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Limited effect of anthropogenic nitrogen oxides on Secondary Organic Aerosol formation

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Abstract

Globally, secondary organic aerosol (SOA) is mostly formed from emissions of biogenic volatile organic compounds (VOCs) by vegetation, but can be modified by human activities as demonstrated in recent research. Specifically, nitrogen oxides ($NO_x = NO + NO_2$) have been shown to play a critical role in the chemical formation of low volatility compounds. We have updated the SOA scheme in the global NCAR Community Atmospheric Model version 4 with chemistry (CAM4-chem) by implementing a 4-product Volatility Basis Set (VBS) scheme, including NO_x-dependent SOA yields and aging parameterizations. The predicted organic aerosol amounts capture both the magnitude and distribution of US surface annual mean measurements from the Interagency Monitoring of Protected Visual Environments (IMPROVE) network by 50 %, and the simulated vertical profiles are within a factor of two compared to Aerosol Mass Spectrometer (AMS) measurements from 13 aircraft-based field campaigns across different region and seasons. We then perform sensitivity experiments to examine how the SOA loading responds to a 50 % reduction in anthropogenic nitric oxide (NO) emissions in different regions. We find limited SOA reductions of 0.9 to 5.6, 6.4 to 12.0 and 0.9 to 2.8 % for global, the southeast US and the Amazon NO_x perturbations, respectively. The fact that SOA formation is almost unaffected by changes in NO_x can be largely attributed to buffering in chemical pathways (low- and high-NO_x pathways, O_3 versus NO_3-initiated oxidation) and to offsetting tendencies in the biogenic versus anthropogenic SOA responses.

1 Introduction

Organic aerosols (OA) account for a substantial fraction of atmospheric fine particulate matter, and can have significant impacts on both air quality (Huang et al., 2014; Zhang et al., 2007) and climate (Carslaw et al., 2010). Previous research suggests that organic compounds make up between 10 to 90 % of the total aerosol mass at conti-

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nental mid-latitudes and in tropical forests (Andreae and Crutzen, 1997; Kanakidou et al., 2005; Putaud et al., 2010; Seinfeld and Pankow, 2003). Aside from primary organic aerosols (POA) that are directly emitted into the atmosphere, another major fraction of OA is composed of secondary organic aerosols (SOA), which are formed through chemical transformation of anthropogenic and biogenic volatile organic compounds (AVOCs and BVOCs). AVOCs include aromatics, alkanes and alkenes of about 25, 44 and 38 TgC per year, respectively, from industrial processes, fossil fuel use, biomass burning and road vehicles (Williams and Koppmann, 2007).. Isoprene and monoterpenes are the dominant BVOC emissions with estimated global source strengths of about 500 and 150 TgC per year, respectively (Guenther et al., 2012). POA can also re-evaporate upon dilution and participate in the chemical oxidation processes leading to the formation of SOA (Robinson et al., 2007).

Biogenic SOA (BSOA) is usually regarded as natural aerosol and as such cannot be addressed by emission control legislation. Recent research implied that anthropogenic compounds facilitate BSOA formation, thus providing the possibility to control BSOA by regulating the emission of other precursor pollutants like AVOCs, POA and nitrogen oxides (Carlton et al., 2010; Emanuelsson et al., 2013; Hoyle et al., 2011; Lin et al., 2013; Rollins et al., 2012; Volkamer et al., 2006). For example, Carlton et al. (2010) have shown that in the southeast US, up to 50 % of the total BSOA surface atmospheric loading is attributed to controllable pollution emissions. Spracklen et al. (2011) found that at the global scale the model with a large human-interfered SOA source was the most consistent with observations, which includes a maximum of 10 % SOA (10 Tg year^{-1}) from fossil sources, and the extra is mostly likely due to an anthropogenic pollution enhancement of BSOA. The potential impacts of human activities are visible in every step of BSOA formation: the amount of naturally emitted BVOCs through land use and land cover change, the oxidative transformation of BVOCs to semivolatiles through altering atmospheric oxidants concentrations, and the partitioning behavior to the aerosol phase through modifying the load and miscibility of pre-existing organic aerosol (Hoyle et al., 2011).

Among the multiple human-induced influences, nitrogen oxides ($NO_x = NO + NO_2$, emitted from many fossil-fuel driven activity sectors) play a critical role in SOA formation through several aspects. First, through the competitive chemistry of organo-peroxy radicals (RO_2) formed from oxidation of AVOC and BVOC precursors, which can react mainly with NO at high NO_x or hydroperoxyl (HO_2) and peroxy radicals (RO_2) at low NO_x conditions (Kroll and Seinfeld, 2008; Ziemann and Atkinson, 2012). Under high NO_x conditions, SOA production is typically reduced because the RO_2 radicals instead react with NO and NO_2 to form higher volatility products, i.e. organic nitrates. Calculating the SOA yield dependence on NO_x is challenging because the OH / O_3 ratio depends on the VOC / NO_x ratio (Presto et al., 2005). Lane et al. (2008) suggested that SOA yields could be calculated by a linear combination of the "pure" mass yields scaled by the strength of each branch. In many SOA models (e.g. Heald et al., 2008; Lane et al., 2008; Pye et al., 2010), the representative reactions for each branch are:

$$\text{Low } NO_x \text{ condition: } RO_2 + HO_2 \rightarrow ROOH \tag{R1}$$

$$\text{High } NO_x \text{ condition: } RO_2 + NO \rightarrow RONO_2 \tag{R2}$$

For both AVOCs like light aromatics (Ng et al., 2007) and BVOCs like isoprene (Kroll et al., 2006) and monoterpenes (Presto et al., 2005), their oxidation products ROOH formed from low-NO_x pathway have a lower volatility than the oxidation products $RONO_2$ under high-NO_x pathway, thus are more likely to condense to form SOA. Second, NO_x can influence SOA formation through the nighttime nitrate radical (NO_3) chemistry. This pathway has a unique chemical signature due to the high yields of organic nitrate ($RONO_2$), which also forms during daytime photooxidation in the presence of NO but with a lower yield. The importance of NO_3-initiated SOA formation have been confirmed by chamber experiments (Griffin et al., 1999; Ng et al., 2008) and field studies, e.g. in Bakersfield California NO_3-chemistry contributes to approximately a third of the nighttime increase in total OA (Rollins et al., 2012). Finally, NO_x levels can impact the atmospheric oxidation capacity. In the NO_x-limited regime, the OH-initiated oxidation of CO, methane (CH_4) and other VOCs in the presence of NO_x produces O_3.

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Thus, increasing NO_x by human activities should, in principle, lead to the increase in atmospheric oxidation capacity (OH and O_3), and result in higher SOA yields. For example, using a chemical transport model PMCAMx, Lane et al. (2008) suggested that a 50 % reduction in NO_x emissions could decrease predicted ground-level BSOA by an average of 0.5 $\mu g\, m^{-3}$ in the eastern US.

Due to the multiple impacts of NO_x on SOA formation, it is important to understand how NO_x emission controls alter the particulate matter surface atmospheric loading. The goal of this study is to improve the SOA scheme in a global climate-chemistry model by incorporating a 4-product Volatility Basis Set (VBS) framework (Pye et al., 2010), which has 4 representative volatility bins to better represent the volatility distribution of all semivolatiles in the atmosphere than the default 2-product scheme (Heald et al., 2008; Odum et al., 1996). The model is then used to investigate the impacts of anthropogenic NO_x emission reduction on SOA formation. Section 2 describes the observational datasets used in this study. In Sect. 3, we describe the default and updated SOA parameterizations embedded within the global chemistry-climate model framework. We perform control simulations using six different model configurations, including the default 2-product scheme and the updated SOA scheme with and without NO_x-dependent yields for monoterpene, and with and without simplified SOA aging parameterizations. Section 4 shows the results. The control simulations are evaluated and assessed against several observational datasets. Then, we perform sensitivity simulations to probe the impacts of a global 50 % anthropogenic NO emission reduction on SOA production. We conduct this experiment as a simplified potential future scenario based on the 50 % NO_x emission reduction from power plants in the southeast US by pollution control programs in the past decade (Frost et al., 2006; Kim et al., 2006). Section 5 summarizes the findings of this study.

2 Terminology and Data sets

The term OA refers to the total organic matter including carbon, hydrogen, oxygen and other possible elements. The term OC usually refers to only the mass of carbon in these organic compounds. Both OA and OC are used based on different measurement techniques. Similarly, primary organic carbon (POC) is the carbon mass in POA; secondary organic carbon (SOC) is the carbon mass in SOA. In this study the term SOA (secondary organic aerosol) and SOG (secondary organic gas) refer to particle phase and gas phase, respectively.

2.1 IMPROVE OC measurements

The US total OC dataset is from the Interagency Monitoring of Protected Visual Environments (IMPROVE, Hand et al., 2011). IMPROVE-OC is measured by semi-online filter analyzer. We choose 120 surface sites from IMPROVE network that are within the bottom layer in corresponding model grids. The original 3-day data from 2005 to 2009 has been averaged to seasonal and annual mean values. OC concentrations from sites within the same model grid cell ($1.9^{\circ} \times 2.5^{\circ}$ latitude by longitude) are averaged for comparison to modeled OC concentrations in corresponding model grid cells.

2.2 Aircraft-based OA measurements from Aerosol Mass Spectrometer (AMS)

The OA datasets come from 13 aircraft field campaigns that took place between 2005 and 2009 (Heald et al., 2011). In these campaigns, total OA density was measured using AMS in standard temperature and pressure conditions, and provides fast on-line submicron aerosol composition(Canagaratna et al., 2007). For each field campaign, the 1-minute raw data is averaged temporally and horizontally along the flight track for comparison to the simulated monthly mean OA vertical profile in corresponding month and location in the model. Each observed OA profile is further averaged vertically to a single value for comparison to the simulated OA concentration averaged over the same range of altitudes.

2.3 Surface OA/OOA/HOA measurements from AMS

We select 42 surface AMS measurements in 2000–2008 from previous studies (Spracklen et al., 2011; Zhang et al., 2007) that differentiate between hydrocarbon-like OA (HOA, a surrogate for POA from combustion and biomass burning) and oxygenated OA (OOA, a surrogate for SOA from all sources). The averaged OOA, HOA and OA data for each campaign have been compared to the simulated monthly mean SOA, POA and total OA in the corresponding model grid. Most of these measurements were taken before 2005. We did not perform simulations in this period due to the lack of GEOS-5 meteorological data (described in Sect. 3.1). Therefore the model results are averaged from 2005 to 2009 as a climatology to compare with this observational dataset.

3 Modeling framework

3.1 CAM4-chem model

The global Community Atmosphere Model Version 4 with chemistry (CAM4-chem) is part of the Community Earth System Model (CESM, version 1.2.2) (Tilmes et al., 2015). Here, we employ CAM4-chem in its specified dynamics mode, in which CAM and the Community Land Model (CLM) are driven by offline Goddard Earth Observing System Model Version 5 (GEOS-5) reanalysis meteorological fields (available since 2004). The prescribed sea surface temperature and sea ice data are from the Climatological/Slab-Ocean Data Model (DOCN) and Climatological Ice Model (DICE) as other components of CESM. In this configuration, CAM4-chem is run in a Chemistry-Transport Model mode, such that direct comparison can be performed without having to consider

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variability associated with internally generated meteorology. CAM4-chem includes interactive simulation of O_3-NO_x-CO-VOC and bulk aerosol chemistry (based on the MOZART-4 chemical mechanism) as described in Lamarque et al. (2012). The default 2-product SOA scheme is described in Sect. 3.2 and in Heald et al. (2008). Updates performed for the purpose of this study are discussed in Sect. 3.3 and 3.4. The emission of isoprene and monoterpenes are calculated online by Model of Emissions of Gases and Aerosols from Nature (MEGAN-2.1), which is embedded in CLM (Guenther et al., 2012). The anthropogenic, biomass burning and other (except biogenic) emissions in CESM are as described in Lamarque et al. (2012). These consist of anthropogenic emissions from the Precursors of Ozone and their Effects in the Troposphere (POET) inventory for 2000 (Granier et al., 2005), with Asia replaced by Regional Emission inventory for ASia (REAS-v1) for each year (Ohara et al., 2007). The biomass burning emissions are from GFED-v2 (van der Werf et al., 2006) for 2005–2008 and from the Fire INventory of NCAR (FINN-v1) for 2009 (Wiedinmyer et al., 2011). All the SOA schemes discussed in this study consider that SOA are only generated from oxidization of gas-phase VOCs. The SOA formation from organic compounds emitted originally in the condensed phase is not considered. Simulations are performed with a 30 minute time step, a horizontal resolution of $1.9^{\circ} \times 2.5^{\circ}$ and 56 levels from the surface to approximately 40 km.

3.2 Default SOA parameterization

In CAM4-chem, the default SOA formation follows the 2-product approach (Odum et al., 1996). Each parent VOC is oxidized to generate 2 semivolatile surrogates, which can partition into pre-existing organic particles including both POA and SOA. The partitioning of the semivolatile products is described by absorptive partitioning theory into carbonaceous aerosol material (Pankow, 1994). CAM-chem tracks POC in its emission, transport and deposition module, and assumes a POA-to-POC ratio of 2.1 (Turpin and Lim, 2001) in the SOA module when calculating the gas- and aerosol-phase partitioning of the semivolatiles. The model simulates anthropogenic SOA (ASOA) from

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NO_x-dependent OH-initiated oxidation of anthropogenic aromatics (benzene, toluene and xylene), BSOA from the OH-initiated oxidation of isoprene, and the ozonolysis, OH- and NO_3-initiated oxidation of monoterpene (Table 1). The surrogate SOA products are assumed to be: $C_{10}H_{16}O_4$ for SOA from monoterpene (SOAM), $C_5H_{12}O_4$ for SOA from isoprene (SOAI), $C_6H_7O_3$, $C_7H_9O_3$, and $C_8H_{11}O_3$ for SOA from benzene, toluene and xylenes. The default 2-product model in CAM4-chem only applies low-NO_x yields parameterization for all OH- and O_3-initiated BSOA formation. The SOA mass yields (summarized in Table S1 in the Supplement) are from Heald et al. (2008) and references therein.

3.3 Updated SOA scheme

We update the SOA model to include a 4-product VBS scheme, which has 4 semivolatile surrogates for each parent VOC species. The saturation concentrations (C^*) at 295 K for the 4 product groups are 0.1, 1, 10, 100 $\mu g\, m^{-3}$, respectively. This VBS has a wider range of volatilities than the default 2-product parameterization that can better represent the volatility distribution of atmospheric semivolatiles. Another goal of implementing this VBS framework is to facilitate implementation of advanced processing including the aging effect. In addition to the current reactions used in the 2-product model, we have added the NO_x-dependent pathway for SOA formation from monoterpenes and the NO_3-initiated oxidation of isoprene into the VBS (see Table 1). SOA formed from OH-initiated photooxidation of isoprene still only has one set of yields following the low-NO_x parameterizations (Pye et al., 2010). The SOA mass yields (summarized in Table S2) are from Pye et al. (2010) and references therein.

In the 4-product VBS model, the partitioning between the high-NO_x (RO_2+NO) and low-NO_x (RO_2+HO_2) pathway is determined by the branching ratio β (Pye et al., 2010):

$$\beta = \frac{[\mathrm{NO}]}{[\mathrm{NO}] + [\mathrm{HO_2}]} \quad (1)$$

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Thus, $100\times\beta\,\%$ of the parent hydrocarbon channels through the high-NO_x pathway, and $100\times(1-\beta)\,\%$ of the parent hydrocarbon channels through the low-NO_x pathway. This format of β is a simplification of:

$$\beta = \frac{\sum k_{RO_2+NO}}{\sum k_{RO_2+NO} + \sum k_{RO_2+HO_2}} \tag{2}$$

where k_{RO_2+NO} and $k_{RO_2+HO_2}$ represent the reaction rate coefficients of RO_2+NO and RO_2+HO_2, respectively.

Field studies that quantified the elemental composition of OA indicate the importance of aged oxygenated OA (Aiken et al., 2008; Chen et al., 2011; Heald et al., 2010). Several regional modeling studies have found the "aging" process necessary to produce reasonable OA mass (Athanasopoulou et al., 2013; Hodzic and Jimenez, 2011; Knote et al., 2015; Lane et al., 2008; Tsimpidi et al., 2010). In this study we implement a simplified aging parameterization into the global model to provide a rough assessment of the SOA sensitivity in VBS to the effect of aerosol aging. At every model time step, each gas-phase SOA product except for the lowest volatility product ($C^* = 0.1\,\mu g\,m^{-3}$) is assumed to be further oxidized by OH with a reaction rate constant k_{OH} of $4\times10^{-11}\,cm^3\,molec^{-1}\,s^{-1}$ (Atkinson and Arey, 2003; Tsimpidi et al., 2010), which reduces its volatility by an order of magnitude. The oxygen-to-carbon ratio (O : C) is assumed to be constant for each surrogate SOA product thus increase in SOA mass due to the addition of oxygen is not considered in the aging process. The aging rate $k_{OH} = 4\times10^{-11}\,cm^3\,molec^{-1}\,s^{-1}$ is at the high end of previously suggested parameters (Lane et al., 2008). We do simulations with and without this aging parameterization to quantify the possible range of global SOA strengths, and do additional simulations (see Sect. 3.4) to examine the effect of different aging parameters.

Particle-phase SOA as well as gas-phase SOG are removed from the atmosphere by wet and dry deposition. Dry deposition follows a resistance-in-series formulation (Heald et al., 2008; Wesely, 1998). SOA and other soluble aerosols are removed by

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both in-cloud scavenging and below-cloud washout (Barth et al., 2000; Lamarque et al., 2012).

3.4 Experiment setup

In this study, we apply six different treatments of SOA formation, as summarized in Table 1. "2-product" is the default SOA model; "VBS" and "VBS_agHigh" are the updated 4-product VBS scheme with and without the aging effect. "VBS_agHigh" applies the high aging rate k_{OH} =4 × 10^{-11} cm^3 $molec^{-1}$ s^{-1} to all species, thus presumably providing the higher bound of simulated SOA loadings. These three schemes (2-product, VBS and VBS_agHigh) are the main SOA schemes that we use to compare with observations (Sect. 4.2) and study the sensitivity to NO_x perturbations. For each of the three schemes, we perform one control run and one sensitivity run in which anthropogenic NO emissions are reduced by 50 % (Sect. 4.3). We perform additional simulations to explore the impact of different aging and NO_x-dependency parameterizations: "VBS_agLow" applies a lower k_{OH} of 5.2 × 10^{-12} cm^3 $molec^{-1}$ s^{-1} (Hu et al., 2013) to all species, which is close to the lower limit suggested by other studies (Hodzic and Jimenez, 2011; Spracklen et al., 2011); "VBS_agAVOC" applies k_{OH} =4 × 10^{-11} cm^3 $molec^{-1}$ s^{-1} to AVOCs only, as suggested by some studies that ASOA ages longer than does BSOA (Lee-Taylor et al., 2015). "VBS_lowNO_x" is the same as "VBS" except that all SOAM is assumed to be formed through the low-NO_x (RO_2+HO_2) pathway. This "VBS_lowNO_x" scheme is done to isolate the influence of the NO_x-dependent pathway for SOAM formation, which is not considered in the default 2-product settings. All simulations are conducted for the years 2004 to 2009 with offline meteorology from GEOS-5 reanalysis and specific monthly anthropogenic emissions. The year 2004 result is discarded as spin-up.

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4 Results

4.1 Comparison of various SOA schemes

The annual mean zonally averaged SOA concentration is shown in Fig. 1. The tropical maximum in the lower troposphere is due to large year-round Amazonian BVOC emissions coupled with extensive seasonal biomass burning that provides ample pre-existing POA onto which the semivolatiles can condense. The second surface maximum in the northern hemisphere mid-latitudes 30–60° is mostly attributed to (1) summertime BVOC emissions from broadleaf deciduous forest in the temperate and boreal zones, especially the southeast US, which has very high BVOC emissions in the summer (Guenther et al., 2006), (2) plentiful supply of anthropogenic and biomass burning emitted POA, and (3) large amounts of AVOC emissions from human activities. In most simulations, indicated by the white contour lines in Fig. 1, the BSOA from isoprene and monoterpenes oxidation accounts for more than 70 % of the total SOA in most latitudes and altitudes, which actually includes both "naturally-formed" and "anthropogenically-influenced" BSOA. The rest is ASOA from the oxidation of AVOCs. In the VBS_agAVOC run, ASOA accounts for a larger fraction in Northern Hemisphere mid-latitudes then other simulations ranging from 30 to 50 % because in this scheme aging process is only applied to ASOA.

Table 2 details the annual global SOA budget in each control experiment. Compared to the default 2-product approach, the VBS scheme predicts a smaller global annual burden of SOA (19 % lower than the 2-product), although the surface concentration is 11 % higher with compensating lower concentrations at higher elevations. Due to the higher yields in the VBS (see Tables S1 and S2), more parent hydrocarbon is consumed near the source location and less is transported to upper troposphere relative to the 2-product scheme. Their different volatility also contributes to the difference in SOA concentrations. Table 2 suggests a shorter SOA lifetime of 8.9 days in the VBS than the lifetime of 11.4 days in the 2-product scheme due to the larger wet-deposition flux, which is consistent with the higher surface concentration. The SOA global burden in

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the VBS_lowNO_x run is 14 % higher than the VBS. This is consistent with the fact that $RONO_2$, the representative semivolatile product under the high-NO_x (RO_2+NO) condition, has a higher volatility than ROOH, the main product under low-NO_x (RO_2+HO_2) condition, and is thus less SOA-producing. The yields of SOAM at $10\,\mu g\,m^{-3}$ under high- and low-NO_x are 0.09 and 0.19, respectively (Table S2).

For present climate, the differences in annual burden between the 2 VBS models without aging effect (VBS and VBS_lowNO_x) and the 2-product model are relatively small (< 20 %), because for most parent hydrocarbon species they are fitted into the same chamber data (see Heald et al., 2008; Pye et al., 2010, and references therein). In contrast, in VBS_agHigh, adding the aging effect accelerates the shift of volatile mass towards lower volatility bins and hence more mass in the particle phase, and results in an overall doubling of the net SOA (particle phase) production, which is important for SOA environmental impacts. We find that the SOA production is sensitive to the assumed OH oxidation rate constant (k_{OH}) for aging of the semivolatile intermediates. For example, using VBS_agLow scheme with a lower k_{OH} of $5.2\times10^{-12}\,cm^3\,molec^{-1}\,s^{-1}$ (Hu et al., 2013), the annual mean SOA production rate would be $44.6\pm2.0\,Tg[C]\,year^{-1}$, in comparison to a production rate of $58.6\pm2.4\,Tg[C]\,year^{-1}$ in the VBS_agHigh scheme with $k_{OH}=4\times10^{-11}\,cm^3\,molec^{-1}\,s^{-1}$, and a production rate of $28.6\pm1.6\,Tg[C]\,year^{-1}$ in the VBS scheme without aging parameterization. This single aging parameter represents the multi-generational aging of hundreds of thousands oxidation intermediate species that are involved in the SOA formation (Lee-Taylor et al., 2015) and is currently not well characterized for individual precursors and chemical environments. In the rest of this study, we will use the three schemes, 2-product, VBS and the VBS_agHigh, to compare with observations and explore the NO_x-dependent effects.

4.2 Evaluation of OA in CAM4-chem simulations

4.2.1 Comparison with the IMPROVE network OC observations

The IMPROVE surface observations and the model outputs are averaged from 2005 to 2009. Modeled OC concentrations are calculated as the sum of primary carbon (directly emitted and transported in the model) and the carbon contained in each SOA species that is calculated assuming the surrogate SOA products described in Sect. 3.2. Figures 2a and 3 show the model-IMPROVE comparison of annual mean surface total OC concentrations using the model 2-product, VBS and VBS_agHigh. The total OC in the 2-product and the VBS are similar to each other and are close to the IMPROVE OC magnitude. They capture the observed spatial distribution within 50 % ($r^2 = 0.45$ and 0.47, respectively). They capture the low OC values in middle and west inland area, and high OC values in the southeast US where considerable BVOC is emitted from forest as well as POC and AVOC emitted from economic sectors. In the northeast US and some coastal polluted regions in California, OC is greatly overestimated by the models. Figure 2c indicates large simulated POC concentration in these regions while IMPROVE total OC (= POC + SOC) is even not as large as the simulated POC concentrations. Therefore the positive bias of the two no-aging simulations in the northeast US is likely due to an overestimate of POC emissions in the inventory, or due to the assumption that all POA are non-volatile once emitted and stay in the particle phase until deposition. The fact that IMPROVE sites are predominantly located in remote clean regions might also contribute to this discrepancy. In Fig. 2b the white contour lines illustrate the annual mean fraction of SOC in total OC. Table 3 summarizes the fractions in each season. In the two no-aging models, annual mean SOC-to-OC ratio ranges from 20 to 30 % in the northeast US and 40 to 60 % in the southeast US. Even in summer, the ratio does not exceeds 50 % in the northeast US and 70 % in the southeast US, which is lower than the suggested values from Ahmadov et al. (2012) and Shrivastava et al. (2008). The aging experiment VBS_agHigh increases the SOC-to-OC ratio greatly (68 and 81 % in summertime northeast and southeast US) and overestimates OC across the entire US

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due to large SOA formation from aging, which is consistent with previous studies that the aging coefficient we apply here ($k_{OH} = 4 \times 10^{-11}\ cm^3\ molec^{-1}\ s^{-1}$) is at the high end of suggested aging rates. The VBS_agHigh scheme slightly improves the replication of spatial distribution of annual mean OC concentrations ($r^2 = 0.53$ as compared to 0.45 and 0.47 in the 2-product and VBS schemes) but not in summer ($r^2 = 0.13$, Table 4). Assuming only ASOA ages, the VBS_agAVOC scheme does not improve the simulated spatial distribution ($r^2 = 0.48$ in annual average and $r^2 = 0.18$ in summer, Table 4).

4.2.2 Vertical profiles of OA from aircraft-based AMS measurements

To assess the simulated OA vertical profile in these models, we select 13 aircraft campaigns that had available AMS measurements between 2005–2009. The comparison of vertical profiles is shown in Fig. 4. The VBS_agHigh scheme provides a higher OA concentration than the other two no-aging simulations. Overall, the inter-model differences are smaller than the model-observation differences. In biomass burning influenced regions, the observed OA profile is usually associated with large variations at elevated altitude, indicating sporadic fire plumes. For example, for the AMMA campaign (west Africa), the aircraft tracked biomass-burning plumes, thus giving several maxima of observed mean OA at multiple altitudes. In this case, the observed median value at each layer is a more reliable value for evaluation of the simulations (Heald et al., 2011). The simulated OA profiles in these fire-influenced regions are close to the observed median OA profiles and all are within one standard deviation of observations except at site DODO (west Africa). The enhanced observed concentrations in DODO in the upper troposphere indicate strong deep convection. The discrepancies are likely caused by biases in sub-grid meteorology and vertical transport rather than the chemical formation of SOA or POA emissions. Polluted regions have high OA concentrations at the surface. All three of the simulations capture both the vertical distribution characteristics and magnitude of concentration with the largest model-observation difference within $3\ \mu g\ m^{-3}$. OA in remote sites is close to zero. The models capture OA at IMPEX (west North America and east Pacific) and OP3 (Borneo) sites but overestimate at

TROMPEX (Cape Verde) and VOCALS-UK (south Pacific). Generally, the simulated OA profiles are all within a factor of 2 of the observed magnitude, indicating a reasonable model performance across different regions and seasons. The model underprediction of total OA is not as large as in Heald et al. (2011) probably due to the high POA-to-POC ratio of 2.1 applied in CAM4-chem (Turpin and Lim, 2001), while other models apply a factor of 1.4 to 1.8. Figure 5 compares OA concentrations averaged across each entire campaign. All the three simulations underestimate observed OA in most campaigns, except in remote sites TROMPEX (Cape Verde) and VOCALS-UK (eastern south Pacific ocean). The VBS_agHigh scheme has the lowest root-mean-square difference (rmsd) of 1.31, and captures 56 % of observed OA mean concentrations, as compared to 49 and 51 % in the 2-product and VBS schemes.

4.2.3 OA, SOA and POA from surface AMS measurements

The observed OOA is a surrogate for SOA, and HOA is a surrogate for POA in AMS measurements. We use 42 short-term surface AMS measurements (Spracklen et al., 2011; Zhang et al., 2007) and classify their locations into four groups: North America (17 sites), Europe (12 sites), East Asia (12 sites) and Amazon (1 site). Most of these measurements were taken before 2005. The 2005–2009 monthly mean model results have been averaged into a climatology to compare to the observations, which may lead to large model-observation differences. Figure 6 compares the measured and simulated OA, OOA(SOA) and HOA(POA). The comparisons between observations and simulations show large discrepancies (in opposite directions) for primary and secondary species. POA is identical in the three simulations. Consistent with the comparison with the IMPROVE network in Sect. 4.2.1, the models overestimate POA in most regions especially in North America, which will likely increase SOA production due to the larger aerosol surface area available for condensation. The SOA concentration in the two no-aging models, 2-product and VBS, are close to observed OOA in North America and are lower in other regions. By including the aging, the VBS_agHigh simulation increases SOA concentration, leading to an overestimation in North Amer-

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ica and still an underestimation in most other regions. The total OA concentrations in all the models exceed observed OA in North America. In Fig. 7 we plot the comparison of SOA(OOA)-to-OA ratios from the observations and simulations. The 2-product and VBS models significantly underestimate the observed OOA-to-OA ratios that range from 0.4 to 1. The VBS_agHigh model makes an improvement but is still lower than the observations due to the large amount of simulated POA. Overall, the inter-model differences are smaller than the model-observation differences. These conclusions are consistent with Sect. 4.2.1 and 4.2.2.

4.3 The impact of anthropogenic NO_x pollution on surface SOA

For each of the 2-product, VBS and VBS_agHigh schemes, we perform a control run and a sensitivity run in which the anthropogenic NO emissions are reduced by 50 % to explore the impact of NO_x pollution on surface SOA concentrations. Other NO sources include biomass burning and soil emissions are not changed. The 50 % reduction in anthropogenic NO emissions leads to a 36 % decrease in annual mean total NO emissions and a 38 % decrease in surface NO_x concentrations at global scale (Fig. S1). The global surface level of oxidants OH, O_3 and NO_3 decrease by 13, 8 and 29 %, respectively (Fig. S2). The surface NO/HO_2 ratio has been greatly reduced by 67 %, while the change in branching ratio $\left(\beta = \frac{NO}{NO+HO_2}\right)$ is small (−3.4 %). The spatial distribution and probability density function of β are plotted in Figs. S3 and S4. We choose a polluted and a clean region as examples: the southeast US [32–40° N, 95–77° W] and the Amazon [17° S–5° N, 77–55° W], both of which are mostly in the NO_x-limited regime due to their large BVOC emissions (Lane et al., 2008;Malm et al., 2005). We examine the dependence of annual mean surface SOA concentrations on β and oxidants level at the global scale, and over the southeast US and the Amazon regions in Fig. 8. The comparison of the sensitivity (red) and the control runs (green) indicates that the 50 % reduction in anthropogenic NO emissions leads to a small decrease in β, oxidation level and SOA concentrations. In Fig. 8, the small SOA concentrations associated with small

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β values ($\beta < 0.6$) mostly happen over the ocean (not shown) or polar regions where VOC precursors hardly exist and NO_x concentrations are low. In the range $0.6 < \beta < 1.0$ which is the common regime over land, the highest SOA concentrations occur at relatively lower β values, which may reflect the fact that low-NO_x pathway has higher SOA yields. The influences of β and oxidation level are tightly related because high β indicating high NO_x is usually associated with high concentrations of oxidants. The dependence of SOA on oxidants concentration indicates a maximum at medium oxidants level of approximately 0.8×10^{12} molecules cm^{-3}. The low SOA concentration at high oxidants level might be explained by, again, the lower yields of high-NO_x pathway, which is associated with high NO_x and oxidants levels.

The SOA production in response to NO_x perturbations is complex as described in Sect. 1. For example, in the VBS_agHigh scheme, we consider monoterpene SOA (SOAM) coming from NO_3-initiated oxidation and the low- and high-NO_x pathway for both OH- and O_3-initiated oxidation. As shown in Fig. 9, with a 50 % reduction in anthropogenic NO emissions, total surface SOAM concentration decreases, dominated by the decrease in NO_3-oxidation branch. This decrease in total SOAM mass is a result of addition or cancellation of various changes in each branch, and the relative importance of different branches may alter with different regions. One interesting phenomenon is that when NO_x emissions are reduced, the low-NO_x OH- and O_3-initiated oxidation branches form less SOAM mass in the Amazon, but more SOAM in human-influenced regions like mid-latitude broadleaf forest in the southeast US, coastal Asia and boreal forest in northern Europe. To further understand and quantitatively evaluate the complex NO_x influence on SOA formation, we examine the predicted change in surface SOA concentrations in different pathways in response to the decrease in anthropogenic NO emissions, as illustrated by Fig. 10. Table 5 details the relative contribution of each pathway to the total SOA change. The results for various SOA types i.e. aromatic SOA, isoprene SOA and monoterpene SOA are discussed below.

4.3.1 Anthropogenic SOAs from benzene, toluene and xylenes: ASOA

ASOA in the three models are assumed to form from OH-initiated oxidation, including both low-NO_x and high-NO_x pathways, i.e. AVOCs + $OH(HO_2)$ and AVOCs + OH(NO). In the southeast US as shown in Fig. 10, all models predict an increase in the low-NO_x pathway and a decrease in the high-NO_x pathway. This is because the model assumes linear interpolation between low- and high-NO_x pathways based on the branching ratio (Sect. 3.3). When NO_x is reduced, more AVOCs are oxidized under the low-NO_x pathway, which has higher yields (see Tables S1 and S2). The total ASOA formation depends on both the low-/high-pathway partitioning and the oxidation capacity, thus can either increase (e.g. 2-product, VBS) or decrease (VBS_agHigh). In the Amazon, the ASOA changes follow the same pattern as in the southeast US, but their relative contributions are very small due to the low concentrations of AVOCs and anthropogenic NO_x. The contributions of ASOA changes to total SOA change $\left(\text{defined as } \frac{\text{change in ASOA}}{|\text{total SOA change}|}\right)$ ranges from −3.7 to 9.2 % in southeast US and from −0.6 to 1.0 % in the Amazon.

4.3.2 Isoprene SOA: SOAI

In our current models, the isoprene only has one set of yields for OH-initiated daytime oxidation following low-NO_x parameterization, and is oxidized by NO_3 during the night (the latter is not considered in the 2-product model). The OH-oxidation is the dominant branch to form SOAI in both regions. When anthropogenic NO emission is halved, both OH- and NO_3- initiated branches decrease in the southeast US and the Amazon due to reduced atmospheric oxidation capacity and the reduction in NO_3 concentration, respectively. The contributions of SOAI changes $\left(\frac{\text{change in SOAI}}{|\text{total SOA change}|}\right)$ are −46.8 to −73.0 % and −30.8 to −43.0 %.

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4.3.3 Monoterpene SOA: SOAM

Monoterpenes are oxidized by OH, O_3 and NO_3 in all models but the 2-product model only consider the low-NO_x pathway (Table 1). In the southeast US with large human interference, the surface SOAM formation is largely attributed to NO_3-initated oxidation as indicated by most models, which dominates the reduction in response to reduced NO_x. This branch itself contributes to the total SOA change $\left(\frac{\text{change in SOAM from } NO_3\text{-oxidation}}{|\text{total SOA change}|}\right)$ by −48.9 to −65.3 %. In the VBS and VBS_agHigh models, the partitioning between high- vs. low-NO_x pathway determines the tendency of increasing yielding from the low-NO_x pathway and decreasing yielding through high-NO_x pathway. The OH-oxidation in the southeast US follows such tendency. However, the SOA formed from both high- and low-NO_x pathway of ozonolysis increases. One possible explanation is the "buffering" between O_3- and NO_3-initiated oxidation, both of which mostly happen at night. Compared to the control run, NO_3 is significantly lower in the sensitivity run, thus more monoterpenes would be oxidized by O_3 under both low- and high NO_x conditions. Adding up the changes in all branches, the SOAM change contributions to total SOA change are about −36.1 to −60.7 %. In the Amazon pristine environment, most branches demonstrate a slight reduction in SOAM in all models. Since the absolute magnitude of anthropogenic NO_x is small, the major influence of the NO_x might be the decline in level of atmospheric oxidants: OH, O_3 and NO_3 decrease by 14, 6 and 16 %, respectively. Despite the minor lessening of oxidation capacity, the SOAM reduction and total SOA reduction are negligible.

4.3.4 Summary of surface SOA concentration change

The changes in total SOA concentration at the surface in different regions are summarized in Table 6. In both human-influenced and clean regions, the 50 % reduction in anthropogenic NO emissions leads to a decline of BSOA, which dominates the overall SOA decrease. The ASOA could either rise (in models without aging parameterization)

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or decline (in models with aging considered). Among the multiple effects of NO_x, BSOA is mostly influenced by changes in NO_3-initiated oxidation. Both BSOA and ASOA are also influenced by the change in atmospheric oxidation capacity and the partitioning between high- vs. low-NO_x pathways.

The annual mean total surface SOA reductions in the southeast US, the Amazon and global average range from 119 to 518, 30 to 153, 3.6 to 43 $ng\,m^{-3}$, respectively. The corresponding percentage reductions are 6.4 to 12.0, 0.9 to 2.8 and 0.9 to 5.6 %. These changes are comparable with previous estimates (Carlton et al., 2010; Lane et al., 2008), but all are smaller than the magnitude of one standard deviation, indicating that such changes are not statistically significant compared to interannual variations caused by climate and emission variations. The column concentrations of tropospheric SOA are also examined (results not shown here), and the conclusion still holds – no significant change of SOA column concentration when anthropogenic NO emissions are reduced by 50 %. The fact that SOA is stable in response to anthropogenic NO_x changes is attributed to the buffering of various branches (e.g. increased ozonolysis and decreased NO_3-oxidation), the partitioning between low- and high-NO_x pathways and the offset from opposite tendencies of BSOA and ASOA responses (in the no-aging models).

5 Summary

NO_x plays a complex role in the chemical formation of SOA. The complexity includes the competition between NO and HO_2 to react with RO_2, its substantial influence on atmospheric oxidation capacity, and the nighttime NO_3 direct oxidation of isoprene and monoterpenes. In this study, we have updated the SOA scheme in the global chemistry-climate model CAM4-chem to include a 4-product VBS scheme that has a broader representation of volatility distribution, and quantitatively evaluated and explained the multiple impacts of anthropogenic NO_x on SOA at global scale.

We updated the SOA scheme in CAM4-chem to a 4-product VBS scheme. Compared to the default 2-product model, the VBS scheme has 11 % higher surface SOA concentration. While the total annual mean SOA burden is 19 % smaller (0.69 ± 0.03 Tg[C] as compared to 0.85 ± 0.04 Tg[C]) and lifetime is shorter (8.9 ± 0.2 days as compared to 11.4 ± 0.4 days). Due to the different volatility and higher yields of SOA in the VBS, more VOC is oxidized near surface and less is transported to higher levels, and more SOA is washed out near surface. We explored an aging parameterization with a constant reaction rate with OH ($k_{OH} = 4 \times 10^{-11}$ cm^3 molec^{-1} s^{-1}, the higher-limit in previous studies), which almost doubles the net annual SOA production and significantly increases the SOA concentration both at surface and in the lower free troposphere. The global SOA burden with aging considered (i.e. VBS_agHigh scheme) increases to 1.08 ± 0.06 Tg[C] and the corresponding lifetime is 6.7 ± 0.1 days. By applying a lower aging reaction rate ($k_{OH} = 5.2 \times 10^{-12}$ cm^3 molec^{-1} s^{-1}, the lower-limit in previous studies), we found that the simulation of SOA is quite sensitive to the assumed k_{OH}. Despite the significance to SOA formation and properties, the aging effect is still poorly understood at the global scale. Further laboratory and process-modeling constraints at different conditions are needed.

The simulated total OC concentrations in the 2-product and the VBS models without aging are similar, and they capture the magnitude and distribution of annual mean surface OC concentrations in the US from the IMPROVE network by 45–47 %, but overestimate OC in the polluted northeast US and west coastal regions. The models with an implementation of aging (VBS_agHigh) slightly improve the replication of annual mean spatial distribution ($r^2 = 53$ %), but overestimate the magnitude. All three models perform poorly in summertime. Compared to AMS measurements from 13 aircraft-based field campaigns, the simulations of OA vertical profiles are within a factor of 2 across different regions and seasons. The VBS_agHigh scheme performs better than the two no-aging models to reproduce these observed OA concentrations ($r^2 = 56$ %, rmsd = 1.31). Further climatological comparisons with surface AMS observations indi-

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cate reasonable simulated total OA concentrations but overestimation of POA in some polluted regions, which is consistent with the comparison to the IMPROVE network. This overestimation of POA may come from higher biased POC from emission inventory in certain regions (e.g. the northeast US) and the assumed high POA-to-POC ratio of 2.1. If so, it would partially conceal the fact that the current parameterized SOA yields and overlooking of aging in the two no-aging models actually lead to the SOA underestimation. Another possible explanation might be POA re-evaporation and subsequent conversion to SOA (Robinson et al., 2007), indicated by the lower fraction of SOA-to-OA ratio in simulations than the AMS observations. Generally, the inter-model differences are smaller than the model-observation differences. We believe that the updated SOA model (e.g. VBS, VBS_agHigh) is superior to the default one because we implemented the NO_x-dependent SOA formation of monoterpenes, whose absence is a major drawback of the default model. The VBS framework also facilitates inclusion of important processes like aging and the future implementation of size-resolved calculations. The model-observation discrepancies come from several reasons: (1) non-consistent O : C ratio assumed in the model and IMPROVE measurements; (2) potential loss of POA due to evaporation and subsequent SOA formation which is currently not considered in this study; (3) uncertainties in chamber-derived SOA yields due to wall losses (Zhang et al., 2014); (4) lack of constraints on dry deposition of organic gases (Hodzic et al., 2014; Knote et al., 2015) or unaccounted photolysis reactions during aging of organics (Hodzic et al., 2015) Other non-chemistry reasons include: (1) the site-level measurement versus coarse model grid ($1.9^{\circ} \times 2.5^{\circ}$); (2) specific observation time period (days to weeks) versus simulated monthly mean values; (3) sub-grid meteorology (e.g. convection events) that the model cannot capture; (4) large uncertainties related to fire activity (e.g. biomass burning plumes).

Finally, we performed sensitivity experiments to examine how the SOA loading responds to a 50 % reduction in anthropogenic NO emissions in different regions. The BSOA generally decreases due to the reduction in NO_3-initiated reaction and the reduced atmospheric oxidation capacity, while the ASOA increases in the two no-aging

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models mainly because of the increased partitioning to the low NO_x pathway, more AVOCs are oxidized through the low-NO_x pathway that has higher yields. In the aging model, ASOA decreases due to the more important effect of reduced oxidation capacity. Decreases in the total surface SOA concentrations are 6.4 to 12.0, 0.9 to 2.8 and 0.9 to 5.6 % for the southeast US, the Amazon and global NO_x perturbations, respectively, which, however, are not significant. The fact that SOA formation is stable to changes in NO_x can be largely attributed to buffering in chemical pathways (e.g. O_3 versus NO_3-initiated oxidation), to the partitioning between low- and high-NO_x pathways and to offsetting tendencies in the biogenic versus anthropogenic SOA responses. Our results, based on the global chemistry-climate model CAM4-chem with simplified SOA schemes, indicate that air quality control on anthropogenic NO_x may not have substantial impacts on organic aerosol loadings at large regional scales. Further modeling studies including both process-based and parameterized schemes need to be done to carefully examine the NO_x impact on SOA formation.

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Table 1. Summary of SOA treatments in CAM4-chem model runs.

SOA scheme	Reactions to form SOA	Description
2-product	MTP + OH(HO_2); MTP + O_3(HO_2); MTP + NO_3; ISOP + OH(HO_2); AVOCs + OH(HO_2); AVOCs + OH(NO)	Default 2-product scheme; SOA mass yields summarized in Table S1; Heald et al. (2008)
VBS	MTP + OH(HO_2); MTP + O_3(HO_2); MTP + NO_3; MTP + OH(NO); MTP + O_3(NO); ISOP + OH(HO_2); ISOP + NO_3; AVOCs + OH(HO_2); AVOCs + OH(NO)	Updated 4-product VBS scheme; SOA mass yields summarized in Table S2; Pye et al. (2010)
VBS_lowNO$_x$	MTP + OH(HO_2); MTP + O_3(HO_2); MTP + NO_3; ISOP + OH(HO_2); ISOP + NO_3; AVOCs + OH(HO_2); AVOCs + OH(NO)	Same as VBS, but assuming all monoterpene SOA (SOAM) is formed under low-NO$_x$ conditions
VBS_agHigh	Same as VBS	Same as VBS, with multi-generational aging applied to all species; $k_{OH} = 4 \times 10^{-11}$ cm^3 molec^{-1} s^{-1}
VBS_agLow	Same as VBS	Same as VBS, with multi-generational aging applied to all species; $k_{OH} = 5.2 \times 10^{-12}$ cm^3 molec^{-1} s^{-1}
VBS_agAVOC	Same as VBS	Same as VBS, with multi-generational aging applied to ASOA only; $k_{OH} = 4 \times 10^{-11}$ cm^3 molec^{-1} s^{-1}

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Table 2. Summary of simulated annual mean global budget of SOA (particle-phase).

	Burden Tg[C]	Net SOA production Tg[C] year^{-1}	Lifetime Day	Wet deposition Tg[C] year^{-1}	Other losses (by SOA dry deposition) Tg[C] year^{-1}
2-product	0.85 ± 0.04	27.3 ± 2.1	11.4 ± 0.4	−24.4 ± 1.8	−2.9 ± 0.3
VBS	0.69 ± 0.03	28.6 ± 1.6	8.9 ± 0.2	−25.3 ± 1.4	−3.3 ± 0.3
VBS_lowNO$_x$	0.79 ± 0.03	33.7 ± 1.8	8.5 ± 0.2	−29.8 ± 1.5	−3.9 ± 0.3
VBS_agHigh	1.08 ± 0.06	58.6 ± 2.4	6.7 ± 0.1	−52.1 ± 2.1	−6.5 ± 0.4
VBS_agLow	0.96 ± 0.05	44.6 ± 2.0	7.8 ± 0.1	−40.0 ± 1.7	−4.8 ± 0.3
VBS_agAVOC	0.75 ± 0.03	31.5 ± 1.6	8.6 ± 0.2	−27.8 ± 1.4	−3.7 ± 0.3

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Table 3. Fraction of SOC in total OC (%) in the southeast US and the northeast US.

		Annual	MAM	JJA	SON	DJF
Northeast US	2-product	24 %	15 %	45 %	20 %	6 %
	VBS	28 %	19 %	49 %	23 %	8 %
	VBS_agHigh	45 %	33 %	68 %	39 %	12 %
Southeast US	2-product	39 %	29 %	62 %	32 %	8 %
	VBS	44 %	34 %	67 %	37 %	10 %
	VBS_agHigh	63 %	55 %	81 %	56 %	18 %

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Table 4. Coefficients of determination (r^2) of IMPROVE measurements versus simulated total OC.

	Annual	MAM	JJA	SON	DJF
2-product	0.45	0.40	0.18	0.41	0.42
VBS	0.47	0.42	0.18	0.43	0.42
fVBS_agHigh	0.53	0.54	0.13	0.49	0.45
VBS_agAVOC	0.48	0.45	0.18	0.44	0.44

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Table 5. The relative contributions (%) of each SOA formation pathway to the total SOA concentration change in the southeast US and the Amazon, defined as $\frac{\text{SOA change in each pathway}}{|\text{total SOA change}|}$. The sums of all numbers in each simulation equal −100 % because the total SOA change in the sensitivity runs compared to the control runs are always negative. The reaction denotations are the same as defined in Fig. 10.

		M1	M2	M3	M4	M5	I1	I2	A1	A2
SE US	2-product	−10.4	–	+15.0	–	−65.3	−46.8	–	+10.6	−3.1
	VBS	+2.9	−13.5	+29.5	+8.8	−63.8	−40.3	−32.7	+13.7	−4.5
	VBS_agHigh	+1.0	−5.3	+8.9	+2.0	−48.9	−35.1	−18.9	+3.5	−7.2
Amazon	2-product	−5.1	–	−0.2	–	−65.0	−30.8	–	+1.4	−0.4
	VBS	+0.4	−7.8	+5.9	−15.8	−45.1	−16.2	−21.9	+0.9	−0.5
	VBS_agHigh	−1.4	−4.3	−9.5	−13.9	−27.2	−30.4	−12.6	0.0	−0.6

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Table 6. Changes in surface SOA concentrations due to a 50 % reduction in anthropogenic NO emissions. Total SOA changes from each model are listed for global average, the southeast US and the Amazon.

		Concentration in Control run ($ng\,m^{-3}$)	Standard deviation ($ng\,m^{-3}$)	Concentration change in sensitivity run ($ng\,m^{-3}$)	Percentage change
SE US [32–40° N, 95–77° W]	2-product	1638	248	−119	−7.3 %
	VBS	2005	286	−127	−6.4 %
	VBS_agHigh	4331	594	−518	−12.0 %
Amazon [17° S–5° N, 77–55° W]	2-product	3360	1383	−30	−0.9 %
	VBS	3884	1197	−46	−1.2 %
	VBS_agHigh	5390	1542	−153	−2.8 %
Global average	2-product	358	40	−3.6	−1.0 %
	VBS	393	37	−3.6	−0.9 %
	VBS_agHigh	774	52	−43	−5.6 %

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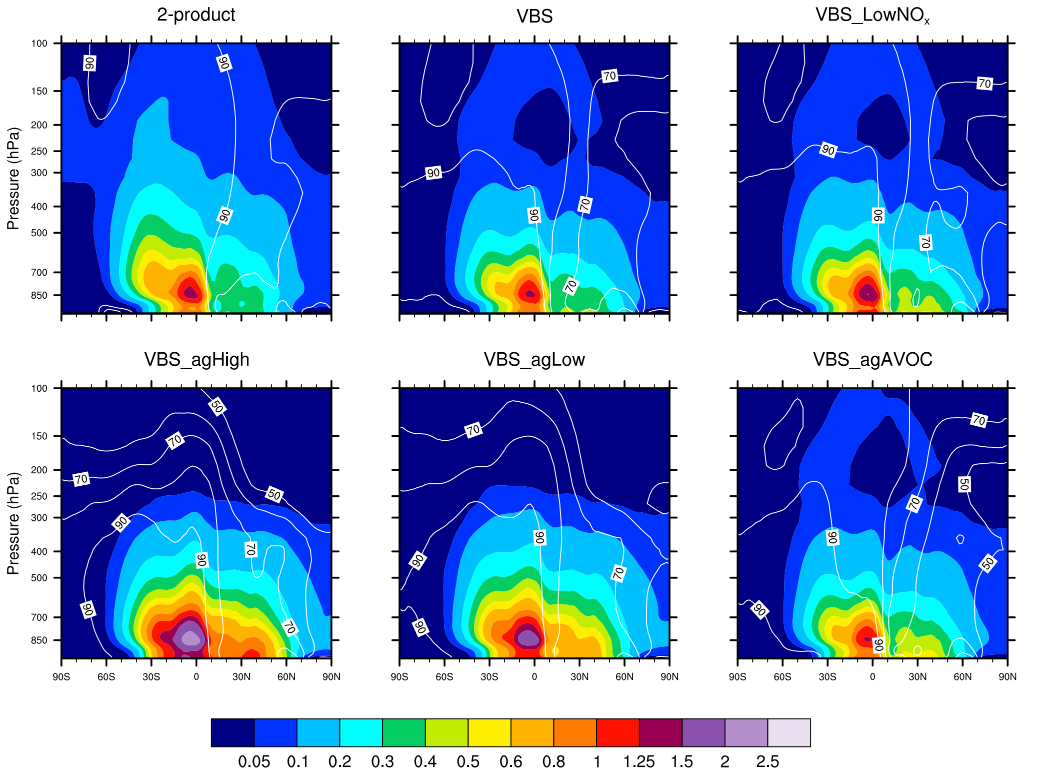

Figure 1. Annual mean zonally averaged SOA concentration ($\mu g\, m^{-3}$) (shown as colored shades) and the fraction of biogenic SOA (%) (shown as white contours) in CAM4-chem for different SOA treatments.

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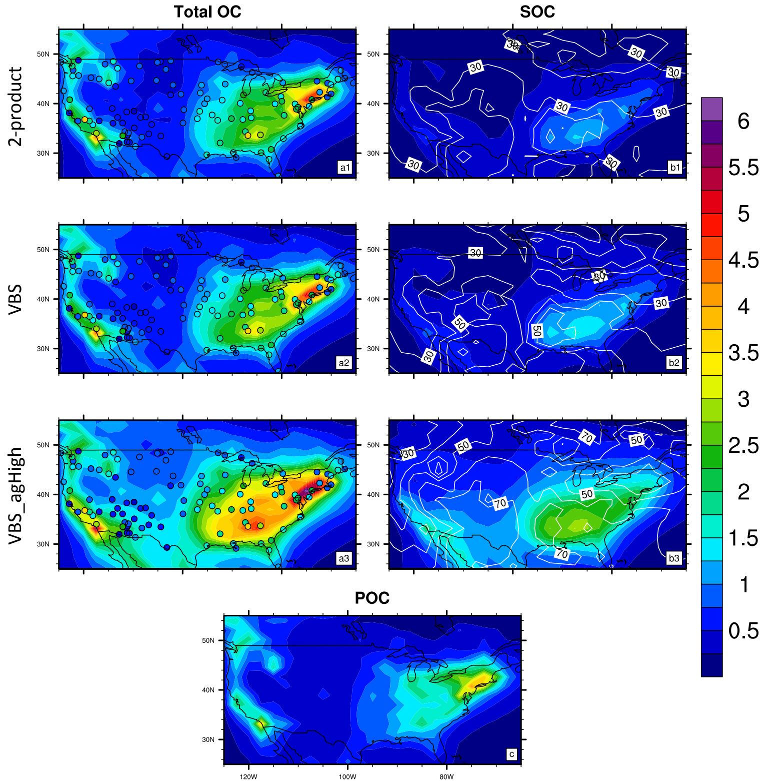

Figure 2. Annual mean surface concentrations (units: µg[C] m^{-3}) of **(a1–a3)** total organic carbon (OC = POC + SOC), **(b1–b3)** secondary organic carbon (SOC) and **(c)** primary organic carbon (POC). The data is averaged from 2005 to 2009. In panel **(a1–a3)**, scatters are IMPROVE observations and color shades are simulated total OC from the model 2-product, VBS and VBS_agHigh. In panel **(b1–b3)**, white contours indicate the fraction of SOC in total OC (%), ranging from 30 to 70 % with an interval of 10 %. Panel **(c)** shows simulated POC, which is identical in the 3 simulations.

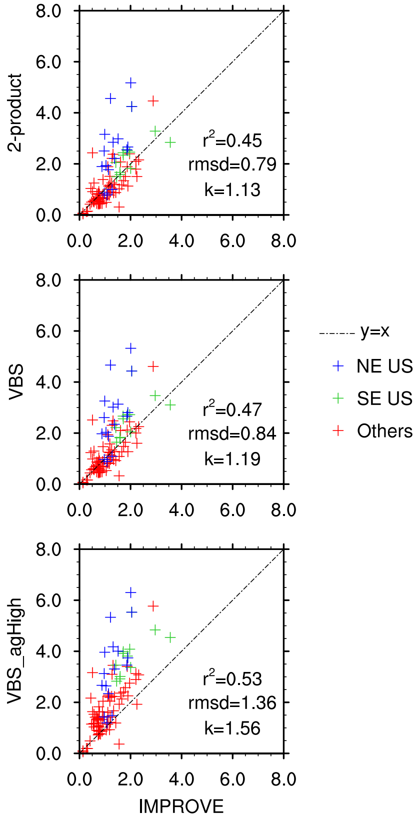

Figure 3. Comparison of averaged annual mean surface OC concentrations (µg[C] m^{-3}) between IMPROVE measurements and the three simulations: 2-product, VBS and VBS_agHigh. Different colors indicate sites in different regions. In each subplot, the dash line is 1-to-1 line. The coefficients of determination (r^2), root-mean-square-difference (rmsd) and the model-to-observation slope (k) are included.

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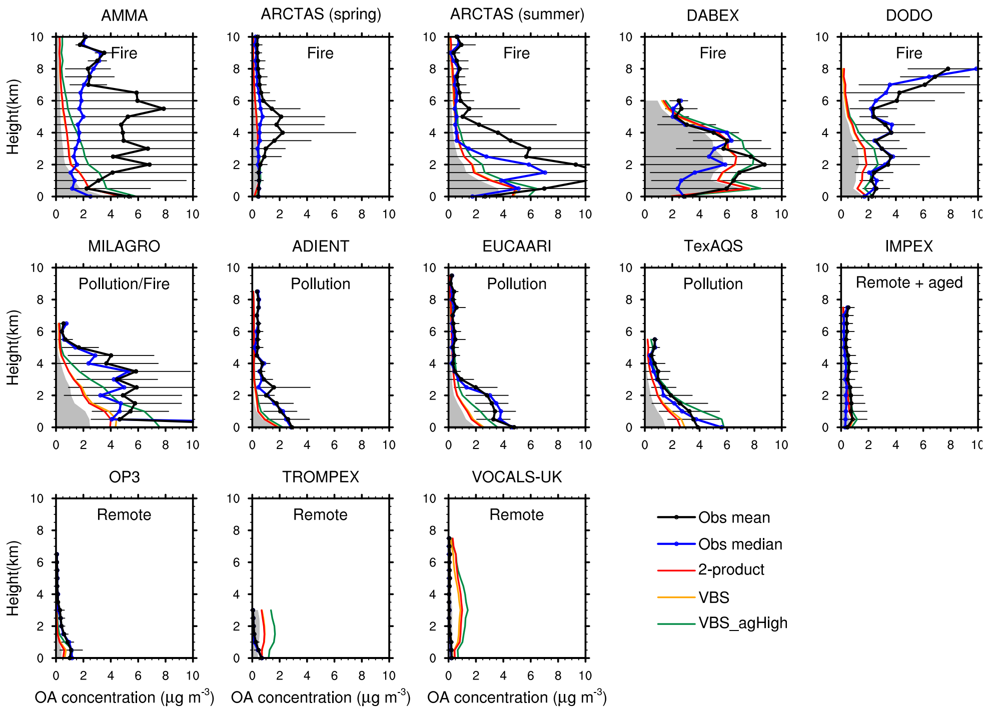

Figure 4. Comparison between observed vertical profile of OA concentration ($\mu g\,m^{-3}$) from 13 AMS field campaigns and the three model simulations: 2-product, VBS and VBS_agHigh. The campaign information is summarized in Heald et al. (2011; Fig. 1 and Table 1 therein). The error bars are one standard deviation of the binned observations for each 0.5 km interval. The grey shades are simulated POA assuming a POA-to-POC ratio of 2.1. The model simulations are sampled for the corresponding months and locations for each campaign. The location and location type for each campaign is included in each subplot.

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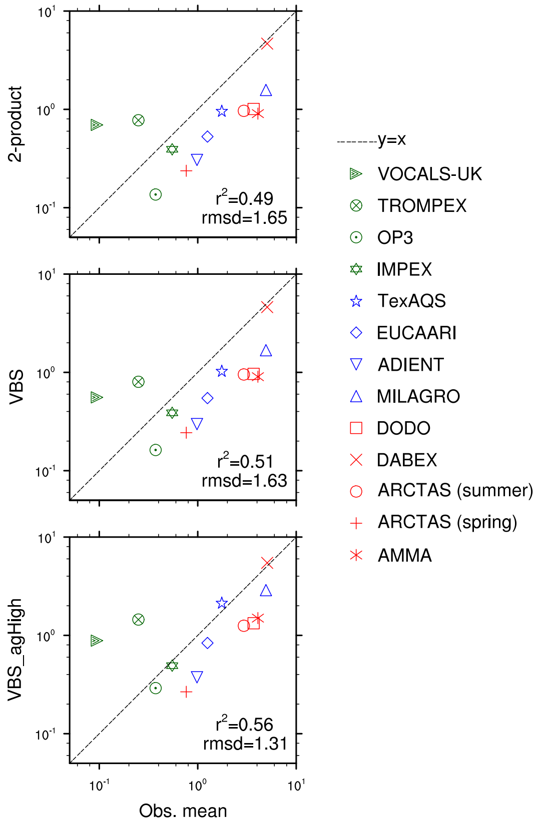

Figure 5. Comparison between averaged OA concentration (µg m^{-3}) from 13 AMS field campaigns and the 3 model simulations: 2-product, VBS and VBS_agHigh. The campaign information is summarized in Heald et al. (2011; Fig. 1 and Table 1 therein). All data in each campaign are temporally, horizontally and vertically averaged to a single value, and compared to the model outputs averaged over the same period and location.

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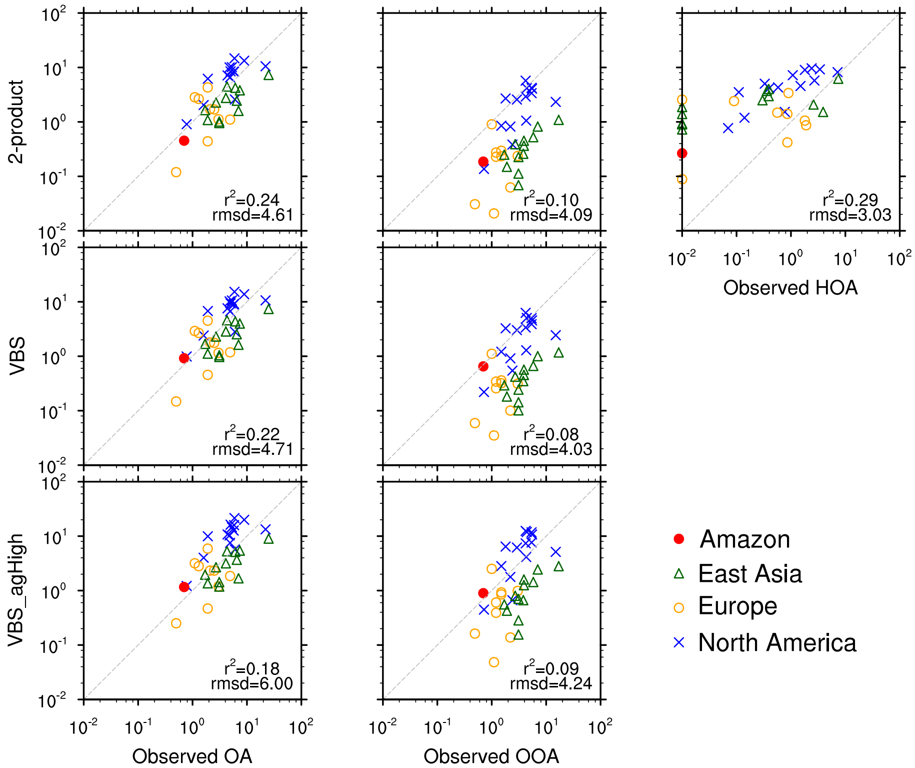

Figure 6. Comparison of surface AMS measurements (units: µg m^{-3}) and three simulations (first column: total OA; second column: SOA(OOA); third column: POA(HOA)). The coefficients of determination (r^2) and root-mean-square-difference (rmsd) are included in each subplot. The observed oxygenated OA (OOA) is a surrogate for SOA from all sources. The observed hydrocarbon-like OA (HOA) is a surrogate for POA from combustion and biomass burning. Simulated POA is identical in the three simulations. In POA-HOA comparison, data points with observed HOA smaller than 0.01 µg m^{-3} have been set to 0.01 µg m^{-3} to be shown in the plots.

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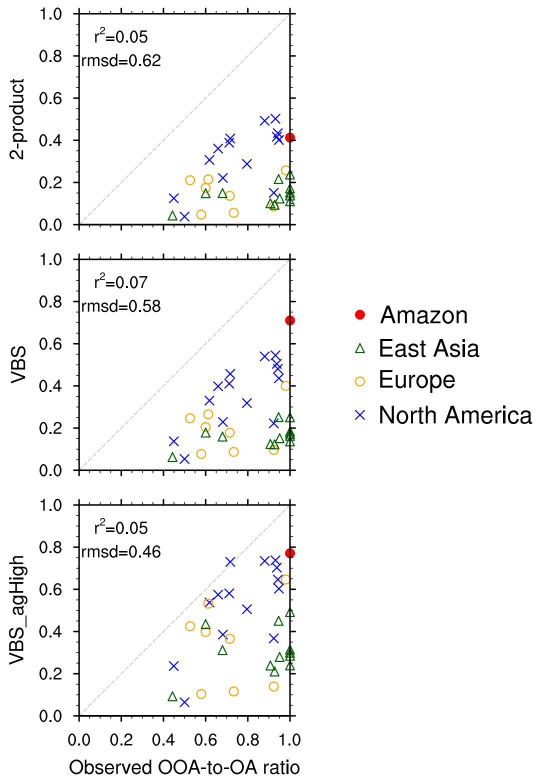

Figure 7. Comparison of observed OOA-to-OA ratio from surface AMS measurements and simulated SOA- to-OA ratio from the 2-product, VBS and VBS_agHigh schemes. The coefficients of determination (r^2) and root-mean-square-difference (rmsd) are included in each subplot.

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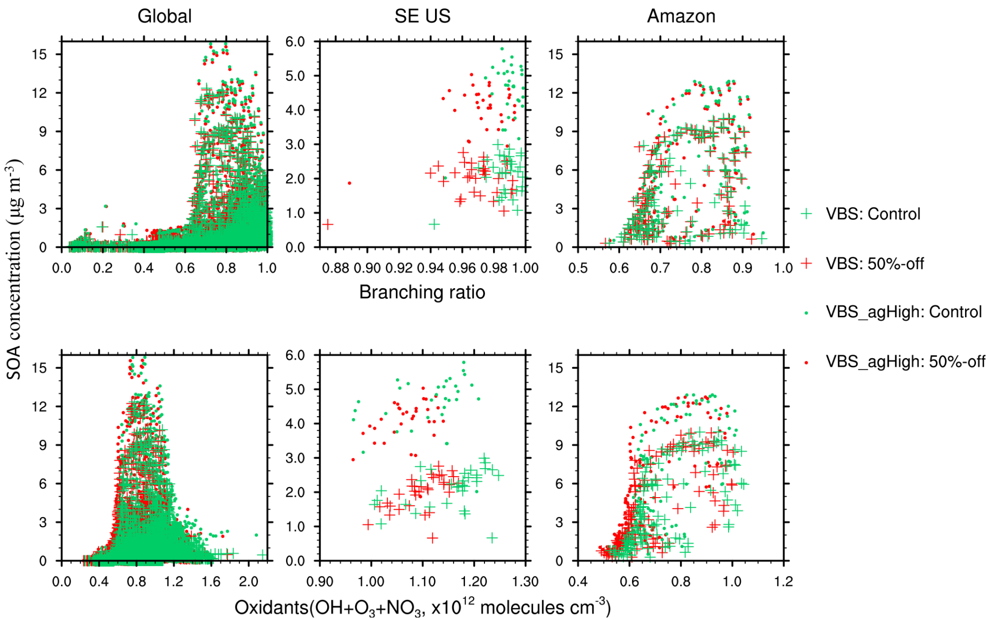

Figure 8. Dependence of annual mean surface SOA concentration ($\mu g\,m^{-3}$) on branching ratio and oxidants level at global scale, in the southeast US and the Amazon. The control runs and the sensitivity runs using VBS and VBS_agHigh schemes are shown. The 2-product results are similar to the VBS results (not shown). Data points over ocean are excluded. Note that the scales for the southeast US and the Amazon are different from the global subplots.

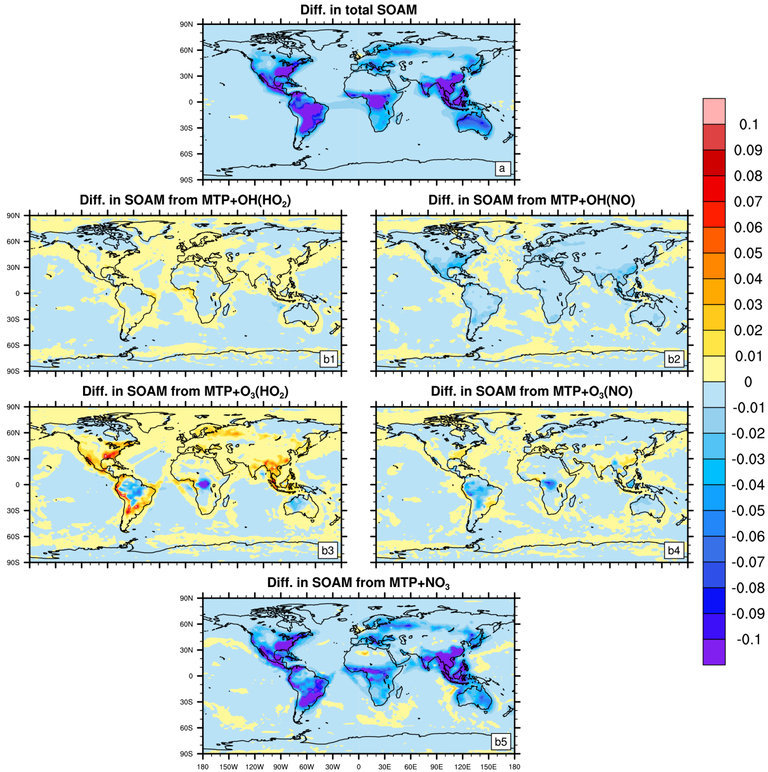

Figure 9. Changes in surface monoterpene SOA (SOAM) concentration ($\mu g\, m^{-3}$) in the sensitivity run with 50 % reductions in anthropogenic NO emissions compared to the control run using VBS_agHigh scheme. The total SOAM change is shown in panel **(a)**. The SOAM change in each formation branch is denoted as: **(b1)**: MTP + OH(HO_2) (low-NO_x OH-photooxidation); **(b2)**: MTP + OH(NO) (high-NO_x OH-photooxidation); **(b3)**: MTP + O_3(HO_2) (low-NO_x ozonolysis); **(b4)**: MTP + O_3(NO) (high-NO_x ozonolysis); **(b4)**: MTP + NO_3 (NO_3-initiated oxidation).

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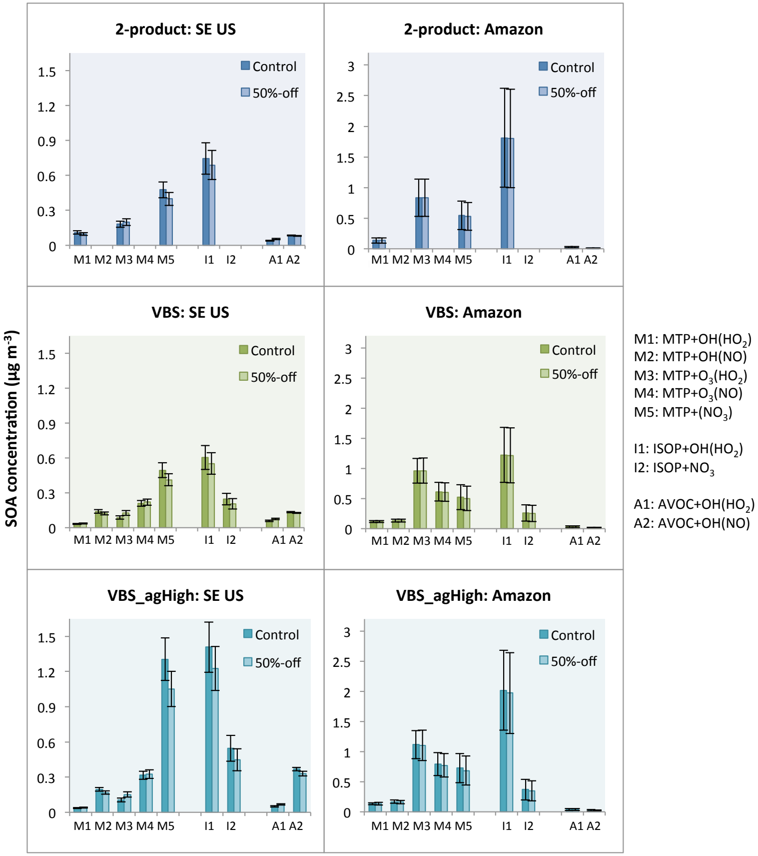

Figure 10. Annual mean surface SOA concentration (µg m^{-3}) in the control runs and the sensitivity runs (with 50 % anthropogenic NO emission off) from different pathways, averaged over the southeast US [32–40° N, 95–77° W] and the Amazon [17° S–5° N, 77–55° W].

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