

To What Extent Can Biogenic SOA be Controlled?

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1 **ABSTRACT**

2 The implicit assumption that biogenic secondary organic aerosol (SOA) is natural
3 and can not be controlled hinders effective air quality management. Anthropogenic
4 pollution facilitates transformation of naturally emitted volatile organic compounds
5 (VOCs) to the particle phase, enhancing the ambient concentrations of biogenic
6 secondary organic aerosol (SOA). It is therefore conceivable that some portion of
7 ambient biogenic SOA can be removed by controlling emissions of anthropogenic
8 pollutants. Direct measurement of the controllable fraction of biogenic SOA is not
9 possible, but can be estimated through 3-dimensional photochemical air quality
10 modeling. To examine this in detail, 22 CMAQ model simulations were conducted over
11 the continental U.S. (August 15 – September 4, 2003). The relative contributions of five
12 emitted pollution classes (i.e., NO_x, NH₃, SO_x, reactive non methane carbon (RNMC) and
13 primary carbonaceous particulate matter (PCM)) on biogenic SOA were estimated by
14 removing anthropogenic emissions of these pollutants, one at a time and all together.
15 Model results demonstrate a strong influence of anthropogenic emissions on predicted
16 biogenic SOA concentrations, suggesting more than 50% of biogenic SOA in the eastern
17 U.S. can be controlled. Because biogenic SOA is substantially enhanced by controllable
18 emissions, classification of SOA as biogenic or anthropogenic based solely on VOC
19 origin is not sufficient to describe the controllable fraction.

20 **INTRODUCTION**

21 Secondary organic aerosol (SOA) forms in the atmosphere from ozone and radical
22 reactions with hydrocarbon precursors that produce nonvolatile and semivolatile organic
23 species that condense onto pre-existing particulate matter or form new particles through

nucleation. SOA produced from naturally-emitted hydrocarbons (e.g., isoprene) is called “biogenic” SOA while other SOA is termed “anthropogenic” when the precursor hydrocarbon (e.g., toluene) is not from natural sources. The relative significance of the various SOA pathways and precursors is uncertain and estimates regarding the importance of secondary contributions to atmospheric organic aerosol vary by season and location [1-4].

Globally, plant foliage contributes more than two-thirds of total volatile organic compound (VOC) emissions to the atmosphere [5]. As a consequence, SOA derived from biogenic VOCs dominates the predicted global atmospheric SOA burden [6, 7] and radiocarbon dating of ambient organic aerosol suggests that SOA indeed consists primarily of non-fossil, modern carbon [8-10], in particular during summer [1]. In many air quality model applications and ambient data analyses, implicit presumptions are made that biogenic SOA can not be controlled by conventional air quality management practices because the precursor VOCs are naturally emitted [11, 12]. However, this same SOA correlates strongly with indicators of anthropogenic pollution, such as CO [13] and alkyl nitrates [14]. Such correlations are suggestive that SOA is predominantly formed through processes that involve modern VOCs strongly linked with anthropogenic components [13]. Anthropogenic emissions can enhance biogenic SOA through a variety of mechanisms (Figure 1). For example, biogenic VOC oxidation in NO_x- and sulfate-rich environments [15] or anthropogenic primary carbonaceous particulate matter (PCM) emissions serving as an absorptive medium available for condensation of semi-volatile species of biogenic origin.

Model investigations of future climate have alluded to the influence of anthropogenic contributions to biogenic SOA. Future projections of biogenic SOA increase 10-30%, largely a result of increased PCM emissions [16-18]. Tsigaridis and Kanakidou [7] found that, globally, biogenic SOA would likely increase in future atmospheres due, not only to changes in PCM emissions, but also due to increases in oxidant levels. Increases in atmospheric concentrations of oxidants (O_3 , OH , NO_3), as a result of increased anthropogenic pollution, can react to convert biogenic VOCs to condensable, SOA-contributing species, thereby enhancing biogenic SOA. Using a volatility basis set approach to SOA modeling, Lane et al. (2008) [19] also found an oxidant effect. Their results suggest that a 50% reduction in NO_x concentrations could decrease predicted biogenic SOA by an average of $0.5 \mu g m^{-3}$ in the eastern U.S. Given these various interactions, the traditional definition of SOA as either anthropogenic or biogenic can be misleading. Rather, we propose classification of SOA as controllable or non-controllable.

Direct measurement of the anthropogenic contribution to biogenic SOA is not possible in field experiments due to the complex preceding chemistry. Quantitative estimates are possible with a 3-dimensional photochemical air quality model that contains advanced mechanisms for biogenic SOA formation. Such models integrate the findings from laboratory and field studies to understand the relative impact of processes over a continental or global scale. To estimate the controllable fraction of biogenic SOA and to evaluate large scale trends, a modeling study, employing the Community Multiscale Air Quality (CMAQv4.7) model (www.cmascenter.org) [20] was conducted.

Because all models are an approximate representation of the physical world, it is important to use care when drawing conclusions from the results. CMAQv4.7 simulations have been shown to capture regional and seasonal variability in observationally-estimated secondary organic carbon (SOC) (annual averages of $r \geq 0.7$ for all regions of the U.S. [21]). However, there is a persistent negative bias [21]. This bias likely arises from a combination of errors and uncertainties, such as inadequate representation of anthropogenic SOA [22], PCM emissions that do not account for intermediate volatility species (IVOC) [23] and uncertain biogenic emissions (e.g., monoterpenes and sesquiterpenes) [24]. Because of these limitations, our modeling experiment is best suited to bounding the enhancement of biogenic SOA from controllable emissions, rather than calculating a single best estimate. Since CMAQv4.7 captures the variability but underestimates the mass, we are most confident in the estimate of the lower bound. Our modeling suggests that despite these uncertainties, this lower bound estimate is substantial.

METHODS

Atmospheric Modeling

CMAQv4.7 was used to simulate air quality in the U.S. from August 15 – September 4, 2003. This date range is representative of polluted conditions typical of the U.S. at a time when biogenic SOA has been measured to be an important component of the atmospheric aerosol [1]. The first three days are excluded from the analysis to allow for model initialization and spin-up. The modeling domain encompasses the continental United States, discretized with a horizontal resolution of 36 x 36 km and 14 vertical layers of variable thickness from the surface up to 100 mbar [25]. The SOA module, as

well as meteorological inputs to drive the CMAQ simulation and biogenic emissions, and boundary conditions for these simulations are described in detail elsewhere [21]. Briefly, biogenic SOA precursors are isoprene, monoterpenes and sesquiterpenes. Formation pathways include oxidation of volatile species to semi-volatile products followed by gas-to-particle partitioning, oligomerization, and acid enhancement of isoprene SOA. NO_x -dependent yields are parameterized for SOA derived from xylene, toluene and benzene, similar dependencies for SOA derived from biogenic VOCs are not included and this may add to the uncertainty. Other processes simulated by CMAQ include advection, dispersion, gas-phase chemistry (SAPRC99), heterogeneous surface chemistry, aqueous chemistry, aerosol thermodynamics and microphysics and wet and dry deposition. When compared with semi-empirical estimates of secondary organic carbon (SOC) this model configuration has a negative bias in the magnitude of predicted organic aerosol mass concentrations, like many atmospheric models, [26, 27] but diurnal, seasonal and regional trends agree with observational estimates [21].

A base model simulation was performed with a complete emissions data set (biogenic and anthropogenic emissions). Twenty-two control simulations were conducted with all biogenic emissions plus a range of emission reduction factors applied to the controllable emissions of selected pollutant classes: RNMC, NO_x , PCM, SO_x and NH_3 . One sensitivity simulation was conducted using 3xPCM emissions for uncontrollable fires, as an upper bound [28] to account for IVOC emissions. Domain wide average changes in predicted biogenic SOA concentrations, as a result of the emissions reduction, are calculated. To better understand and characterize potential human exposure, population-weighted values are also analyzed. We define the

population (P_i) in each CMAQ grid cell (i) as the sum of all census tracts whose centroid is within the cell. The domain-wide, population weighted concentration (\bar{C}) is calculated according to equation 1:

$$\bar{C} = \frac{\sum_i C_i P_i}{\sum_i P_i} \quad [1]$$

where C_i is the concentration in CMAQ grid cell, i .

Emissions Characterization

Emission sources can be broadly categorized into 1) those that can be controlled by changes in human activity and 2) those that result from natural processes plus preventative, accidental, and illegal activities. We refer to the latter as uncontrollable emissions and define them as the sum of biogenic VOCs, emissions of NO from unfertilized fields and lightning, emissions of PCM and NO_x from wildfires and prescribed burn events, and sea salt from salt water bodies.

Cloud-to-ground lightning NO emissions are spatially and temporally distributed using National Lightning Detection Network strike data. The NO production per flash and vertical distribution of emissions are parameterized using cloud properties [29] extracted from the same meteorological fields used in the CMAQ simulations. Emissions from cloud-to-cloud lightning are estimated from the cloud-to-ground strikes using climatological ratios [30].

The Biogenic Emissions Inventory System Version 3.14 (BEIS) [31] is used to estimate biogenic emissions of VOCs, such as isoprene, monoterpenes, and sesquiterpenes, as well as the emissions of NO from unfertilized fields.

Wildfires arise from both natural processes (lightning) and human activity (accidents, arson). Because they are not an intentional outcome of social policy, we classify wildfires as “uncontrollable”. Prescribed burning is a necessary part of land management, so we classify it as uncontrollable. On the other hand, agricultural burning is classified as controllable. Because fires are episodic and have large year-to-year variability, our simulations used a “climatological” fire emission inventory that is a seven-year average for conditions from 1996-2002 (http://www.epa.gov/air/interstateairquality/pdfs/Fire_Temporal_Documentation.pdf).

Remaining sources are defined as controllable and are estimated from the USEPA National Emission Inventory 2002 (<http://www.epa.gov/ttn/chief/net/critsummary.html>). Updates include year 2003 specific data for motor vehicle emissions derived using MOBILE6 (<http://www.epa.gov/otaq/m6.htm>) and power plant emissions are directly calculated from continuous emissions monitors (CEM) observations at each facility.

To estimate the impact of reductions in controllable emissions, we generated a series of sensitivity cases with a fixed percentage reduction of controllable emissions. The emission reductions were implemented by applying a fixed scaling factor to all controllable emissions across the domain for the length of the simulation. Five scaling factors were used: 1.0 (equivalent to the “total” case), 0.75, 0.5, 0.25, and 0.0 (equivalent to only uncontrollable emissions). To investigate the impacts and interactions between chemical species, we divide the emitted controllable chemical species into five categories: reactive non methane carbon (RNMC) is the sum of non-methane hydrocarbons, NO_x is the sum of NO and NO_2 , primary carbonaceous matter (PCM) is the sum of the carbonaceous particle emissions, including elemental carbon (i.e., EC +

POC), SO_x is the sum of SO_2 gas and SO_4^{2-} particles, and NH_3 is ammonia. We apply the same five factors to the controllable emissions of the species in that category, and leave all other emissions as in the total case. The domain total fractions of several emitted species are shown in Figure 2. Species that have both grey and white fractions (e.g., alkanes, CO, NO_x) are emitted from both controllable and uncontrollable sources.

RESULTS and DISCUSSION

CMAQ predictions of total and biogenic SOA decreases substantially when controllable emissions are eliminated (Figures 3, 4). Figure 3a illustrates the difference in predicted biogenic SOA between the base case (total emissions) and the simulation when all controllable emissions are removed (i.e., uncontrollable emissions only). Figure 3b depicts that difference as a fraction of biogenic SOA in the base case. These results suggest that a substantial fraction of biogenic VOCs are converted to SOA only when there is sufficient anthropogenic pollution to facilitate formation. At the surface layer, when all controllable emissions were removed, biogenic SOA is reduced by more than 50% or $\sim 1 \mu\text{g m}^{-3}$ in the eastern U.S. (Figures 3 and 4). The general underprediction of secondary aerosol by CMAQ [21] suggests that while there is uncertainty in the $\sim 1 \mu\text{g m}^{-3}$ estimate, it is likely a lower bound. Biogenic SOA reductions for individual pollution classes were observed to be approximately -30%, -20%, and -10% (Table 1; Figure 4b; Figure S-1) for PCM, NO_x and RNMC respectively. Because CMAQ predicts trends and patterns in biogenic SOA well [21], we have more confidence in the relative fractional decreases than in the absolute predicted mass concentrations.

Biogenic SOA (Figure 4b) is most sensitive to controllable PCM and NO_x emissions, in agreement with previous findings [16, 17, 19, 32]. Even when PCM

emissions from uncontrollable fires are tripled to account for the maximum IVOC emission potential, biogenic SOA sensitivity to controllable PCM emissions is still the largest, though it decreases by ~20% (as an extreme) for the population-weighted value. Similar findings arise, in part, due to similar model formulations, though Lane and Pandis [19] used a volatility basis approach to model SOA unlike the other studies. Reductions in NO_x emissions decrease oxidant levels and consequently the formation of semi-volatile species from VOC oxidation. PCM emissions have the largest effect by limiting the organic material available for condensable semi-volatile species. Biogenic SOA is less sensitive to controllable RNMC emissions due to the large source strength of biogenic VOC emissions. Also, reductions in controllable RNMC emissions result in less SOA from those precursors (Figure 4c) and therefore less material is available for condensation of semi-volatile biogenic species, as for the PCM case described above. Conversely, when less controllable RNMC is emitted, there is less competition for oxidants and more oxidation of biogenic VOCs and formation of semi-volatile, SOA-forming species. Effects from SO_x and NH₃ on total biogenic SOA were small. Only a fraction of total biogenic SOA, (i.e., acid-enhanced isoprene SOA) was affected by changes in emissions of these species. Because acid-enhanced isoprene SOA is a small fraction of the total predicted biogenic SOA, these species had a limited effect.

While PM_{2.5} contains large amounts of sulfate and nitrate, substantial reductions in PM_{2.5} are achieved through PCM controls and to some extent limits in NO_x emissions (Figure 4d). The domain-average PM_{2.5} reductions are largest for SO₂. However, sulfate concentrations are regionally homogeneous, while PCM is simulated and observed in much higher concentrations in urban centers [33]. When weighted by population, the

average $PM_{2.5}$ decrease due to PCM is ~40%, slightly larger than the decrease due to SO_x emission controls (Table 1). Species with substantial emissions contributions from mobile sources (i.e., VOCs, NO_x and ammonia) [34, 35] affect the population-weighted averages of $PM_{2.5}$ more strongly than the domain-average estimates (Table 1). These findings suggest the effectiveness of $PM_{2.5}$ control strategies aimed at mitigating population exposure that reduce PCM emissions would be on par with those aimed at reducing sulfur emissions.

To improve this assessment, future work should focus on resolving key uncertainties relevant to the impact of controllable emissions on organic aerosol. Emissions of all the biogenic VOC precursors are uncertain. The preceding gas phase oxidation chemistry as well as the chemical and physical processes leading to SOA formation is not settled [36]. Some SOA-forming material has been shown to condense on inorganic aerosol [37] and organo-sulfur SOA compounds form [38], but these are not presently represented. CMAQ does not include SOA formation through nucleation because this process does not contribute appreciably to mass in the U.S. Further, there are sources of uncontrollable PCM emissions (e.g., vegetative detritus, pollen grain fragments, wind blown dust) not included currently in the emission estimates, but in certain areas these sources might be important [39]. In CMAQ, all organic aerosol is assumed to have the same effectiveness as a condensation site, but recent empirical evidence suggests not all organic material is equally miscible [40]. Including additional sources of uncontrollable PCM and simulating SOA condensation to inorganic aerosol would likely decrease the simulated sensitivity of biogenic SOA to PCM. However, missing species of intermediate volatility [23] of controllable origin (e.g., motor vehicles)

would increase the amount of biogenic SOA and this provides further confidence in the lower bound estimate of $1 \mu\text{g m}^{-3}$. Other SOA species have recently been reported to have an acidic influence [41] and including these pathways would increase the effect of SO_x and NH_3 emissions. Resolving these uncertainties is critical to improved understanding of the impact of controllable emissions on biogenic SOA.

It is frequently assumed that biogenic SOA can not be controlled by conventional air quality management practices because the precursor VOCs are naturally emitted. The simulations presented here demonstrate that biogenic SOA is substantially enhanced by controllable emissions, especially PCM and NO_x . For the purposes of air quality management, the methods demonstrated here can be used to more accurately partition SOA into a controllable and non-controllable fraction. Recognition by regulators that a substantial fraction of SOA is controllable regardless of biogenic or anthropogenic VOC origin will lead to more effective control strategies and improved air quality management plans.

DISCLAIMER

Although this paper has been reviewed by EPA and approved for publication, it does not necessarily reflect EPA's policies or views.

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Table 1. Changes in predicted PM_{2.5} due to controllable emissions.

	Population-weighted change (%)	Domain - average change (%)
RNMC	-1.8	-1.5
NO_x	-14	-7.2
PCM	-40	-28
SO_x	-39	-35
NH₃	-14	-8.6
Total	-82	-64

Note: Reported values are calculated at the surface and averaged from Aug. 18th – Sep. 4th, 2003. The percent change is calculated as the difference between predicted PM_{2.5} in the base case (total emissions) and the case where 100% of controllable emissions of each particular species is removed divided by the base case prediction.

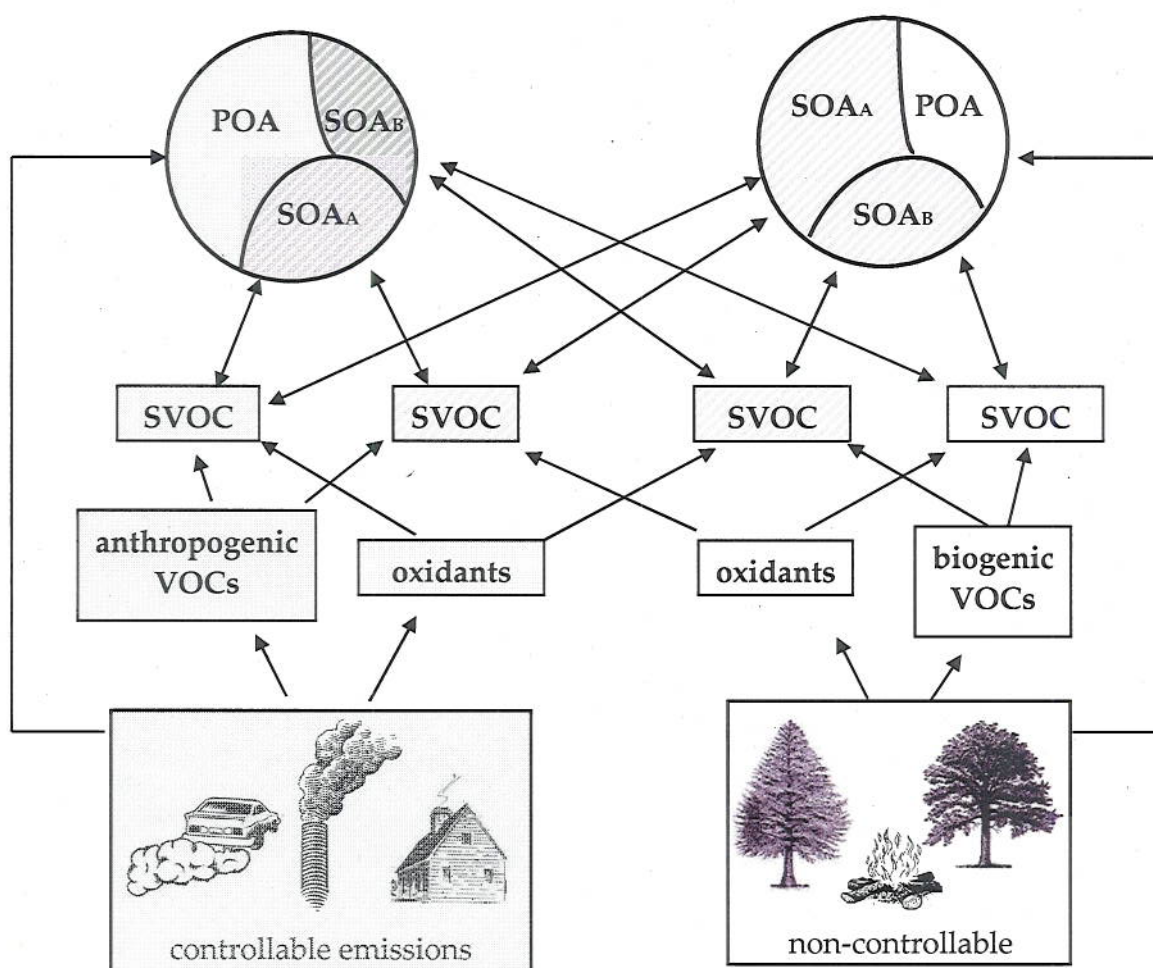


Figure 1. Biogenic SOA Production

Grey or grey-and-white shaded areas are potentially controllable fractions of SOA. Anthropogenic pollution enhances biogenic SOA through increasing oxidant and POM concentrations. Oxidants facilitate conversion of biogenic VOC to semi-volatile, condensing species and POM increases available sites for “semi-volatile” VOC condensation. Note: not shown are direct NO_x effects (e.g., high- NO_x or low NO_x pathways) and H^+ effects. SOA_A denotes anthropogenic SOA and SOA_B denotes biogenic SOA.

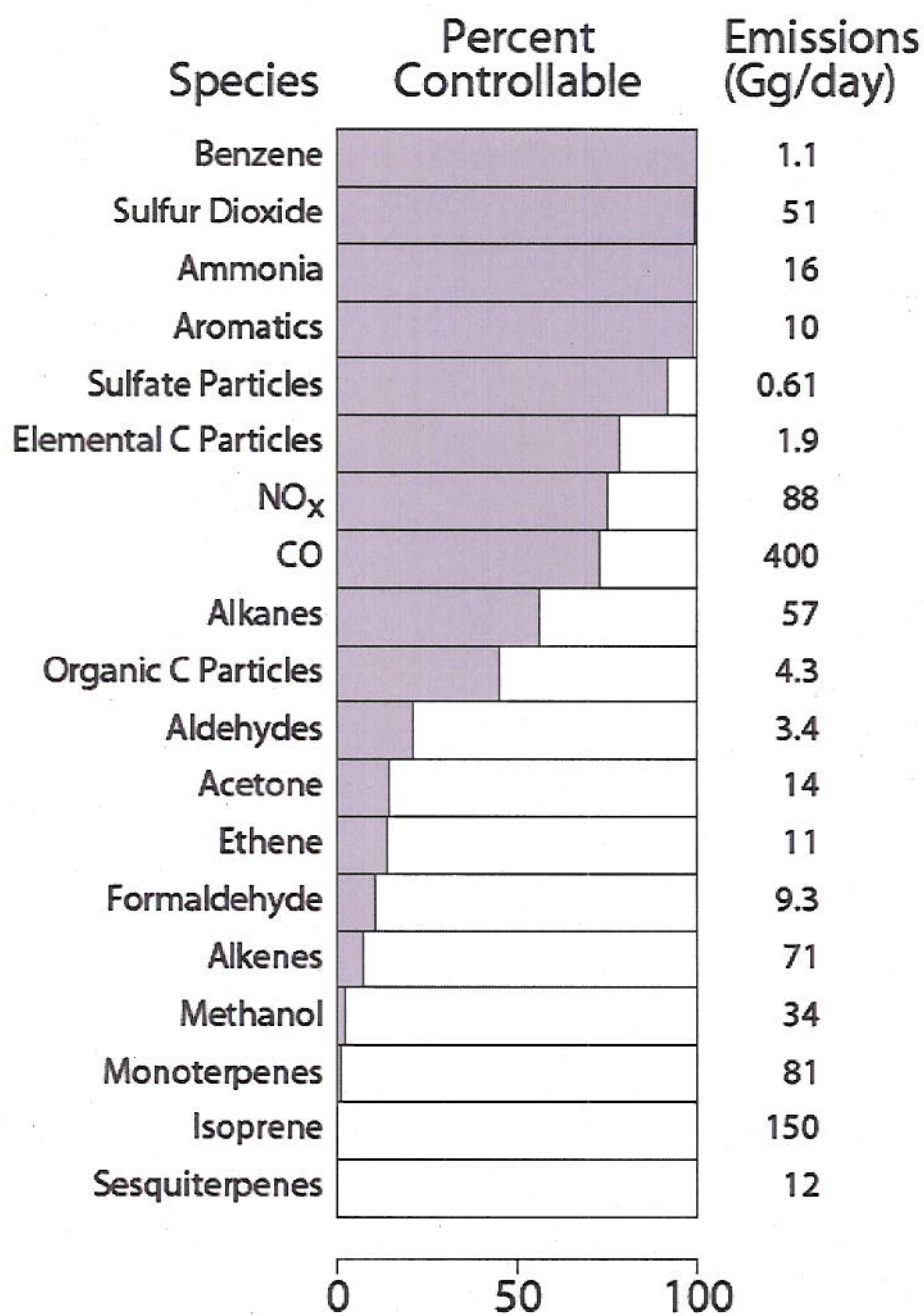


Figure 2: Percent of emitted species from controllable (grey) and uncontrollable (white) sources.

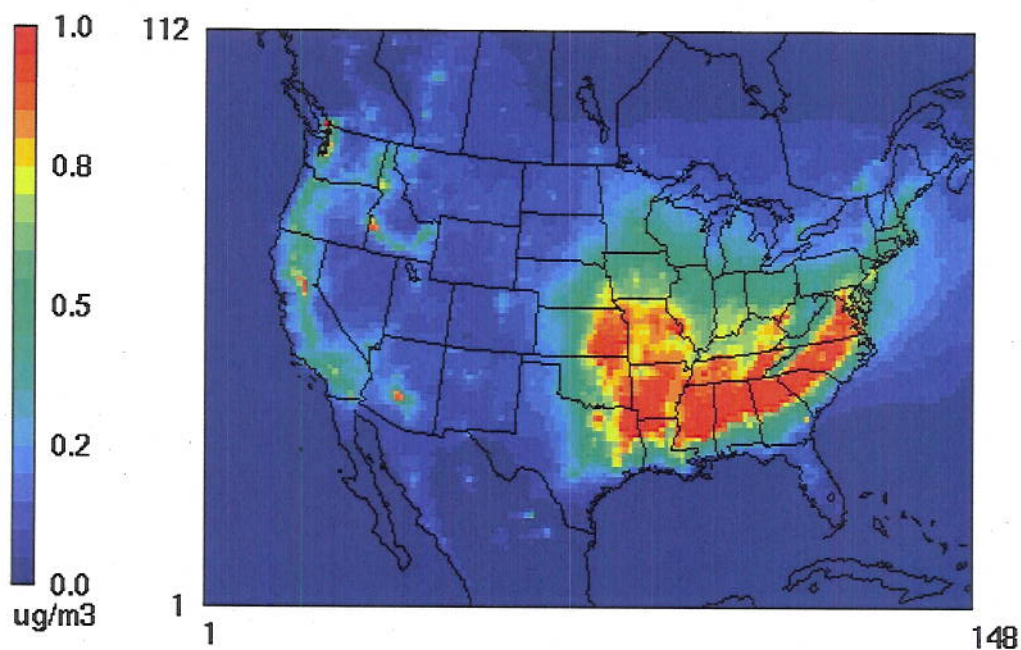


Figure 3a. Average concentration of biogenic SOA, at the surface, due to controllable emissions. Values are averaged from Aug. 18th – Sep. 4th, 2003.

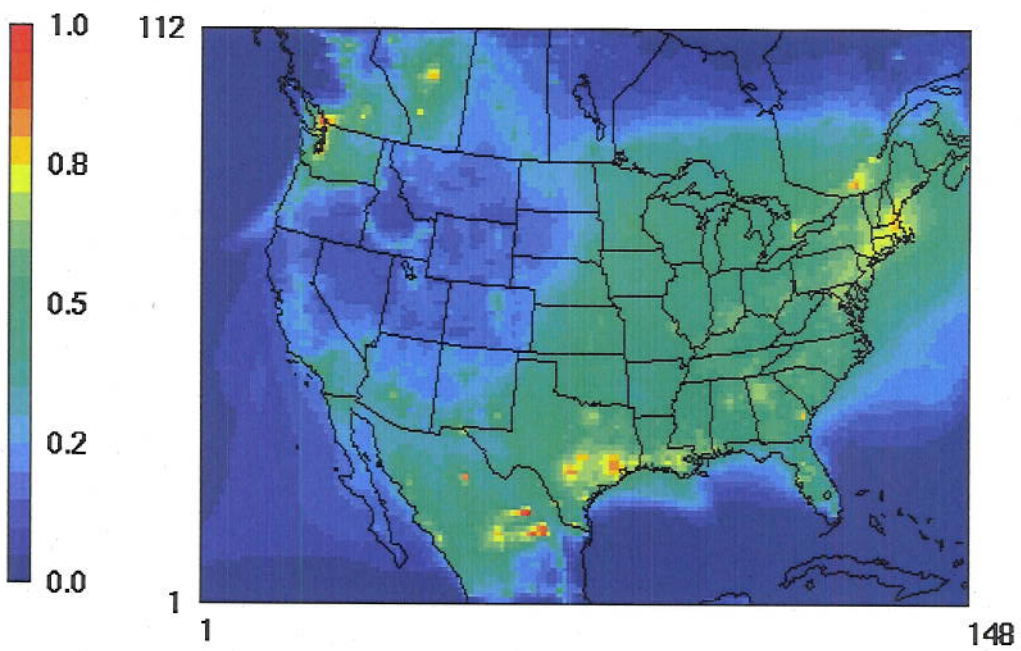


Figure 3b. Fraction of biogenic SOA, at the surface, due to controllable emissions. Values are averaged from Aug. 18th – Sep. 4th, 2003.

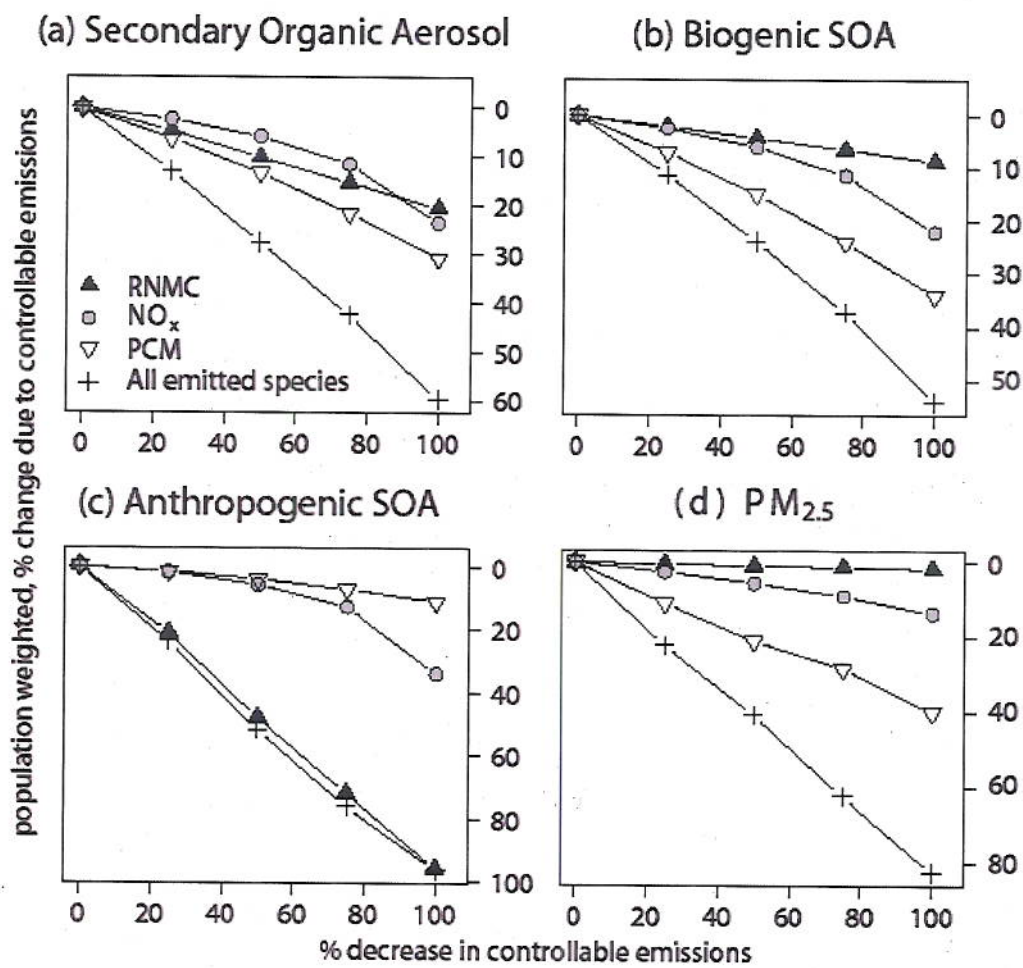


Figure 4: Change in population-weighted (a) total SOA, (b) biogenic SOA, (c) anthropogenic SOA and (d) PM_{2.5} due to reductions in controllable emissions