonium mass concentrations over the US based on the updated wet scavenging parameterization (i.e., $ICCW_t$_EW) are in much better agreement with in-situ measurements.

4. Summary and discussions

We present an improved wet scavenging parameterization for ~~use in~~using in GEOS-Chem by considering cloud condensation water variability and an empirical washout rate. The updated parameterization significantly reduces the overestimation of simulated annual mean mass concentrations of nitric acid, nitrate, and ammonium at CASTNET, IMPROVE, and CSN sites in US, from 2.04 to 1.03 (observation: 0.83) μg m^{-3}, 1.89 to 0.88 (observation: 0.70) μg m^{-3}, 1.09 to 0.68 (observation: 0.60) μg m^{-3}, respectively. In addition, the agreement of model simulated seasonal variations of corresponding species with measurements is also improved. The updated wet scavenging scheme provides a partial solution to the persistent problem of nitric acid and nitrate overestimation in the widely used community model GEOS-Chem (e.g., Heald et al.,

2012) and thus improve the skill of the model in predicting nitric acid, nitrate, and ammonium concentrations. It should be noted that in the present study the cloud condensation water variability is considered only for stratiform cloud rainout. Convective cloud removal is important (especially for tropical regions) and is necessary to be studied as well, calling for the output of convective cloud fraction and cloud water content fields in future GMAO reanalysis products.

The empirical washout rate suggested in the present work will also help to resolve the significant over-prediction of nitric acid by most of the 9 global models participating in the Aerosol Comparisons between Observations and Models (AeroCom) phase III study (Bian et al., 2017). Due to large difference in nitric acid washout rate based on theoretical and field studies and the importance of this rate, further research is needed to better understand the underlying reasons and reduce the difference. At the time being, we recommend the empirical values to be used in models.

~~While the present study focused on the US where abundant relevant measurements are available, the updated wet scavenging parameterization impacts model simulated nitric acid, nitrate and ammonium concentrations in other regions as well, particularly over land.~~ The revised rainout scheme presented in this study can be applied to other atmospheric chemistry models assuming constant cloud condensation water. The changes of nitrate and ammonium mass concentrations not only impact particle growth but also influence ammonia concentrations which are important for aerosol nucleation (Kirkby et al., 2011; Yu et al., 2018), via the equilibrium of sulfate-nitrate-ammonium. The updated scheme presented in this study has potential implications to new particle formation, particle growth, aerosol size, CCN number concentration and associated radiative forcing, which will be the subjects of future research.

In this study, we only evaluated the impacts of the updated wet scavenging parameterization on nitric acid, nitrate, and ammonium concentrations at the surface level over the US. The updated wet scavenging parameterization can also impact other soluble tracers. For example, as shown in the supporting material (table S1 and figure S1), the applying of ICCW and empirical washout rate can reduce the simulated annual mean mass concentrations of sulfate at IMPROVE and CSN sites in US from 1.56 to 1.18 (observation: 1.30) μg m^{-3}. The NMB is changed from 20 % to -9 %. The impacts of the updated wet scavenging parameterization on the concentrations all major aerosols over the whole globe should be carefully assessed against relevant measurements in future studies. In addition, the impact of the updated treatment of wet scavenging on aerosol vertical profile and mass loading shall be investigated. Previous study by Liu et al. (2001) indicate that Pb-210 is a good tracer for testing wet deposition in GEOS-Chem. It will be helpful to carry out Pb-210 simulation to further evaluate the updated wet scavenging parameterization.

Code and data availability. The code of GEOS-Chem 12.0.0 is available through the GEOS-Chem distribution web-page http://wiki.seas.harvard.edu/geos-chem/index.php/GEOS-Chem_12. All measurement data are publicly available.

Author contributions. GL and FY proposed and implemented the revised wet scavenging scheme and validated model simulations with surface observations. JS provided useful suggestions to improve this work. All authors contributed to the writing and editing of the paper.

Competing interests. The authors declare that they have no conflict of interest.

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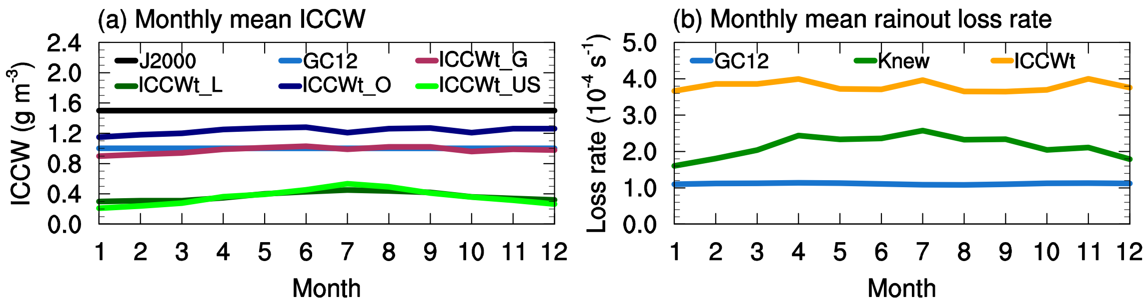
Table 1. Observed annual mean surface concentrations of HNO_3, nitrate, and ammonium at CASTNET, IMPROVE, and CSN sites. Annual mean surface concentrations (Mean), normalized mean bias (NMB), and correlation coefficient (*r*) between observed and simulated annual mean values for the 3 species by GC12, Knew, $ICCW_t$, and $ICCW_t$_EW cases.

	HNO_3			NIT			NH4		
	Mean ($\mu g\ m^{-3}$)	NMB (%)	*r*	Mean ($\mu g\ m^{-3}$)	NMB (%)	*r*	Mean ($\mu g\ m^{-3}$)	NMB (%)	*r*
Observation	0.83			0.70			0.60		
GC12	2.04	145.1	0.73	1.89	168.1	0.53	1.09	81.4	0.75
Knew	2.05	146.8	0.73	1.90	170.5	0.53	1.11	84.5	0.75
$ICCW_t$	1.87	125.0	0.74	1.29	83.5	0.57	0.86	42.7	0.78
$ICCW_t$_EW	1.03	24.2	0.72	0.88	25.0	0.57	0.68	12.8	0.78



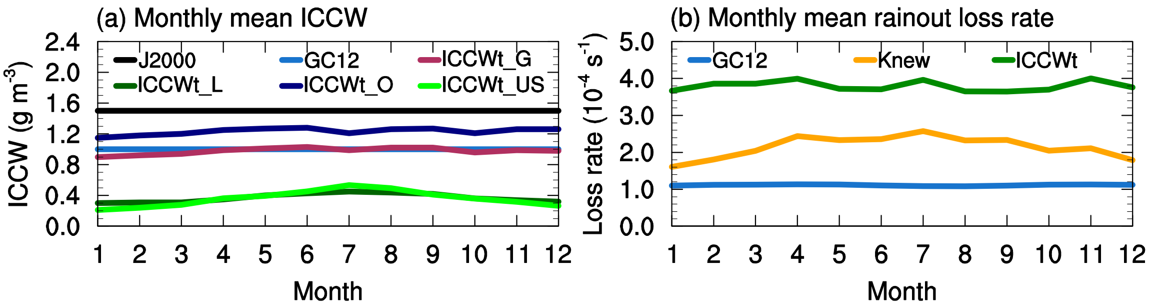


Figure 1. (a) Monthly variations of ICCW averaged over the lower troposphere layers of the whole globe (maroon), global land areas (olive), global oceans (navy), and continental US (green) from MERRA2, along with constant ICCW values assumed in J2000 (black) and GC12 (blue). (b) Monthly variations of the rainout loss rate averaged in the lower troposphere layers of the continental US based on Eq. (2) (i.e, GC12) and Eq. (3) with constant ICCW of 1 g m^{-3}, and Eq. (3) with MERRA2 ICCW (Eq. 4).

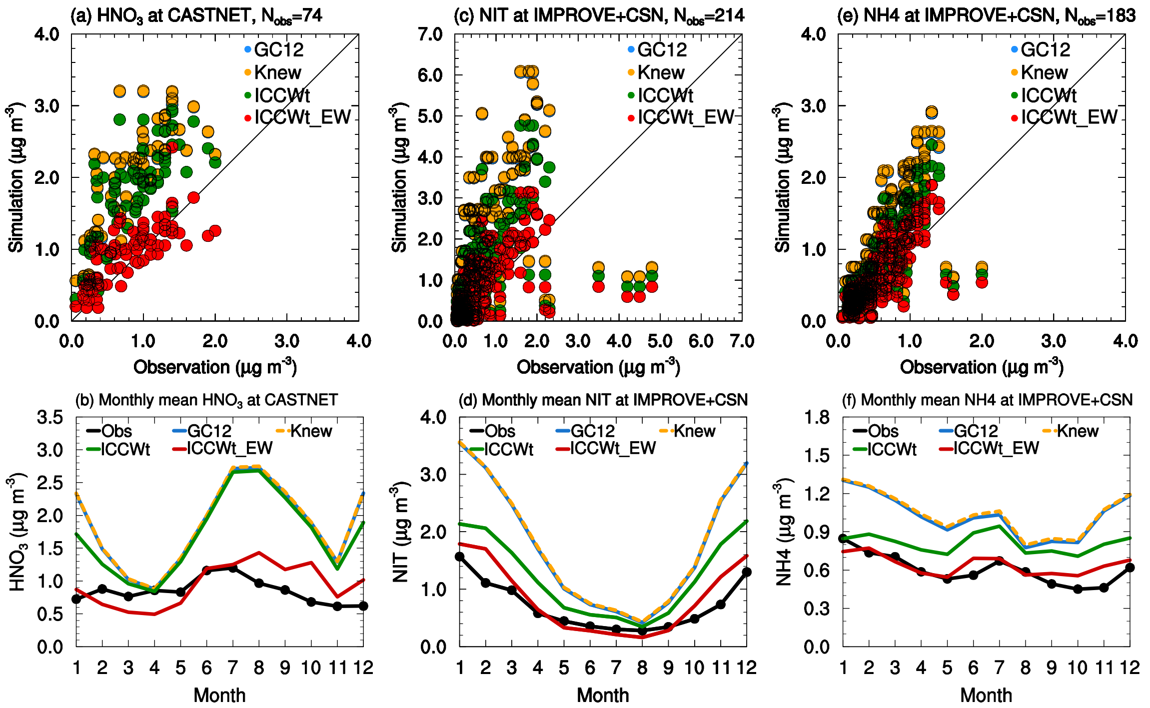


Figure 2. (a) Scatter plot of observed and simulated annual mean HNO_3 at CASTNET sites and (b) ~~monthly ~~variations of ~~median~~monthly mean for year 2011 showing the comparison between nitric acid mass concentrations observed at CASTNET sites (black) and simulated by GC12 (blue), Knew (~~green~~yellow dash), ICCW$_t$ (~~yellow~~green), and ICCW$_t$_EW (red) cases. (c) and (d) are the same as (a) and (b) but for nitrate at IMPROVE+CSN sites. (e) and (f) are the same as (a) and (b) but for ammonium at IMPROVE+CSN sites. It is worthy of note that the differences between G12 (blue) and Knew (yellow dash) are small.

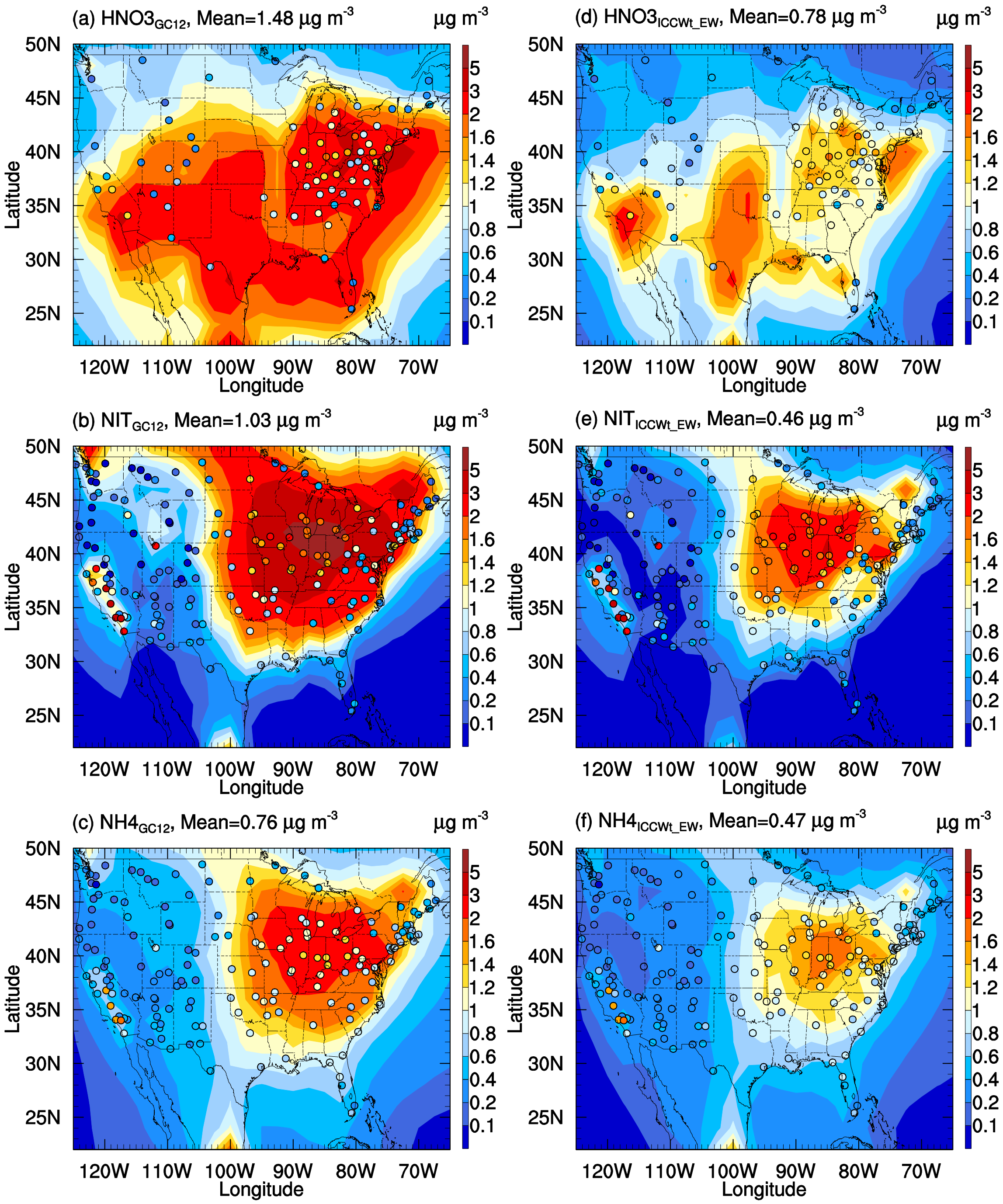


Figure 3. Horizontal distributions of surface layer nitric acid, nitrate, and ammonium simulated by the GC12 case (a-c) and the ICCW$_t$_EW case (d-f). Filled circles are annual mean surface mass concentrations observed at CASTNET, IMPROVE, and CSN for corresponding species.