

# Secondary organic aerosol importance in the future atmosphere

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## Abstract

In order to investigate the secondary organic aerosol (SOA) response to changes in biogenic volatile organic compounds (VOC) emissions in the future atmosphere and how important will SOA be relative to the major anthropogenic aerosol component (sulfate), the global three-dimensional chemistry/transport model TM3 has been used. Emission estimates of biogenic VOC (BVOC) and anthropogenic gases and particles from the literature for the year 2100 have been adopted.

According to our present-day model simulations, isoprene oxidation produces  $4.6 \text{ Tg SOA yr}^{-1}$ , that is less than half of the  $12.2 \text{ Tg SOA yr}^{-1}$  formed by the oxidation of other BVOC. In the future, nitrate radicals and ozone become more important than nowadays, but remain minor oxidants for both isoprene and aromatics. SOA produced by isoprene is estimated to almost triple, whereas the production from other BVOC more than triples. The calculated future SOA burden change, from  $0.8 \text{ Tg}$  at present to  $2.0 \text{ Tg}$  in the future, is driven by changes in emissions, oxidant levels and pre-existing particles. The non-linearity in SOA formation and the involved chemical and physical feedbacks prohibit the quantitative attribution of the computed changes to the above-mentioned individual factors. In 2100, SOA burden is calculated to exceed that of sulfate, indicating that SOA might become more important than nowadays. These results critically depend on the biogenic emissions and thus are subject to the high uncertainty associated with these emissions estimated due to the insufficient knowledge on plant response to carbon dioxide changes. Nevertheless, they clearly indicate that the change in oxidants and primary aerosol caused by human activities can contribute as much as the change in BVOC emissions to the increase of the biogenic SOA production in the future atmosphere.

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**Keywords:** Secondary organic aerosol; Biogenic emissions; Global modeling; Future; Anthropogenic impact

## 1. Introduction

Vegetation emits large amounts of reactive carbon to the atmosphere that in the presence of  $\text{NO}_x$  and light can form ozone (Crutzen, 1995). Several BVOC

are also involved in SOA formation (Kanakidou et al., 2005). Both ozone ( $\text{O}_3$ ) and SOA are radiatively active constituents of the troposphere.  $\text{O}_3$  is a greenhouse gas and contributes to the global warming of the atmosphere, SOA are scattering solar radiation and can also act as cloud condensation nuclei affecting cloud properties and the hydrological cycle in the atmosphere (Kanakidou et al., 2005). Therefore, BVOC emitted by vegetation

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<b>Nomenclature</b>	SOAt SOA from terpenes oxidation
SOA( = SOAb + SOAa) secondary organic aerosols	SOAb( = SOAi + SOAt) SOA from biogenic VOC oxidation
SOAi SOA from isoprene oxidation	SOAa SOA from aromatic (anthropogenic VOC) oxidation

via procedures that are driven by climate (temperature and light) and vegetation type, form oxidation products that, in turn, affect climate (Guenther et al., 1995). This feedback can be more intensive than earlier thought, since recent findings have demonstrated the key role played by isoprene, the major single compound emitted by vegetation, and producing SOA (Claeys et al., 2004; Henze and Seinfeld, 2006). Note that according to global three-dimensional model estimates the SOA chemical present-day source is highly uncertain and ranges from 12 to 70 Tgyr<sup>-1</sup> (Kanakidou et al., 2005). The lowest estimates are based on the so-called two-product yield approach (Odum et al., 1997) to which the present study belongs. The highest estimates include detailed chemistry with a couple of lumped SOA products. According to this second group of estimates, the SOA burden nowadays already exceeds that of sulfate, the major individual anthropogenic aerosol component. It is an open question how the biosphere–climate–chemistry feedback (iLEAPS, 2005) will evolve in the future and, in particular, what the SOA composition will be, and how important will SOA be relative to sulfate. The present three-dimensional global model work aims to investigate SOA changes in the future atmosphere with particular focus on the sensitivity of the results to the future biogenic emission scenarios and points out topics where further research is needed.

## 2. Model description

The model used in the present study is the well-documented chemistry/transport model TM3 (Tsigaridis and Kanakidou, 2003; Tsigaridis et al., 2005, 2006 and references therein). The model has a horizontal resolution of 3.75° × 5° in latitude and longitude and 19 vertical hybrid layers from the surface to 10 hPa. Roughly, five layers are located in the boundary layer, eight in the free troposphere and six in the stratosphere. The model is driven by ECMWF ERA15 re-analysis meteorological data archive (Gibson et al., 1997, [http://www.ecmwf.](http://www.ecmwf.int/research/era/ERA-15)

[int/research/era/ERA-15](http://www.ecmwf.int/research/era/ERA-15)) updated every 6 h. The ozone boundary conditions are based on TOMS data convoluted with climatological vertical ozone profiles as described in Lelieveld and Dentener (2000).

The model uses a modified CBM4 chemical mechanism to describe the gas-phase tropospheric chemistry together with all main aerosol components, including the SOA formation and nitrate (Tsigaridis et al., 2006 and references therein). As suggested by Griffin et al. (1999), 32% of the emitted other reactive biogenic VOC (ORVOC) are SOA precursors, including compounds like sesquiterpenes and terpenoid alcohols. However, these numbers are highly uncertain and should be improved as soon as appropriate emission data will become available. In the model, the oxidation of isoprene, terpenes and aromatics by all three main oxidants (OH radicals, O<sub>3</sub> and NO<sub>3</sub> radicals) is taken into account in TM3. However, SOA formation is considered to occur from the oxidation paths of aromatics and isoprene by OH and O<sub>3</sub>, and for terpenes and ORVOC forming SOA from O<sub>3</sub> only, consistent with the experimentally derived parameters that have been adopted in the present study. Assuming that terpenes reactions with all oxidants are yielding SOA could increase the SOA global production by about 16% (Tsigaridis et al., 2006). A two-product model has been adopted to parameterize the SOA formation, taking into account the change in VOC/NO<sub>x</sub> conditions, as described in detail in Tsigaridis et al. (2006) and references therein. The recently experimentally derived effective enthalpy of vaporization of SOA formed from isoprene oxidation (Kleindienst et al., 2007) has been adopted in the present study. Due to lack of appropriate kinetic data, the dependence of SOA formation from isoprene on the VOC/NO<sub>x</sub> conditions has been taken into account by scaling the SOA yields from isoprene reported by Henze and Seinfeld (2006) on the SOA yields of α-pinene, as described by Tsigaridis et al. (2006) for β-pinene. Consideration of the VOC/NO<sub>x</sub> dependence of aerosol yields is reducing the SOA forming potential of the precursor VOC due to formation of more

volatile product distribution as VOC/NO<sub>x</sub> decreases (Kroll et al., 2005; Presto et al., 2005; Song et al., 2005). These assumptions are important for the model results and have to evolve in parallel with our understanding of the SOA chemical formation and the availability of appropriate data.

### 2.1. Present-day simulation

For the present day, we used a reference model simulation for the year 1990 as described by Tsigaridis et al. (2006) extended to include SOA<sub>i</sub> formation from isoprene oxidation as above explained. The emissions adopted are given in Table 1. Anthropogenic emissions, biomass burning emissions of gases, and the emissions of NO<sub>x</sub> from soils are based on EDGAR-HYDE 1.3 (van Aardenne et al., 2001). Methane surface concentrations are fixed to the year 1990 conditions following Hein et al. (1997). The ORCHIDEE dynamic global vegetation model (Lathière et al., 2006) computed monthly varying biogenic emissions for the year 1990 (isoprene, monoterpenes and other reactive biogenic VOC) that are used in the TM3 model. These global plant emissions are associated with

Table 1  
Present (year 1990) and future (year 2100) emissions adopted in the model

	Present	Future	Units
NO <sub>x</sub>	43.7	101.1	Tg N yr <sup>-1</sup>
Carbon monoxide	1051.8	1764.5	Tg yr <sup>-1</sup>
VOC <sup>a</sup>	316.6	659.6	Tg C yr <sup>-1</sup>
Formaldehyde	19.2	22.9	Tg yr <sup>-1</sup>
Isoprene	467.5	638.7	Tg C yr <sup>-1</sup>
Monoterpenes	137.1	300.8	Tg yr <sup>-1</sup>
ORVOC <sup>b</sup>	80.3	141.2	Tg yr <sup>-1</sup>
POA	44.4	81.8	Tg yr <sup>-1</sup>
BC	7.5	13.6	Tg yr <sup>-1</sup>
Aromatic VOC	15.8	45.9	Tg yr <sup>-1</sup>
DMS	18.5	18.5	Tg S yr <sup>-1</sup>
Anthropogenic SO <sub>2</sub>	73.0	139.1	Tg S yr <sup>-1</sup>
Volcanic SO <sub>2</sub>	9.2	9.2	Tg S yr <sup>-1</sup>
Ammonia	44.1	115.6	Tg yr <sup>-1</sup>
Sea-salt <sup>c</sup>	7804.2	7804.2	Tg yr <sup>-1</sup>
Dust <sup>c</sup>	1704.1	1704.1	Tg yr <sup>-1</sup>

<sup>a</sup>Excluding biogenic species line isoprene, monoterpenes and other reactive VOC (ORVOC) that produce SOA (32% of total ORVOC; Griffin et al., 1999).

<sup>b</sup>The fraction of reactive biogenic VOC (excluding monoterpenes and isoprene) that is able to produce SOA is notated as ORVOC, while the non-SOA producing ORVOC (68% of total ORVOC) are added to the VOC species.

<sup>c</sup>Both present and future emissions are based on the year 2000.

high uncertainty. For the case of isoprene, the global annual fluxes are estimated to range at present from 440 to 660 Tg C yr<sup>-1</sup>, depending on the driving variables used (Guenther et al., 2006). Lathière et al. (2006) present-day emission inventory adopted in the present study of 467.5 Tg C yr<sup>-1</sup> falls close to the low edge of that range. Dimethyl sulfide (DMS) emissions are driven by the ERA-15 ECMWF 10 m wind speed and surface sea-water DMS concentrations compiled by Kettle et al. (1999). Black carbon (BC) and primary organic aerosol (POA) emissions are based on the estimates of Ito and Penner (2005), which are similar with the average emissions given by Bond et al. (2004). Particulate nitrate and aerosol-associated water (AAW) are computed online with the equilibrium model EQSAM (Metzger et al., 2002). The AAW calculation is based only on the inorganic *n*-sulfate, ammonium and nitrate components of the total aerosol mass. The daily emissions of sea-salt and dust aerosol components compiled for the AEROCOM-B experiment for the year 2000 (Dentener et al., 2006) are adopted for the present study. Following the AEROCOM recommendations, we consider three modes for sea-salt (aitken, accumulation and coarse) and two for dust (accumulation and coarse) aerosol (Tsigaridis et al., 2006).

### 2.2. Future simulation

The year 2100 is used as reference year for the future atmosphere. However, the meteorological fields for the year 1990 used for the present-day simulation have been also applied for the Future simulation to avoid any impact of changes of the meteorological conditions in our results. Stratospheric ozone is forced based on the 1980 TOMS ozone column, assuming the optimistic scenario that the ozone hole will have recovered in the future atmosphere. The emissions used in this simulation are also given in Table 1. Anthropogenic surface emissions of gases are from Lelieveld and Dentener (2000). BVOC emissions in 2100 come from Lathière et al. (2005) and show a moderate increase of about 40% in isoprene emissions that is smaller than the factor of two estimated by the MEGAN model based on temperature changes (Guenther et al., 2006). The seasonality of biomass burning was kept the same as for the Present simulation, whereas the emission strength from Lelieveld and Dentener (2000) has been adopted. Methane surface concentration is assumed to be 85% higher than in

the year 1990, based on IPCC (2001). No changes in the surface spatial emissions distribution of POA and BC since 1990 have been assumed, whereas the global emissions are increased by 65% (IPCC, 2001). The non-consideration of the spatial distribution changes in emissions of methane and carbonaceous aerosols can be overlooked, due to the large uncertainty in the future emission projections. Lightning  $\text{NO}_x$  and DMS emissions were kept constant for consistency with the adopted meteorological fields, although we know that DMS emissions might be subject to change with climate (Gabric et al., 1996). However, the assumption of constant DMS flux is not expected to significantly affect our results. Indeed, according to Bopp et al. (2004), who performed coupled ocean–atmosphere simulations in a  $2 \times$  carbon oxide ( $\text{CO}_2$ ) scenario, only a small increase in the DMS burden is predicted accompanied by a very small decrease in sulfate burden. The authors explain this result by a possible shift of sulfate production to areas where wet deposition is more efficient. For aviation  $\text{NO}_x$  emissions, in the absence of any estimate for the year 2100, a 59% increase has been adopted, as suggested by IPCC (2001) for the year 2050.

### 2.3. Sensitivity on biogenic VOC emissions (FuturePBE)

Lathière et al. (2005) estimated the future BVOC assuming the same crop distribution and land use in the year 2100 as in the year 1990 due to the high uncertainty in several factors like the future crop yield improvement and the evolution of agricultural practices. The calculated change in emissions results from the  $\text{CO}_2$  increase in the atmosphere and the subsequent climate change. Even knowing the evolution of the vegetation distribution, the prediction of the future emissions from vegetation is difficult, since the plant fertilization effect due to  $\text{CO}_2$  increase might be compensated by smaller size of the plant stomata that will reduce the  $\text{CO}_2$  uptake (Murray, 1995). In particular, Arneth et al. (2007) suggest that inhibition of leaf metabolism due to the increasing  $\text{CO}_2$  could offset the stimulation of isoprene emissions. Therefore, in order to investigate uncertainties in the future biogenic emissions, an additional simulation has been performed similar with the above-described Future one, but using the BVOC emissions of the present atmosphere. This simulation is further called FuturePBE (Future, Present Biogenic Emissions).

### 2.4. Temperature effect on partitioning (FutureT)

Since TM3 is a chemistry/transport model, it is not possible to examine the changes in climate, like those in wind speed and precipitation that are expected to occur in the future atmosphere and to affect both primary natural emissions and wet removal of particles. Nevertheless, SOA occurrence in the atmosphere is highly affected by temperature (Tsigaridis and Kanakidou, 2003; Tsigaridis et al., 2005). This impact occurs not only via the changes in VOC emissions (effect taken into account in the previously described Future simulation) but also via changes in the atmospheric reaction rates and in the gas-to-particle partitioning. In order to investigate the changes in SOA partitioning due to a potential tropospheric temperature increase in the future, an additional simulation similar with the Future one has been performed. For this, the temperature has been arbitrarily modified as follows: in the boundary layer the temperature has been increased by 2 K, in the free troposphere by 1 K and in the lower stratosphere the temperature was kept the same. This simulation is further called FutureT simulation (Future, Temperature). The choice of the 2 K increase in the boundary layer is based on the average of the different scenarios estimate of the temperature increase from nowadays to the year 2100 reported by IPCC (2001). In this model run, that increase affects only the temperature dependence of the partitioning coefficient of the SOA gaseous precursors and not the atmospheric reaction rates or any other temperature-dependent process.

### 2.5. Temperature effect on chemistry and partitioning (FutureTR)

To further investigate potential chemical feedbacks in changes with air temperature, an additional simulation has been performed. For this, the temperature changes described earlier also affect the temperature dependence of the chemical reactions. Since the rate of the oxidation of BVOC is enhanced with increased temperature, it is expected that the production of semi-volatile SOA precursors will be faster, if oxidant levels are the same, or increased. The net effect on the semi-volatile SOA precursor levels due to the changes in the partitioning coefficients, in the oxidants and in the reaction rates of VOC oxidation, resulting from the increase in temperature, has been investigated by this

simulation, further called FutureTR (Future, Temperature + Reactions).

### 2.6. Effect of oxidants and primary carbonaceous aerosol emissions (FuturePC)

Distinguishing the effect of oxidant levels on the calculated SOA enhancement in the future from that of the increase of aerosol concentrations is not an easy task, since increased oxidants will alter the chemical composition of aerosols, and thus their lifetime. Increased ozone will result to faster conversion of aerosols from hydrophobic to hydrophilic and faster oxidation of  $\text{SO}_2$  to sulfate aerosols. In an effort to separate the chemical effects from those due to changes in primary emissions of aerosols, we made an additional simulation, similar to the Future one, but keeping the primary carbonaceous aerosol emissions at the present-day levels. This simulation is further called FuturePC (Future, Present Carbonaceous). Its results have to be treated as lower limits for the primary aerosol impact on the future SOA levels,

since important feedbacks are involved as above outlined.

## 3. Results and discussion

### 3.1. SOA concentration change

The annual mean surface concentration of SOA in the Present simulation is shown in Fig. 1a, where maximum SOA concentrations are calculated above source regions. This figure highlights the importance of boreal and tropical forests on SOA formation. The calculated SOA distributions are however subject to the uncertainties in the modeled oxidant fields that can lead to differences of at least 20% in the global estimates of SOA chemical production (Myriokefalitakis et al., 2007). In the FuturePBE simulation, an increase in the SOA concentrations is calculated (Fig. 1b) due to the increased anthropogenic primary and secondary inorganic aerosols and oxidant levels caused by anthropogenic activities following the IS92a IPCC scenario that corresponds to about 20% burden increase in the model domain.

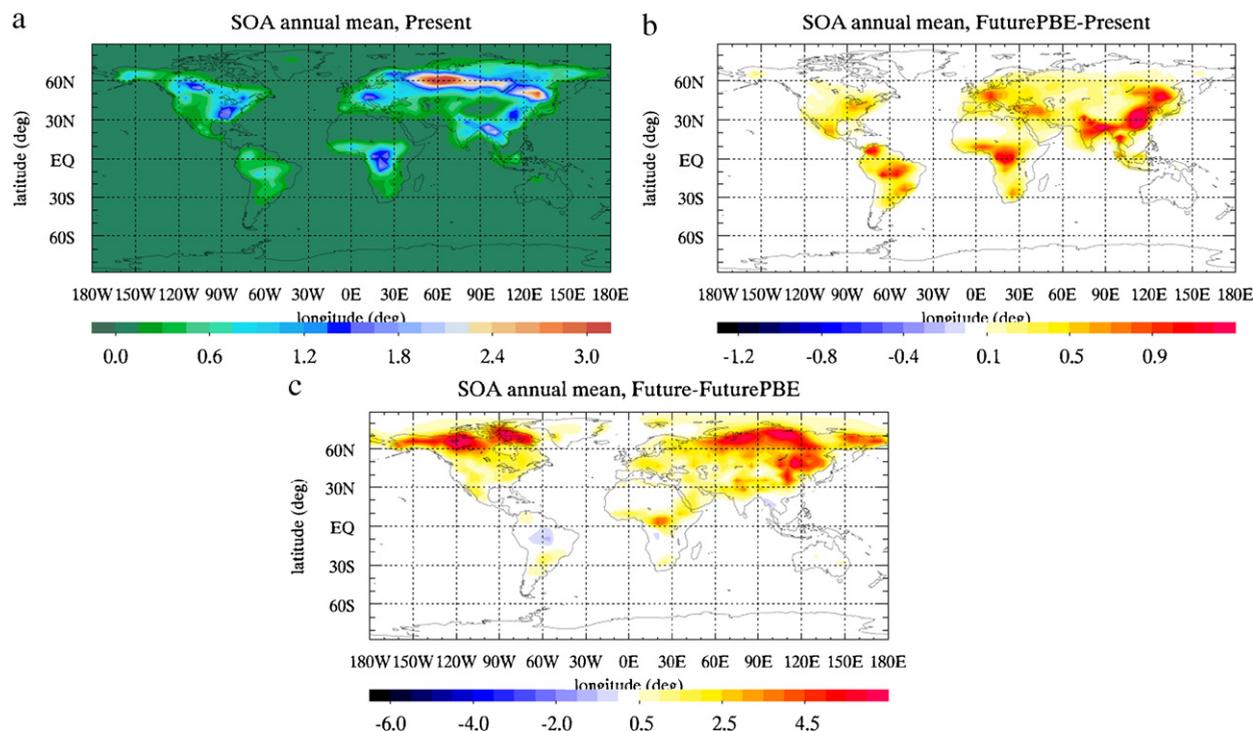


Fig. 1. Annual mean SOA concentration in the present atmosphere (a), difference of SOA annual mean concentration in the FuturePBE simulation when compared to the Present one (b) and difference of SOA annual mean concentration in the Future simulation when compared to the FuturePBE one (c). Warm colors indicate increase in the Future (or FuturePBE) simulation, while cold colors indicate decrease. All units are  $\mu\text{g m}^{-3}$ . Notice the difference in the scales.

Taking into account the enhanced biogenic emissions for the Future simulation, a much stronger increase in the SOA concentrations is calculated (Fig. 1c) that corresponds to a two-fold burden increase. This change presents an interesting pattern when comparing the Future with the FuturePBE simulations; over boreal forests SOA is more abundant in the Future simulation, while over tropical forests (South America, Africa and Indonesia) is less abundant. This is attributed to the predicted by Lathière et al. (2006) future decrease in the tropical VOC emissions, for all BVOC, and especially over Amazon that is caused by a reduction of both the coverage of tropical trees and leaf area index. On the other hand, temperate and boreal forests expand in the future scenario of Lathière et al. (2006), leading to higher BVOC emissions from these forests in the future.

### 3.2. SOA composition change

Fig. 2 shows the contribution of SOAi to the SOAb distribution for the Present simulation and the changes calculated for the Future simulation. The SOA produced from isoprene oxidation appears to contribute to the total SOA by about 30% over the oceans. Note however that the SOA concentrations in these regions are very low. In addition, in our simulation a potentially important oceanic source of isoprene (Bonsang et al., 1992; Palmer and Shaw, 2005) is neglected. Over tropical forests the model calculates that SOAi significantly contributes to the total SOAb mass, though over boreal forests the contribution of SOAt highly dominates. This reflects both the chemical composition of the emissions and the dominant oxidant in these regions.  $O_3$  is more abundant in the northern

hemisphere than in tropical forests. In the future, the model simulates almost everywhere a decrease in the contribution of SOAi to SOAb, which is attributed to the stronger increase of SOAt precursor emissions (100%) compared to isoprene emissions (37%). An exception to this general pattern is areas of intense isoprene emissions like Central America, the Amazon basin and central Africa.

The relative contribution of SOA that comes from anthropogenic aromatic precursor VOC (SOAa) at present is shown in Fig. 3, together with the change in its contribution calculated by the model for the Future simulation. According to these model calculations, SOAa from anthropogenic VOC gas-phase oxidation is minor contributor to the total SOA except downwind of the industrialized areas of the northern hemisphere, where the SOA concentrations are very low. The contribution of SOAa is calculated to increase in the future atmosphere. Our results are consistent with  $^{14}C$  measurements and regional modeling over Europe (Simpson et al., 2007). Note however that our results rely on the actual kinetic knowledge on SOA formation from anthropogenic VOC. Recent field experiments (de Gouw et al., 2005; Volkamer et al., 2006; Takegawa et al., 2006) suggest that SOAa might be more important than previously thought.

### 3.3. Temperature effect on SOA production

The comparison between simulations FutureT and Future shows that the reduction in the partitioning coefficients due to temperature increase in the future leads to slightly lower SOA concentrations in the boundary layer and the lower troposphere in the FutureT scenario. The calculated

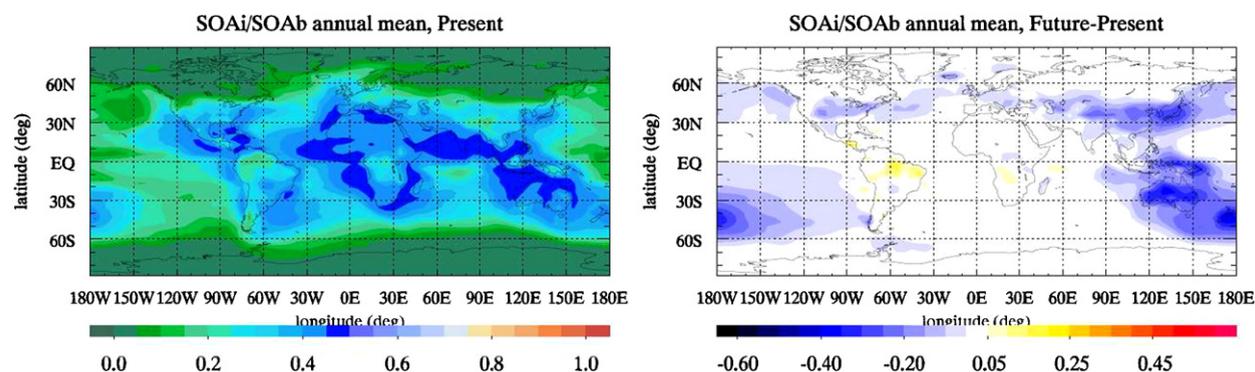


Fig. 2. Annual mean ratio of SOAi over SOAb for the present atmosphere (left) and corresponding change in the Future simulation (right). Warm colors indicate increase in the future atmosphere, while cold colors indicate decrease.

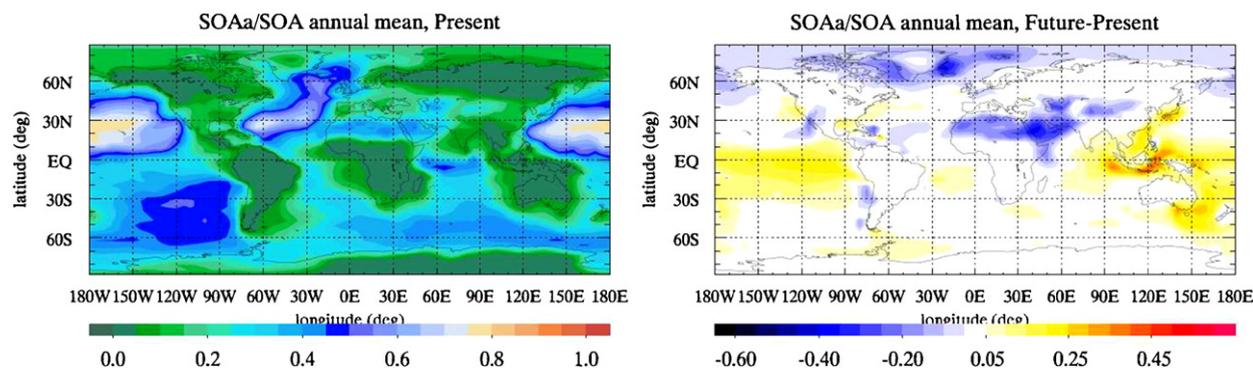


Fig. 3. Annual mean ratio of SOAa over SOA for the present atmosphere (left) and corresponding change in the Future simulation (right). Warm colors indicate increase in the future atmosphere, while cold colors indicate decrease.

increase by a factor of 3.9 of the SOA burden in the boundary layer for the Future simulation since nowadays is still important in the FutureT simulation (factor of 3.5). However, this increase is suppressed compared to the Future case due to increased evaporation of the semi-volatile SOA compounds, leading to an 11% decrease in the tropospheric SOA burden in the FutureT simulation compared to the Future.

Assuming that the temperature increase, in addition to partitioning, also affects all reaction rates of the gas-phase chemistry (FutureTR), a general increase in oxidant levels is calculated over continental areas and a decrease above oceans. This oxidant increase close to VOC source regions affects the production rate of the semi-volatile SOA precursors and further decreases the tropospheric SOA burden by 10%. Therefore, temperature changes are expected to affect the SOA abundance not only due to changes in the evaporation rates of the SOA compounds, but also due to chemistry.

### 3.4. Feedback mechanisms

The non-linearity in SOA formation and the involved chemical and physical feedbacks prohibit the quantitative attribution of the computed changes to the various individual factors driving them. In particular, the increased oxidant levels in the future atmosphere will faster oxidize hydrophobic to hydrophilic aerosol. These result from both increased anthropogenic and natural emissions. Increased oxidants will also produce more sulfate aerosol (that in addition is enhanced due to the increase in  $\text{SO}_2$  emissions) as can be seen in Table 1 when comparing Future with present-day simulations. About 15% of this increase in sulfate

chemical production in the Future simulation is due to the oxidant changes induced by the BVOC emissions (comparing Future and FuturePBE simulations, Table 1). These changes will affect the conversion of carbonaceous aerosols from hydrophobic to hydrophilic, and thus their lifetime. Increased oxidants and sulfate production lead to shorter lifetime for carbonaceous aerosols. This effect is restricting the SOA occurrence in the atmosphere whereas on the opposite the increased oxidants are enhancing the chemical production of SOA gas-phase precursors. Thus, only 6% of the SOA chemical production future change is the net result of the increased carbonaceous primary emissions (comparing Present, Future and FuturePC simulations).

### 3.5. Importance of *nss*-sulfate vs. SOA

Fig. 4 shows the importance of *Nss*-sulfate aerosol compared to the total SOA, which is mostly biogenic. *Nss*-sulfate is mainly of anthropogenic origin, with natural contributions being volcanic emissions and oxidation of marine DMS. SOA contribution dominates above forested areas, both tropical and boreal, and also to the South Pole where both SOA and *nss*-sulfate are very low. In the Future simulation, the importance of *nss*-sulfate decreases in most regions due to the 58% increase of the BVOC emissions, which are SOA precursors, and to the increase of pre-existing particles (about a factor of 2.3) and oxidizing agents, most notably ozone (about 50%). On the other hand, based on the IS92a IPCC scenario,  $\text{SO}_2$  emissions will increase up to 2050 and then will start to decline reaching 90% higher than present levels in 2100. However, these emissions cannot counterbalance

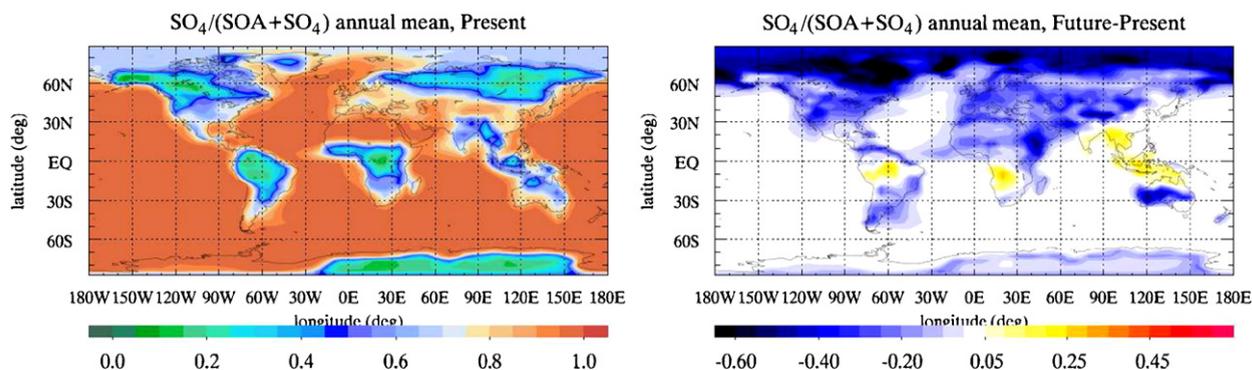


Fig. 4. Annual mean ratio of sulfate over the sum of sulfate + SOA for the present atmosphere (left) and corresponding change in the Future simulation (right). Warm colors indicate increase in the future atmosphere, while cold colors indicate decrease.

the total SOA increase. Interestingly, above-forested regions in the tropics, sulfate aerosol appears to gain importance relative to SOA in the future. This is because although primary carbonaceous aerosol emissions increase, the biogenic emissions decrease due to reduced forest coverage (as discussed in Section 3.1) and thus SOA is reduced. The resulting SOAb reduction is not compensated by the enhancement of SOAa.

### 3.6. Global budgets

According to our present-day model simulations, isoprene oxidation produces  $4.6 \text{ Tg SOA yr}^{-1}$ , that is less than half the  $12.2 \text{ Tg SOA yr}^{-1}$  formed by the oxidation of other BVOC, taking into account the dependence of SOA yields on the VOC/NO<sub>x</sub> ratio. The model calculates that at present, on an annual base OH is responsible for about 81%, 14% and almost 100% of the oxidation of isoprene, terpenes and aromatics, respectively. Ozone accounts for about 16% and 81% of isoprene and terpene oxidation. The remainder is consumed by NO<sub>3</sub> radicals. These results are subject to the uncertainty of the calculated oxidant fields, which vary significantly between models (Stevenson et al., 2006). In the future, NO<sub>3</sub> radicals and O<sub>3</sub> become more important than today, but remain minor oxidants for both isoprene and aromatics; SOA produced by isoprene is estimated to almost triple ( $12.6 \text{ Tg yr}^{-1}$ ) in the Future simulation, whereas the production from other BVOC more than triples ( $40.4 \text{ Tg yr}^{-1}$ ). These changes reflect both the different emission changes of isoprene compared to the other VOC (Table 1) and the above-discussed oxidant level changes from the present to the future atmosphere. SOAa production, also affected by the

VOC/NO<sub>x</sub> ratio, is calculated to increase from  $1.8 \text{ Tg yr}^{-1}$  at present to  $5.5 \text{ Tg yr}^{-1}$  in the future. The future SOA burden changes are driven by changes in emissions, oxidant levels and pre-existing particles, while the temperature changes impact on reaction rates and partitioning of gases to the particulate phase has a minor effect (Table 2). These simulations do not consider additional changes in aerosol removal by precipitation that is expected to increase in a warmer climate (Liao et al., 2006). The emission scenario adopted by our model indicates that anthropogenic SO<sub>2</sub> emissions will increase in the future by about 90% while DMS fluxes remain constant, resulting in a burden increase of sulfate by 68%. Liao et al. (2006) calculated that sulfate will be reduced by about 3% in 2100, reflecting the 1% decrease in the sum of industrial SO<sub>2</sub> and DMS emissions adopted in their modeling study. For SOA, our calculations indicate a factor of 2.5 increase in the SOA burden in the future since present time (increase in monoterpenes emissions of 120%) while Liao et al. (2006) estimate an increase by a factor of 1.5 (resulting from a 58% increase in monoterpenes emissions). Our model additionally includes the contribution of isoprene to the total biogenic SOA. These results are subject to high uncertainty in the input biogenic emissions due to the insufficient knowledge on plant response to CO<sub>2</sub> changes (Arneeth et al., 2007). Nevertheless, they clearly indicate that the change in oxidants and primary aerosol caused by human activities is the major contributor to the increase of the biogenic SOA production in the future atmosphere. Similar response for SOA was also found for the pre-industrial-to-present changes (Kanakidou et al., 2000; Tsigaridis et al., 2006).

Table 2  
Burden and chemical production of species (SOA<sub>x</sub> and SO<sub>4</sub>)

		SOAi	SOAt	SOAa	SOA	SO <sub>4</sub>
Chemical production (Tgyr <sup>-1</sup> )	Present	4.6	12.2	1.8	18.6	84.9
	Future	12.6	40.4	5.5	58.5	140.5
	FuturePBE	8.3	14.2	5.5	28.0	132.8
	FutureT	11.6	36.8	5.3	53.7	140.5
	FutureTR	10.9	33.4	5.1	49.4	141.3
	FuturePC	11.4	39.2	5.4	56.0	140.5
Burden (Tg)	Present	0.08	0.69	0.04	0.82	1.05
	Future	0.24	1.65	0.13	2.02	1.75
	FuturePBE	0.12	0.71	0.13	0.95	1.69
	FutureT	0.22	1.58	0.13	1.94	1.75
	FutureTR	0.21	1.51	0.13	1.85	1.76
	FuturePC	0.22	1.63	0.13	1.98	1.75

#### 4. Conclusions

Hydroxyl radical is calculated to be the dominant oxidant for isoprene degradation and almost the exclusive oxidant for aromatics at present, while for terpenes the main oxidizing agent is ozone followed by OH and NO<sub>3</sub> radicals. In the future, NO<sub>3</sub> radicals and O<sub>3</sub> become more important than today, but still remain minor oxidants for both isoprene and aromatics. According to our model calculations, SOA burden (0.8 Tg at present) more than doubles in 2100. To this increase, isoprene, other biogenic VOC and aromatics contribute by 13%, 80% and 7%, respectively. Interestingly, while at present SOA is almost as abundant as *nss*-sulfate, in the future the model calculates higher SOA burden (that is mostly SOAb) than *nss*-sulfate. The burden increase of *nss*-sulfate can be directly regulated by reduction of anthropogenic sulfur emissions, while for SOAb this can occur via controlling ozone precursors and primary particle emissions.

Our model results neglect any potential oceanic source of SOA. They are subject to high uncertainties related to the future biogenic VOC emissions since it is still an open question how the climate change will affect them in terms of intensity, chemical composition and spatial distribution. The SOA chemical composition and formation pathways in the atmosphere are poorly understood, their dependence on NO<sub>x</sub> conditions is not sufficiently documented and the SOA chemical and physical properties like chemical reactivity, solubility and volatility.

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