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Particle partitioning potential of organic compounds is highest in the Eastern US and driven by anthropogenic water

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Particle partitioning potential of organic compounds

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Abstract

Gas phase water-soluble organic matter ($WSOM_g$) is ubiquitous in the troposphere. In the summertime, the potential for these gases to partition to particle phase liquid water (H_2O_{ptcl}) where they can form secondary organic aerosol (SOA_{AQ}) is high in the Eastern US and low elsewhere, with the exception of an area near Los Angeles, CA. This spatial pattern is driven by mass concentrations of H_2O_{ptcl}, not $WSOM_g$. H_2O_{ptcl} mass concentrations are predicted to be high in the Eastern US, largely due to sulfate. The ability of sulfate to increase H_2O_{ptcl} is well-established and routinely included in atmospheric models, however $WSOM_g$ partitioning to this water and subsequent SOA formation is not. The high mass concentrations of H_2O_{ptcl} in the southeast (SE) US but not the Amazon, may help explain why biogenic SOA mass concentrations are high in the SE US, but low in the Amazon. Furthermore, during the summertime in the Eastern US, the potential for organic gases to partition into liquid water is greater than their potential to partition into organic matter (OM) because concentrations of $WSOM_g$ and H_2O_{ptcl} are higher than semi-volatile gases and OM. Thus, unless condensed phase yields are substantially different ($> \sim$ order of magnitude), we expect that SOA formed through aqueous phase pathways (SOA_{AQ}) will dominate in the Eastern US. These findings also suggest that H_2O_{ptcl} is largely anthropogenic and provide a previously unrecognized mechanism by which anthropogenic pollutants impact the amount of SOA mass formed from biogenic organic emissions. The previously reported estimate of the controllable fraction of biogenic SOA in the Eastern US (50 %) is likely too low.

1 Introduction

Liquid water is the most abundant particle phase species in the atmosphere, 2–3 times total aerosol dry mass globally (Liao and Seinfeld, 2005). Yet, chemical mechanisms employed in atmospheric photochemical models largely under-represent the impact of partitioning and oxidation reactions in aqueous media, in particular for organic species.

This hinders development of effective strategies for air quality management and climate mitigation because important processes, feedbacks and anthropogenic influences are missing from model predictions.

Formation of SOA through partitioning of semivolatile products of gas-phase photochemical reactions into preexisting particulate OM (SOA$_{gas}$) is well established. For more than twenty years empirical relationships developed from relatively dry SOA smog chamber studies conducted with little particle phase liquid water (e.g., relative humidity (RH) < 20 %, Griffin et al., 1999; Ng et al., 2007), have provided critical data for atmospheric modeling of organic aerosol (Pankow, 1994; Odum et al., 1996; Seinfeld and Pankow, 2003). However, extending these relationships beyond the chamber studies from which they are developed remains problematic (Chang et al., 2010), possibly in part because derived empirical formulations do not include the potential for polar organic gases to partition to polar solvents such as water and react in that medium. Parikh et al., find that when an Odum 2-product or volatility basis set (VBS) SOA model is applied to independent smog chamber studies where relative humidity (RH) and particle phase liquid water concentrations (H$_2$O$_{ptcl}$) are more typical of general atmospheric conditions, SOA parameterizations cannot reproduce observed amounts or trends in SOA mass (Parikh et al., 2011, 2012). In a series of experiments conducted in an outdoor chamber, accounting for gas phase formation of water-soluble gases followed by partitioning into aerosol water was necessary to accurately describe observed SOA mass (Parikh et al., 2011, 2012). It is important to note available H$_2$O$_{ptcl}$ is not only a function of RH, but also of particle concentration and hygroscopicity (Zhou et al., 2011). Measurement of RH alone is not sufficient to determine H$_2$O$_{ptcl}$.

Gas phase photochemistry oxidizes and fragments biogenic and anthropogenic VOCs resulting in the ubiquitous and abundant presence of small, water-soluble organic compounds (e.g., formic and acetic acids, glyoxal, methylglyoxal, acetone) (Spaulding et al., 2003). These compounds are too small to form SOA through traditional semi-volatile partitioning theory in atmospheric models (e.g., SOA$_{gas}$). However, it is now accepted that water-soluble compounds react in atmospheric waters (clouds,

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fogs and wet aerosols) to form SOA (Blando and Turpin, 2000; Ervens et al., 2011; Liu et al., 2012). Evidence for SOA formation from gas followed by aqueous chemistry (SOA$_{AQ}$) is provided by laboratory experiments conducted at concentrations typical of atmospheric waters (e.g., with OH radicals and other reactants) that demonstrate for-

5 mation of compounds found predominantly in the particle phase in the atmosphere: organic acids/salts (e.g., oxalate), high molecular weight compounds (HMWC) including oligomers, and sulfur- and nitrogen-containing organics (Carlton et al., 2006, 2007; Altieri et al., 2006, 2008; Guzman et al., 2006; Noziere and Cordova, 2008; Volkamer et al., 2009; Galloway et al., 2009; Shapiro et al., 2009; De Haan et al., 2009a,b; El

10 Haddad et al., 2009; Perri et al., 2009, 2010; Liu et al., 2009, 2012b,c; Noziere et al., 2009, 2010; Yasmeen et al., 2010; Tan et al., 2010, 2012; Sun et al., 2010; Sareen et al., 2010; Grgic et al., 2010; Poulain et al., 2010; Zhang et al., 2010; Huang et al., 2011; Lee et al., 2011; Ortiz-Montalvo et al., 2012; Zarzana et al., 2012; Nguyen et al., 2012).

15 The analysis herein suggests that, as is the case for SOA$_{gas}$ (Lane et al., 2008; Carlton et al., 2010b), anthropogenic pollution enhances the formation of biogenic SOA$_{AQ}$. We propose that this anthropogenic enhancement of biogenic SOA$_{AQ}$ occurs because sulfur pollution increases the amount of H$_2$O$_{ptcl}$ at a given relative humidity (RH) (Malm et al., 1994). In many locations including the Eastern US, SOA is predomi-

20 nantly formed from biogenic hydrocarbons (Lewis et al., 2004; Kleindienst et al., 2007; Ding et al., 2008). However, correlations between biogenic SOA mass and tracers of anthropogenic pollution are strong suggesting that anthropogenic pollution plays an important role in biogenic SOA formation (De Gouw and Jimenez, 2009). In fact anthropogenic aerosol water could potentially drive biogenic SOA formation in high RH

25 locations by providing the partitioning medium (H$_2$O$_{ptcl}$) for SOA$_{AQ}$ formation. There is observational evidence suggesting enhancement of biogenic SOA mass derived from isoprene oxidation products when sulfate is present in the Eastern US (Chan et al., 2010), in particular when RH is high (Hatch et al., 2011). Anthropogenic pollution has been estimated to be responsible for roughly half of the biogenic SOA mass in the

Eastern US (Carlton et al., 2010b). While anthropogenic H_2O_{ptcl} was estimated in those simulations, $WSOM_g$ partitioning and subsequent SOA_{AQ} formation in wet aerosol was not included, thus the 50 % estimate is likely too low.

To explore potential drivers of spatial differences in observed SOA mass, we use a 3-D photochemical transport model to predict mixing ratios of gas phase organic compounds and mass concentrations of particulate species. We use these predictions to evaluate spatial trends in the overall solubility of organic gas-phase inventories, particle phase concentrations of liquid water (H_2O_{ptcl}), and particulate OM. We use these predictions to estimate the chemical potential of organic gases to partition into liquid water. We also compare this potential (qualitatively) to the partitioning of semi-volatile organic gases into OM.

2   Methods

Version 4.7 of the Community Multiscale Air Quality (CMAQ) (www.cmascenter.org) model is applied to predict the photochemistry and transport of atmospheric trace species over the continental US for July 2003. Observational estimates during this time period indicate that secondary organic carbon is a substantial fraction of total particle carbon mass (Kleindienst et al., 2007).

2.1   CMAQ model simulations

CMAQ simulation details and inputs are described in detail elsewhere (Carlton et al., 2010b). Briefly, CMAQv4.7, with SOA formation (Carlton et al., 2010a) and aqueous phase chemistry of sulfur, glyoxal and methylglyoxal in clouds (Carlton et al., 2008) is applied. The MM5 meteorology model, EPA's 2002 National Emissions Inventory (NEIv2) and the Biogenic Emission Inventory System (BEIS) (Pierce et al., 1998) are used to drive transport and develop anthropogenic and biogenic emissions, projected hourly for input to CMAQ with SMOKE (Houyoux et al., 2000). The SAPRC99 gas

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phase chemical mechanism was used to simulate gas phase photochemistry. The model domain is resolved horizontally with 36 km × 36 km grid cells and vertically up to 100 mb with 14 vertical layers, with most resolution near the surface. Presented results are averages for July 2003. Aerosol free acidity is calculated in nmol m^{-3} from CMAQ predictions of Aiken and accumulation mode aerosol as:

$$H^+ = 1000 \left[2\frac{SO_4^{2-}}{96} + \frac{NO_3^-}{62} + \frac{Cl^-}{35} - \frac{Na^+}{23} - \frac{NH_4^+}{18} \right] \tag{1}$$

The ion mass concentrations are calculated from the following CMAQ species: SO_4 = ASO4I + ASO4J; NO_3 = ANO3I + ANO3J; Cl = ACLJ; Na = ANAJ; NH_4 = ANH4I + ANH4J.

2.2 Water soluble and semi-volatile gases

Organic gases listed in Table 1 are simulated in the CMAQ model when SAPRC is employed. Mixing ratios of each species are converted from ppb$_V$ to ppb$_v$C and mass concentrations are calculated in µg m^{-3} using the ideal gas law and MM5 predicted air density. For the purposes of this work, WSOM$_g$ is calculated as the sum of water soluble gases simulated by CMAQ and shown in laboratory experiments to make SOA through aqueous phase processes at concentrations typical of wet aerosol: glyoxal (Carlton et al., 2007), methylglyoxal (Tan et al., 2010), acetaldehyde (Li et al., 2011), methacrolein (El Haddad et al., 2009), phenols (Sun et al., 2010), acetone (Poulain et al., 2010), acetic acid (Tan et al., 2012) and glycolaldehyde (Perri et al., 2010). Glycolaldehyde is not an explicit species in SAPRC99 and is counted as half of model species "RCHO". It should be recognized that this summation is a lower bound estimate of WSOM$_g$ with the potential to form SOA$_{AQ}$. Formaldehyde, an abundant water soluble gas, forms particle phase hydroxymethansulfonate in the presence of sulfur through aqueous phase processes (Munger et al., 1984), but is not counted here. Only half of model species "RCHO" (C3 aldehydes and higher) was counted in the sum,

but the uncounted RCHO mass will also likely form SOA_{AQ} to some degree similar to aldehydes that are considered (glyoxal, methylglyoxal, glyocolaldehyde). The semi-volatile gas phase species are the 1st and 2nd products from isoprene, monoterpenes, sesquiterpenes, benzene, long chain alkanes, toluenes and xylenes that form SOA in CMAQ (Carlton et al., 2010a) through semi-volatile partitioning (Odum et al., 1996) (SOA_{gas}).

2.3 Methylglyoxal equivalent solubility

In order to account for the combined effects of compound specific water solubility and concentration, a solubility index for describing organic gas concentrations was adopted. Methylglyoxal is used as a reference compound because, as an oxidation product of both biogenic and anthropogenic hydrocarbons (Paulson and Seinfeld, 1992; Smith et al., 1999; Atkinson and Arey, 2003; Ham et al., 2006), it is found widely in urban and rural environments (Spaulding et al., 1999, 2003; Moortgat et al., 2002; Wang et al., 2002; Li and Yu, 2005; Ho et al., 2006). In this method, analogous to the propylene equivalent concentration used in reactivity calculations (Chameides et al., 1992), a methylglyoxal equivalent concentration is calculated for each organic species J in the SAPRC99 mechanism using values in Table 1.

$$MGLY_{equiv}(J) = [C_J]\frac{H_{L,J}}{H_{L,MGLY}} \tag{2}$$

Where C_J is the concentration of organic species J, $H_{L,J}$ is the Henry's Law constant for species J and $H_{L,MGLY}$ is the Henry's Law Constant for methylglyoxal. Henry's Law constants are adjusted to hour specific model-predicted temperature when appropriate (Table 1). $MGLY_{equiv}$ is the concentration of species J on a scale normalized to the solubility of methylglyoxal. $MGLY_{equiv}$ is the gas phase mass concentration of methylglyoxal needed to generate an equal amount of partitionable (gas-to-aqueous) organic mass of species J. The concentration is calculated in $\mu g\,m^{-3}$ to investigate trends and

patterns in gas phase water-soluble organic matter (WSOM$_g$). In this context, if gas phase organic species J has an atmospheric abundance of $10\,\mu g\,m^{-3}$ and is twice as soluble as methylglyoal, it would have a MGLY$_{equiv}$ concentration of $20\,\mu g\,m^{-3}$; if the species was half as soluble as methylglyoxal, it would have a MGLY$_{equiv}$ concentration of $5\,\mu g\,m^{-3}$. Because this solubility-based method accounts for a species' solubility as well as its atmospheric concentration, it provides an estimate of the relative contribution each organic species can make to the flux of gas phase organic matter to aerosol water. It also provides a framework to compare spatial differences in the overall gas phase organic solubility for a particular inventory.

2.4 Instantaneous aqueous partitioning potential

The overall potential for organic gas-to-liquid water partitioning is dependent not only on the concentration and water solubility of organic gases, but also the spatial and temporal colocation (or not) of liquid water. In this work we consider only particle phase liquid water (H$_2$O$_{ptcl}$). The mass concentration of H$_2$O$_{ptcl}$ is predicted in CMAQ with ISORROPIA from water vapor mixing ratios and concentrations of inorganic species. In ISORROPIA, partitioning of inorganic species and atmospheric water between the gas- and aerosol-phase is calculated using relative humidity and molality of an aqueous binary solution of species containing sulfate, nitrate, chlorine, sodium and ammonium (Nenes et al., 1999). The partitioning potential of WSOM$_g$ to liquid water is calculated with a thermodynamic equilibrium assumption as is done for gas-phase organic species that partition to OM (Pankow, 1994). The potential is calculated here:

$$P_{WSOM_P}(J) = [C_J][C_{H_2O}]\frac{H_J}{H_{MGLY}}\Phi_J = MGLY_{equiv}[C_{H_2O}]\Phi_J \qquad (3)$$

where C$_J$ is the concentration of organic species J ($\mu g\,m^{-3}$), C$_{H_2O}$ is the liquid water concentration (H$_2$O$_{ptcl}$) ($\mu g\,m^{-3}$). Φ_J is referred to as the SOA$_{AQ}$-forming potential, analogous to incremental reactivity in ozone studies (Chameides et al., 1992). Φ_J

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represents the likelihood organic mass will remain in the condensed phase after partitioning, for example by being transformed into low volatility products. Φ_J depends on a variety of factors including the presence of other species/reactants (e.g., OH radicals, NH_3) and local meteorology (e.g., temperature and RH). Values of Φ_J are not currently known and are likely not constant. Here a value of 1 is assigned to all species. This assumption is not correct and represents a non-trivial limitation of the framework, but regardless, the partitioning potential is useful as an index that identifies areas where SOA_{AQ} is likely to be important. In assessing this partitioning potential, the relative importance of one organic species to another will depend not only upon the relative concentrations of the compound in the $MGLY_{equiv}$ index, but also the liquid water content of the air mass. For this reason, a highly soluble species with a large concentration will not necessarily be an important precursor if not colocated with H_2O_{ptcl} in space and time.

2.5 Limitiations

There are uncertainties when calculating partitioning potentials and comparing pathways. First, the degree to which CMAQ accurately represents particle phase liquid water mass is not well understood. CMAQ might underpredict H_2O_{ptcl} because ISORROPIA, the thermodynamic partitioning model implemented in CMAQ and employed to predict particle phase liquid water, includes only inorganic species. In laboratory studies, organic compounds ubiquitous in the troposphere (methylglyoxal and acetaldehyde) increase particle hygroscopicity (Sareen et al., 2013) and particle phase organic material is reported to contribute to H_2O_{ptcl} in several locations (Dick et al., 2000; Canepari et al., 2013). Second, it is well established that CMAQv4.7 underpredicts secondary organic aerosol mass (Carlton et al., 2010a; Carlton and Baker, 2011). The uncertainties in H_2O_{ptcl}, OM, $WSOM_g$ and semi-volatile gas phase species constitute the major limitations of this assessment.

Organic species are often found in the aerosol aqueous phase at concentrations higher than predicted by Henry's Law (e.g., glyoxal, Kroll et al., 2005). Nevertheless,

Henry's Law constants are predictors of organic gas-to-aqueous partitioning and there-fore useful in a "partitioning potential" calculation. The assumption $\Phi_J = 1$ for all organic species is not correct. Appropriate values for Φ are not well understood. The results herein provide a framework to identify species, locations and times where SOA_{AQ} for-mation is likely to be important and further investigation is warranted.

3   Results

3.1   Ubiquity of water-soluble organic gases

In the summertime, throughout the troposphere over the continental US water-soluble organic gases, demonstrated to form SOA in laboratory experiments through aque-ous phase chemistry, are ubiquitous (Fig. 1). This finding is consistent with a vari-ety of ambient measurements that indicate $WSOM_g$ is abundant (Chebbi and Carlier, 1996; Nolte et al., 1999; Hennigan et al., 2009). At the surface, mass concentrations of $WSOM_g$ in $MGLY_{equiv}$ are high throughout the US, typically $> 20\,\mu g\,m^{-3}$ (Fig. 2). $MGLY_{equiv}$ concentrations suggest organic gas phase inventories are soluble through-out the US (Fig. 2a). When the entire model column is considered (up to 100 mb), mass concentrations of WSOM in $MGLY_{equiv}$ are ubiquitously large (typically $> 500\,\mu g\,m^{-2}$) and greatest in the Western US ($> 1\,mg\,m^{-2}$) (Fig. 2b). Tropospheric gas phase or-ganic inventories over the continental US are highly water soluble, whether evaluated in mixing ratios, mass concentrations or $MGLY_{equiv}$.

3.2   WSOM aqueous partitioning potential is high in the Eastern US

The instantaneous potential for gas phase water-soluble organic matter to partition to particle phase liquid water is large in surface air in the Eastern US and small elsewhere, with the exception of an area near Los Angeles, CA (Fig. 3) and "hot spots" in Mexico. A similar trend is observed when the entire column is considered. Unlike water soluble

gas concentrations ($WSOM_g$, $MGLY_{equiv}$), this "liquid water partitioning potential" is not spatially ubiquitous. This phenomenon is explained by spatial patterns in H_2O_{ptcl} mass concentrations (Fig. 4). The abundance of H_2O_{ptcl} is a function of the mixing ratio of water vapor in the atmosphere and the concentration and hygroscopicity of the aerosol.

5　Water vapor mixing ratios are highest in the Eastern US, as are aerosol free acidity concentrations (Fig. 5). The abundance of aerosol free acidity in the Eastern US is influenced to a large degree by anthropogenic SO_2 emissions and the subsequent sulfate aerosol mass concentrations (see Supplement). In these simulations, particle phase acidity and the resulting H_2O uptake are anthropogenic in surface air over the

10　continental US.

The simulated increase in partitioning potential when liquid water is available is consistent with ambient observations. Hennigan et al. and Sorooshian et al., find that when liquid water is available, there is increased partitioning of gas phase water-soluble organic compounds with increasing sub-saturated relative humidity (Hennigan et al.,

15　2008, 2009; Sorooshian et al., 2010). Gas phase WSOM partitioning also increases with increasing aerosol hygroscopicity (Sorooshian et al., 2010). This work suggests that because gas phase WSOM is ubiquitous and H_2O_{ptcl} is not, the availability of particle phase liquid water caused by anthropogenic influences, is the limiting factor in SOA_{AQ} formation over the continental US.

20　CMAQ-estimated polar, water-soluble gases are more abundant than semi-volatile organic gases and particle phase liquid water is more abundant than dry organic aerosol mass in the summertime over the US. In many locations, in particular the Eastern US, the chemical potential for aqueous partitioning (water soluble gases to particle liquid water) appears to be greater than the potential for semi-volatile gases to partition to dry OM (Fig. 6). And it seems that the overall geographic distribution of SOA_{gas}

25　and SOA_{AQ} are driven predominantly by the geographic distribution of OM and H_2O_{ptcl}, which are spatially limited compared to the organic precursor gases.

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3.3 Biogenic SOA is controllable

Insights gained from this work lead us to hypothesize that biogenic SOA is abundant in the Southeastern US (Kleindienst et al., 2007, 2010; Lewandowski et al., 2007; Hennigan et al., 2008, 2009) but low in the Amazon (Pöschl et al., 2010) because H_2O_{ptcl} concentrations are high (and anthropogenic) in the SE US but low in the Amazon. Global predictions of H_2O_{ptcl} by Liao and Seinfeld (2005) support this idea. This work suggests SO_2 pollution contributes to biogenic SOA mass concentrations in the Eastern US through mechanisms not currently accounted for in atmospheric models. Carlton et al. (2010b) previously estimated that anthropogenic pollution accounts for approximately half of biogenic SOA (SOA formed from biogenic hydrocarbons) in the Eastern US. The framework herein identifies another mechanism by which anthropogenic pollution can facilitate "biogenic" SOA production, and suggests that previous estimates of the controllable fraction of biogenic SOA are too low.

Supplementary material related to this article is available online at: http://www.atmos-chem-phys-discuss.net/13/12743/2013/ acpd-13-12743-2013-supplement.pdf.

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Particle partitioning potential of organic compounds

A. G. Carlton and B. J. Turpin

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Table 1. Values used in MGLY$_{equiv}$ calculations for gas phase organic species in the SAPRC99 gas phase chemical mechanism as applied in CMAQv4.7.

Species Mechansim Name	Species Description	MW g mol^{-1}	No. of C atoms	H$_i$ mol atm^{-1}
HCHO	formaldehyde	30	1	$3.2e03 \times \exp(6.8e03 \times T_{fac})$
CCHO	acetaldehyde	44	2	$1.4e01 \times \exp(5.6e03 \times T_{fac})$
RCHO	lumped C3+ aldehydes	58	3	4.20×10^3
ACET	acetone	58	3	$3.0e01 \times \exp(4.6e03 \times T_{fac})$
MEK	ketones (and other non-aldehydes) with $k_{OH} < 5 \times 10^{-12}$ cm^3 molec^{-2} sec^{-1}	72	3	$2.0e01 \times \exp(5.0e03 \times T_{fac})$
MEOH	methanol	32	1	2.20×10^2
COOH	methyl hydroperoxide	48	1	$3.1e02 \times \exp(5.2e03 \times T_{fac})$
ROOH	lumped higher organic hydroperoxides	62	2	$3.1e02 \times \exp(5.2e03 \times T_{fac})$
GLY	glyoxal	58	2	3.60×10^5
MGLY	methylglyoxal	72	3	3.20×10^4
BACL	biacetyl	86	4	$7.4e01 \times \exp(5.7e03 \times T_{fac})$
PHEN	phenol	94	6	$1.9e03 \times \exp(7.3e03 \times T_{fac})$
CRES	cresols	108	7	8.20×10^2
BALD	aromatic aldehydes (e.g., benzaldehyde)	106	7	$3.9e01 \times \exp(4.8e03 \times T_{fac})$
METHACRO	methacrolein	70	4	6.50
MVK	methyl vinyl ketone	70	4	4.10×10^1
ISOPROD	lumped isoprene products	70	4	4.10×10^1
PROD2	ketones (and other non-aldehydes) with $k_{OH} > 5 \times 10^{-12}$ cm^3 molec^{-2} sec^{-1}	100	4	4.10×10^1
DCB1	reactive aromatic fragmentation products that do not undergo significant photodecomposition	58	3	8.20
DCB2	reactive aromatic fragmentation products that photolyze with α-dicarbonyl-like action spectrum	72	4	8.20
DCB3	reactive aromatic fragmentation products that photolyze with acrolein action spectrum	72	4	8.20

Table 1. Continued.

Species Mechansim Name	Species Description	MW g mol^{-1}	No. of C atoms	H$_l$ mol atm^{-1}
HCOOH	formic acid	46	1	$8.9e03 \times \exp(6.1e03 \times T_{fac})$
CCO_OOH	acetic acid	76	2	$4.1e03 \times \exp(6.3e03 \times T_{fac})$
RCO_OH	higher organic acids	74	3	5.70×10^3
CCO_OH	peroxy acetic acid	60	2	$8.4e02 \times \exp(5.3e03 \times T_{fac})$
RCO_OOH	higher organic peroxy acids	90	3	5.70×10^3
ETHENE	ethene	28	2	4.70×10^{-3}
ISOPRENE	isoprene	68	5	2.80×10^{-2}
ALK1	alkanes (and other non-aromatics) that react only with OH, $k_{OH} < 5 \times 10^2$ ppm^{-1} min^{-1} (primarily ethane)	30.1	2	$1.9 \times 10^{-3} \times \exp(2.3e3 \times T_{fac})$
ALK2	alkanes (and other non-aromatics) that react only with OH, $5 \times 10^2 < k_{OH} < 2.5 \times 10^3$ ppm^{-1} min^{-1} (primarily propane and acetylene)	36.7	3	$0.0015 \times \exp(2.7e3 \times T_{fac})$
ALK3	alkanes (and other non-aromatics) that react only with OH, $2.5 \times 10^3 < k_{OH} < 5 \times 10^3$ ppm^{-1} min^{-1}	58.6	4	1.10×10^{-3}
ALK4	alkanes (and other non-aromatics) that react only with OH, $5 \times 10^3 < k_{OH} < 1 \times 10^4$ ppm^{-1} min^{-1}	77.6	5	1.10×10^{-3}
ALK5	alkanes (and other non-aromatics) that react only with OH, $k_{OH} > 1 \times 10^4$ ppm^{-1} min^{-1}	118.9	8	1.40×10^{-4}
ARO1	aromatics with $k_{OH} < 2 \times 10^4$ ppm^{-1} min^{-1}	98.6	7	$1.5e-01 \times \exp(4.0e03 \times T_{fac})$
ARO2	aromatics with $k_{OH} > 2 \times 10^4$ ppm^{-1} min^{-1}	118.7	8	$1.9e-01 \times \exp(4.0e03 \times T_{fac})$
OLE1	alkenes (other than ethene) with $k_{OH} < 7 \times 10^4$ ppm^{-1} min^{-1}	72.3	6	4.70×10^{-3}
OLE2	alkenes with $k_{OH} > 7 \times 10^4$ ppm^{-1} min^{-1}	75.8	6	4.70E-03
TRP1	terpenes	136	10	4.90×10^{-2}
SESQ	sesquiterpenes	204	15	4.90×10^{-2}
BENZENE	benzene	78	6	$1.6e-01 \times \exp(4.1e03 \times T_{fac})$

$T_{fac} = (298 - \text{Temp})/(298 \times \text{Temp})$
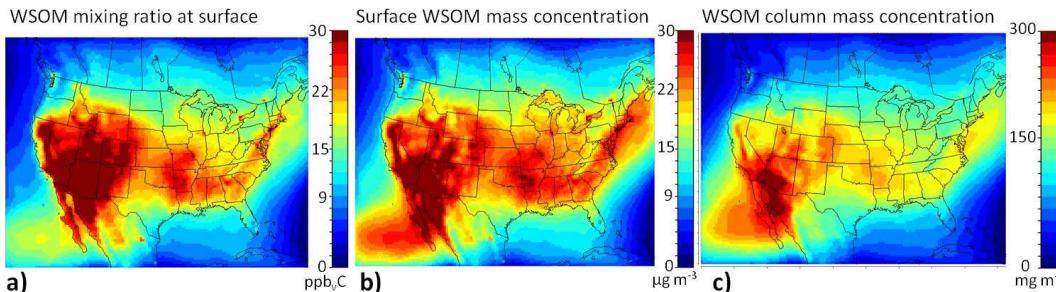
Fig. 1. (a) Sum of gas phase CMAQ water-soluble organic gases shown in lab experiments to make SOA$_{aq}$: glyoxal (Carlton et al., 2007), methylglyoxal (Tan et al., 2010), acetaldehyde (Li et al., 2011), phenols (Sun et al., 2010), acetone (Poulain et al., 2010), acetic acid (Tan et al., 2012), methacrolein (El Haddad et al., 2009) and glycolaldehyde (Perri et al., 2010). Note that glycolaldehyde is not an explicit species in SAPRC99 (used in this simulation) and is counted as half of model species "RCHO". For the mixing ratio **(a)**, all gases are presented in ppb$_V$-carbon. The mass concentrations in **(b)** and **(c)** are converted from the molar ratios using the ideal gas law. Values are July 2003 averages.
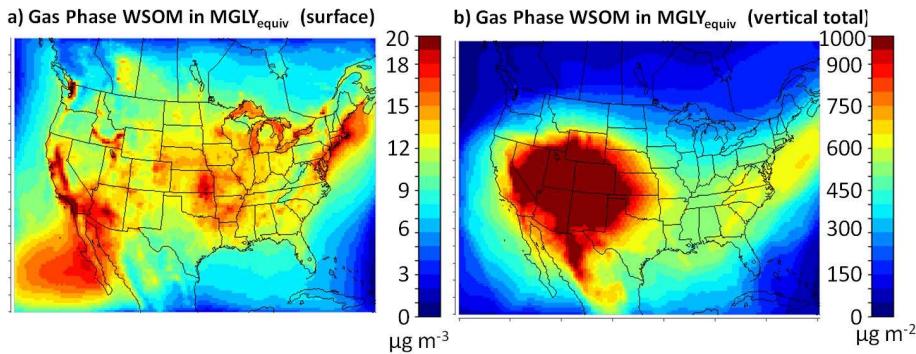
Fig. 2. MGLY$_{equiv}$ mass concentrations for gas phase water-soluble organic matter (WSOM) at the surface **(a)** and for the model column (surface to 100 mb) **(b)**. Note that all species included in Table 1 are used in this calculation. Values are July 2003 averages.

MGLY$_{equiv}$ Partitioning Potential to H$_2$O$_{ptcl}$ (surface) MGLY$_{equiv}$ Partitioning Potential to H$_2$O$_{ptcl}$ (vertical total)
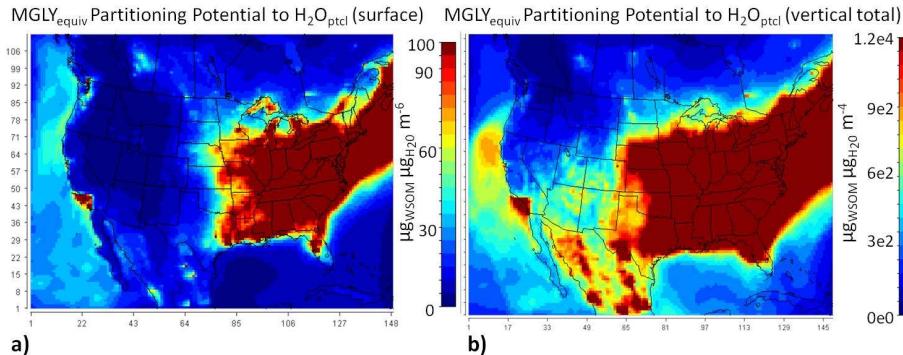
Fig. 3. Instantaneous partitioning potential for gas water soluble organic matter (WSOM) as MGLY$_{equiv}$ to partition to particle phase liquid water at the surface **(a)** and for the model column (up to 100 mb) **(b)**. Values are July 2003 averages.

a) Particle Phase Liquid Water (surface)   b) Particle liquid phase water (vertical total)
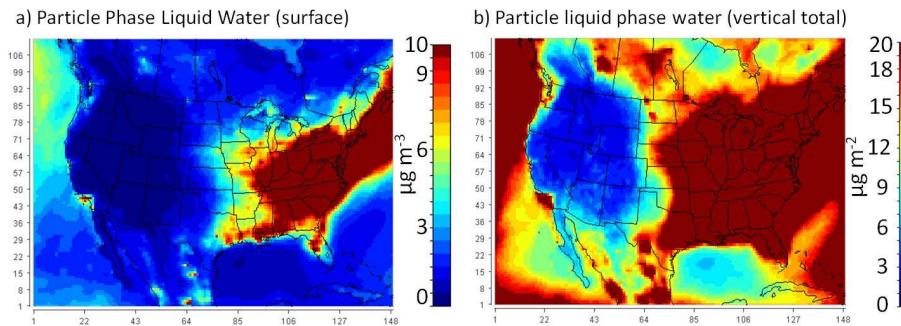
**Fig. 4.** Particle phase liquid water concentrations at the surface ($0 \sim 34$ m) and for the model column (surface up to 100 mb). Values are July 2003 averages.
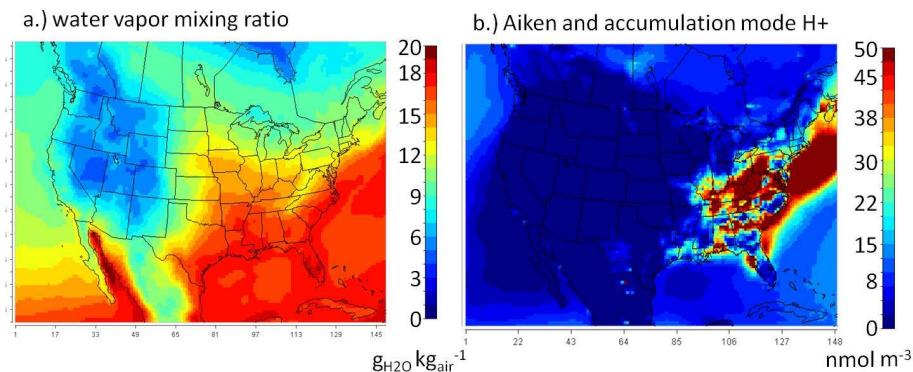
Fig. 5. Water vapor mixing ratio **(a)** and aerosol free acidity **(b)** at the surface averaged for July 2003.
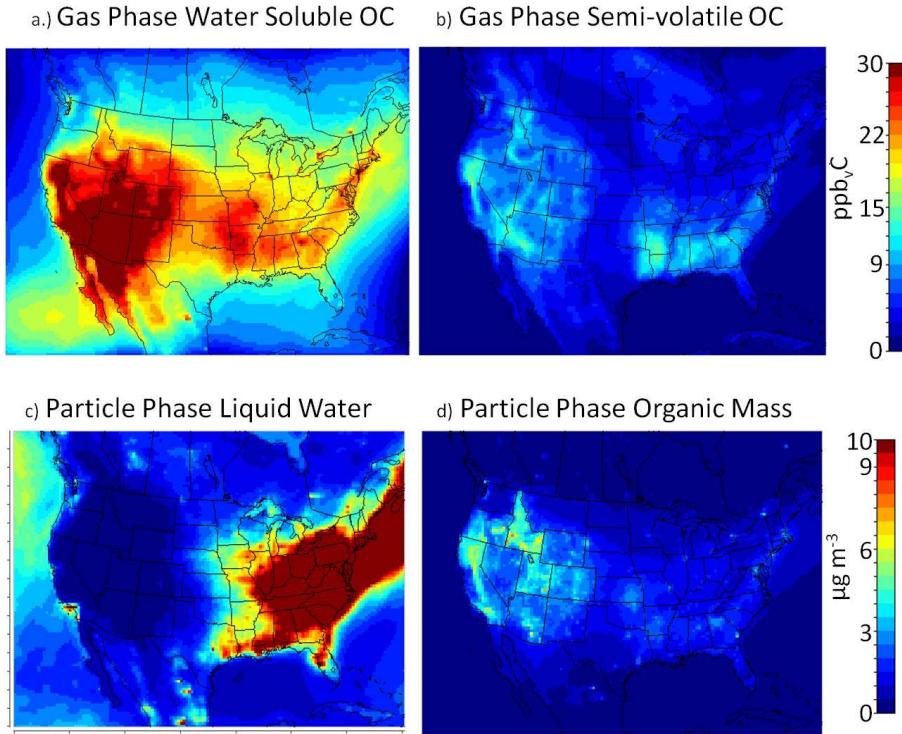
**Fig. 6.** Qualitative comparison of the potential of water soluble gases to partition to aerosol water (left) versus the potential of semi-volatile gases to partition particle phase organic matter (right). All values are averaged for July 2003.