Investigating aqueous production pathways of particulate sulfur in CMAQ with AQCHEM-KMT (version 2) and the sulfur tracking method

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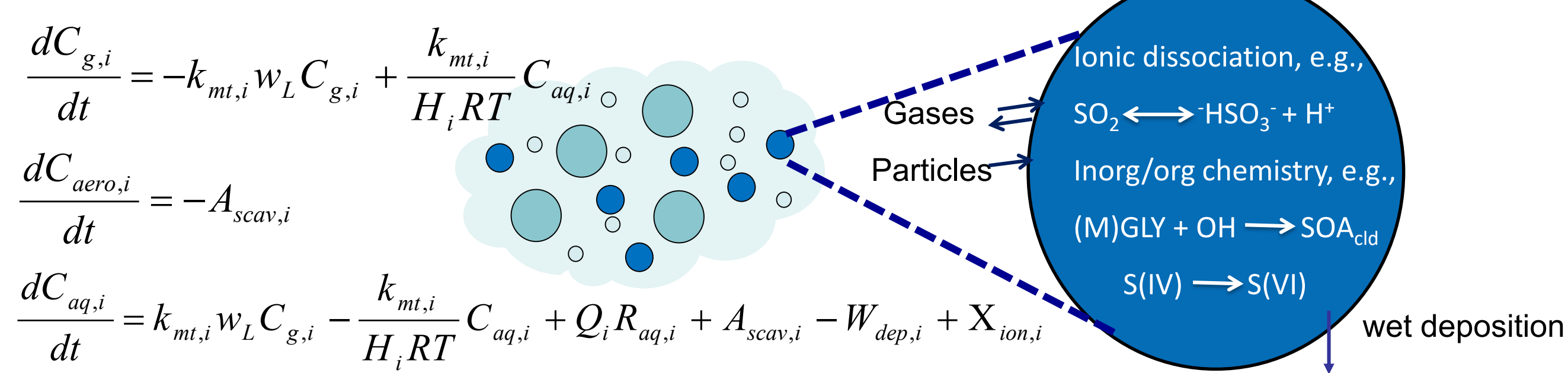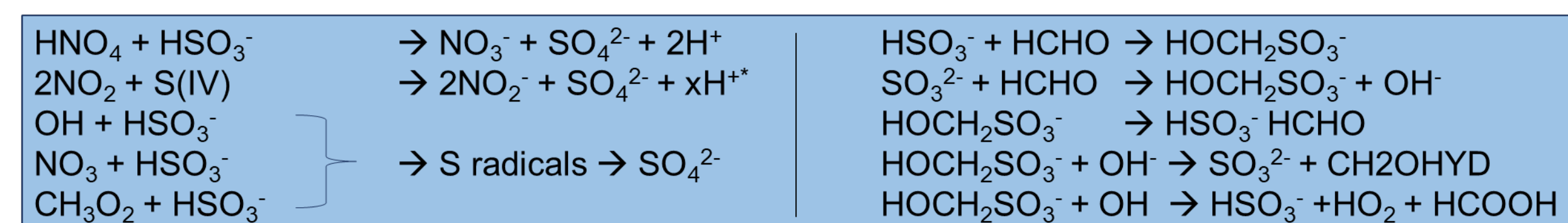Kathleen Fahey I fahey.kathleen@epa.gov I 919-541-3685

1. Background

- Particulate sulfur (most often attributed to SO_4^{2-}) remains a major contributor to $PM_{2.5}$ levels around the globe
  - Aqueous conversion of SO_2 to SO_4^{2-} dominates in the presence of cloud/fog
  - Major SO_2 oxidation pathways (i.e., gas phase oxidation by OH and aqueous oxidation via H_2O_2 and O_3) are well understood; however conventional oxidation pathways in existing models are unable to accurately represent high SO_4^{2-} levels observed in some regions (e.g., wintertime Beijing, Fairbanks, AK)

- CMAQv5.3 includes an optional cloud chemistry treatment, AQCHEM-KMT, v2 (KMT2),[1],[2] that treats additional chemistry for S, N, C, and O-H species beyond CMAQ's default cloud chemistry module
  - Includes additional in-cloud S(IV) oxidation pathways via HNO_4, NO_2, and radicals (e.g., OH), as well as formation and destruction of the S(IV)-HCHO adduct, hydroxymethanesulfonate (HMSA), recently suggested to be a possible contributor to the high particulate S levels observed during Beijing winter haze[3]

- Here we extend the Sulfur Tracking Method, v5.3, to include the additional S(IV) oxidation pathways in KMT2, implement HMSA as an explicitly tracked/transported species, and investigate the contributions to particulate S concentrations for new and old pathways with an ***annual 2016 CMAQv5.3 simulation over the N. Hemisphere***
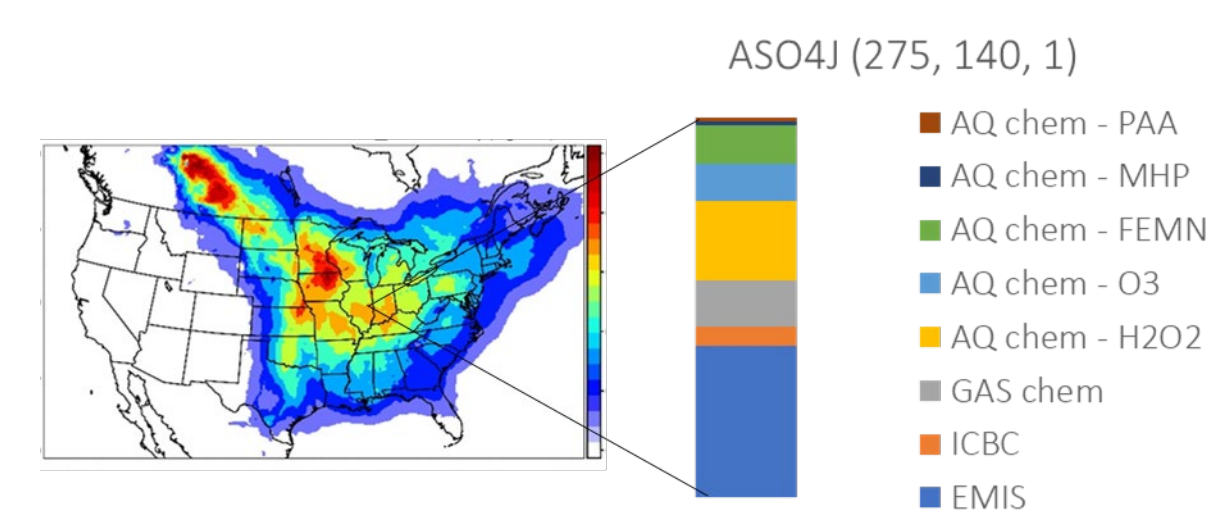
2. KMT2 and the Sulfur Tracking Method (STM)

$$\frac{dC_{g,i}}{dt} = -k_{mt,i}w_L C_{g,i} + \frac{k_{mt,i}}{H_i RT}C_{aq,i}$$

$$\frac{dC_{aero,i}}{dt} = -A_{scav,i}$$

$$\frac{dC_{aq,i}}{dt} = k_{mt,i}w_L C_{g,i} - \frac{k_{mt,i}}{H_i RT}C_{aq,i} + Q_i R_{aq,i} + A_{scav,i} - W_{dep,i} + X_{ion,i}$$

Gases / Particles

Ionic dissociation, e.g., $SO_2 \leftrightarrow \cdot HSO_3^- + H^+$

Inorg/org chemistry, e.g., (M)GLY + OH → SOA_{cld}

S(IV) → S(VI)

wet deposition

Figure 1. AQCHEM-KMT. AQCHEM-KMT uses the Kinetic PreProcessor (KPP)[4] to generate the code/integrator for a user-specified chemical mechanism to solve a system of differential equations that describe the evolution of the gas, aqueous, and interstitial aerosol concentrations due to the processes of kinetic mass transfer, ionic dissociation, chemical kinetics, interstitial aerosol scavenging, and wet deposition

In-cloud S chemistry: KMT2 includes standard in-cloud S(IV) oxidation pathways of H_2O_2, O_3, O_2 catalyzed by Fe^{3+}/Mn^{2+} (FEMN), CH_3OOH (MHP), $CH_3C(O)OOH$ (PAA), as well as NO_2[5], HNO_4, and OH, NO_3, and CH_3O_2 radicals[4]. Also included is the formation + destruction of HMSA[6], added to the list of explicitly tracked CMAQ aerosol species for this work

$HNO_4 + HSO_3^- \rightarrow NO_3^- + SO_4^{2-} + 2H^+$	$HSO_3^- + HCHO \rightarrow HOCH_2SO_3^-$
$2NO_2 + S(IV) \rightarrow 2NO_2^- + SO_4^{2-} + xH^{+*}$	$SO_3^{2-} + HCHO \rightarrow HOCH_2SO_3^- + OH^-$
$OH + HSO_3^- \rightarrow S$ radicals $\rightarrow SO_4^{2-}$	$HOCH_2SO_3^- \rightarrow HSO_3^- + HCHO$
$NO_3 + HSO_3^-$	$HOCH_2SO_3^- + OH^- \rightarrow SO_3^{2-} + CH_2OHYD$
$CH_3O_2 + HSO_3^-$	$HOCH_2SO_3^- + OH \rightarrow HSO_3^- + HO_2 + HCOOH$

STM: STMv5.3 is a diagnostic option included in CMAQv5.3 for tracking sulfate production from individual gas- and aqueous-phase chemical reactions (extended here to include the additional oxidation pathways from KMT2), as well as emissions and IC/BCs

ASO4J (275, 140, 1)

AQ chem - PAA
AQ chem - MHP
AQ chem - FEMN
AQ chem - O3
AQ chem - H2O2
GAS chem
ICBC
EMIS

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3. Quarterly particulate S contributions for 2016
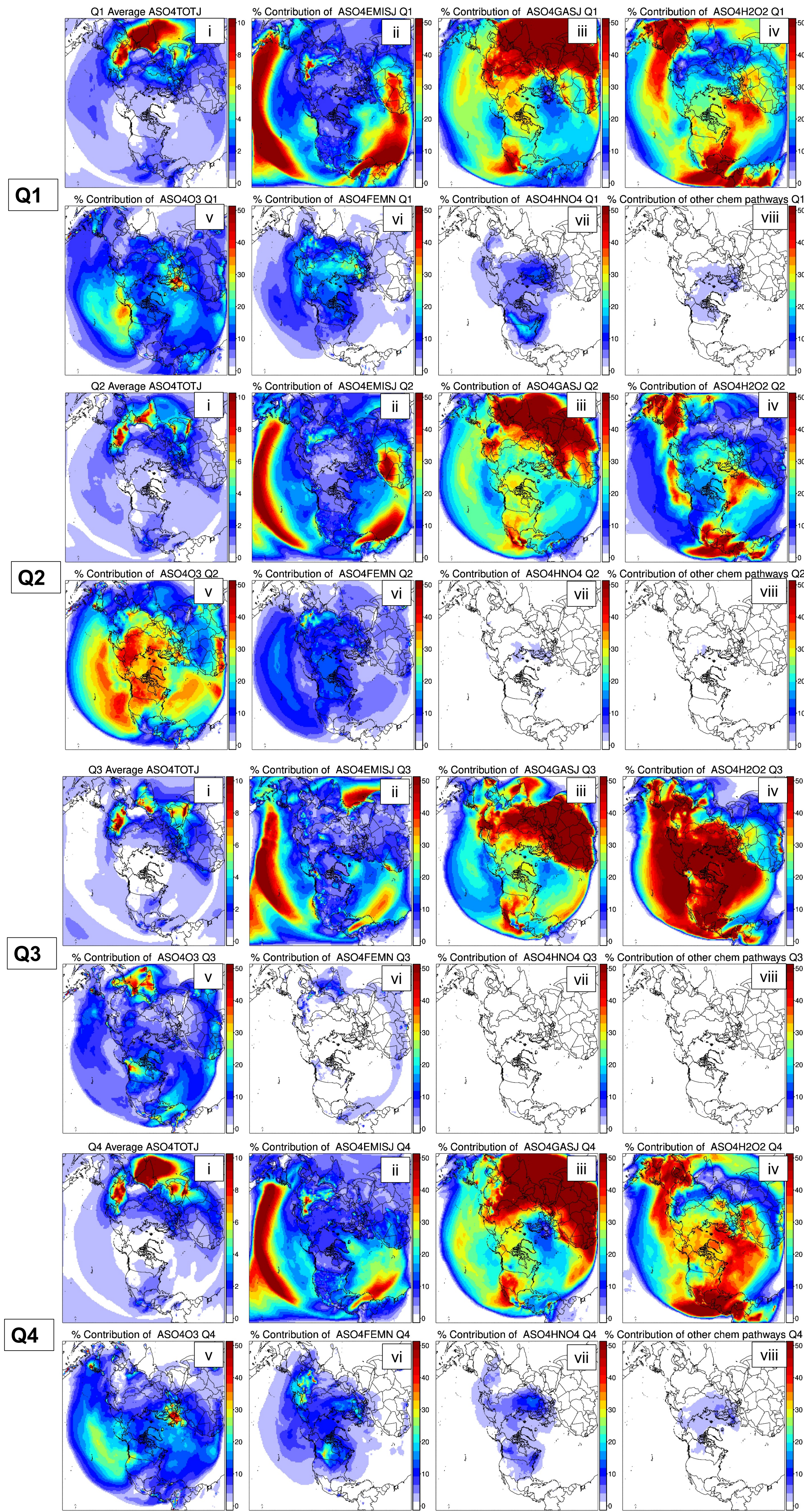
Sulfate

Figure 2. (Q1) Jan-Mar 2016, **(Q2)** Apr-Jun 2016, **(Q3)** Jul-Sep 2016, and **(Q4)** Oct-Dec average *(i)* accumulation mode SO_4^{2-} concentrations and percent contributions from *(ii)* primary emissions, *(iii)* gas phase chemistry (OH), and aqueous chemical pathways *(iv)* H_2O_2, *(v)* O_3, *(vi)* metal catalyzed oxidation with Fe^{3+} and Mn^{2+}, *(vii)* HNO_4, and *(viii)* sum of MHP, PAA, NO_2 and S radical pathways via OH, NO_3, and CH_3O_2. Not shown are contributions from ICBC or contributions for Aitken and coarse modes.
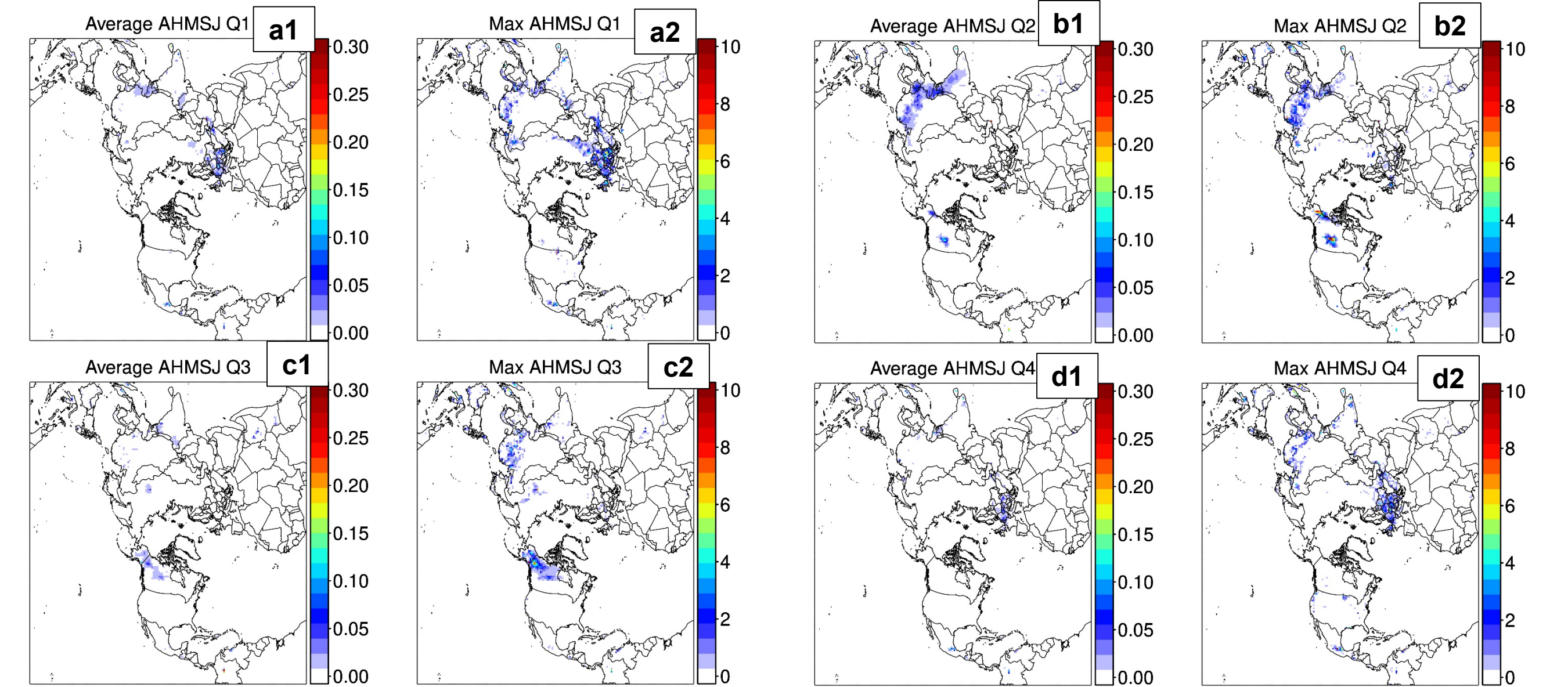
Hydroxymethanesulfonate (HMSA)

Figure 3. (1) Average and **(2)** Maximum HMSA for **(a)** Q1, **(b)** Q2, **(c)** Q3, and **(d)** Q4 2016 for the base mechanism

Figure 5. Jan 2016 **(a)** average HMSA and **(b)** change in SO_4^{2-} between runs with and without HMSA chemistry/tracking. Inclusion of HMSA leads to a lowering of predicted SO_4^{2-} concentrations.
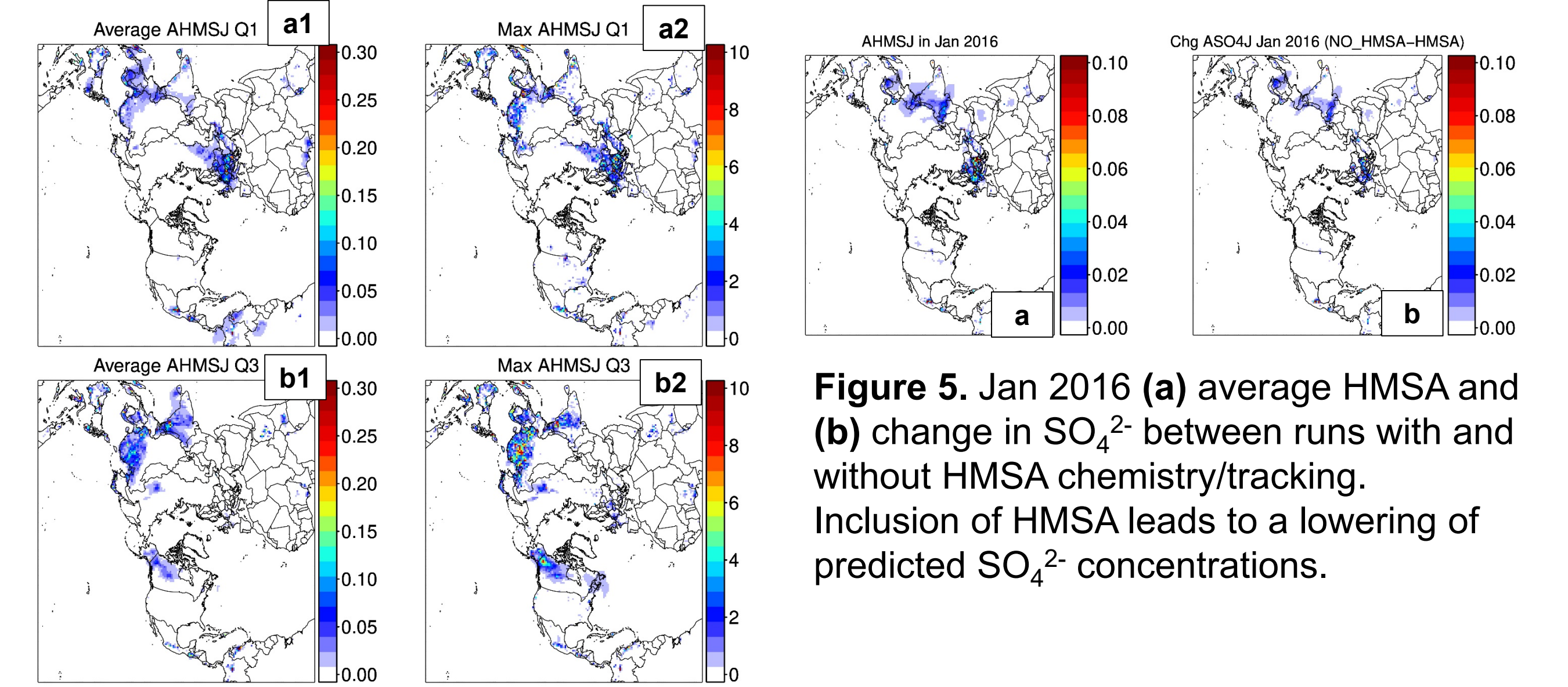
Figure 4. (1) Average and **(2)** max HMSA for **(a)** Q1 and **(b)** Q3 2016 for a sensitivity run without HMSA loss to HSO_3^- + HCHO. This reaction is absent from some other published mechanisms[3].

4. Discussion

- Direct emissions, gas phase production, and aqueous oxidation via O_3, H_2O_2, and FEMN account for the majority of modeled SO_4^{2-}, with relative contributions varying across locations and seasons
  - Gas phase oxidation represents a major contribution for all quarters, followed by direct emissions and aqueous production via H_2O_2. In quarters 1 and 4, there are localized areas where FEMN might contribute as much as or more than H_2O_2 or O_3 pathways
  - SO_4^{2-} production from HNO_4 can contribute a significant amount of average total SO_4^{2-}, up to 22% (0.8 μg/m³), particularly in colder months (Q1, Q4); however the new particulate S pathways in KMT2 do not have large average impacts in wintertime model underperformance areas like Beijing

- While HMSA average concentration is often ≤ 0.1 μg/m³, hourly values can reach over 10 μg/m³. A sensitivity run where the degradation of HMSA to HSO_3^- and HCHO was neglected (Fig 4) shows an increase in quarterly average HMSA values up to ~1 μg/m³, though most remain ≤ 0.2 μg/m³
  - Spatiotemporal distribution is highly variable and depends on the amount of LWC and precursors available, droplet pH, and the relative amount of competing oxidants
  - HMSA observations may help reduce any uncertainties in the mechanism or rates

- The increase in particulate S that comes from including HMSA is offset by a loss of SO_4^{2-} (Fig. 5). HMSA serves as a reservoir for S(IV) in cloud/fog water and can prevent the oxidation to S(VI). Addition of HMSA to the model thus can lead to an increase in particulate S from HMSA while SO_4^{2-} decreases.

References: [1] Fahey et al., 2017, Geosci. Mod. Dev. ▪ [2] Fahey et al., 2017, CMAS ▪ [3] Moch et al., Geophys. Res. Lett. ▪ Damian et al., 2002, Computers and Chemical Engineering ▪ [5] Lee and Schwartz, 1983, Precipitation Scavenging, Dry Deposition, and Resuspension, v1 ▪ [6] Leriche et al., 2013, Geosci. Mod. Dev.