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**Changes of  
emissions and  
temperature in  
Europe**

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# Response of fine particulate matter concentrations to changes of emissions and temperature in Europe

**A. G. Megaritis<sup>1,2</sup>, C. Fountoukis<sup>2</sup>, P. E. Charalampidis<sup>3</sup>, C. Pilinis<sup>3</sup>, and S. N. Pandis<sup>1,2,4</sup>**

<sup>1</sup>Department of Chemical Engineering, University of Patras, Patras, Greece

<sup>2</sup>Institute of Chemical Engineering Sciences (FORTH/ICE-HT), Patras, Greece

<sup>3</sup>Department of Environment, University of the Aegean, University Hill, 81100, Mytilene, Greece

<sup>4</sup>Department of Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA 15213, USA

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Correspondence to: S. N. Pandis (spyros@andrew.cmu.edu)

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## Abstract

PMCAMx-2008, a three dimensional chemical transport model (CTM), was applied in Europe to quantify the changes in fine particle ( $PM_{2.5}$ ) concentration in response to different emission reductions as well as to temperature increase. A summer and a winter simulation period were used, to investigate the seasonal dependence of the  $PM_{2.5}$  response to 50 % reductions of  $SO_2$ ,  $NH_3$ ,  $NO_x$ , anthropogenic VOCs and anthropogenic OA emissions and also to temperature increases of 2.5 and 5 K. Reduction of  $NH_3$  emissions seems to be the most effective control strategy for reducing  $PM_{2.5}$ , in both periods, resulting in a decrease of  $PM_{2.5}$  up to  $5.1 \mu g m^{-3}$  and  $1.8 \mu g m^{-3}$  (5.5 % and 4% on average) during summer and winter respectively, mainly due to reduction of  $NH_4NO_3$  (20 % on average in both periods). The reduction of  $SO_2$  emissions decreases  $PM_{2.5}$  in both periods having a significant effect over the Balkans (up to  $1.6 \mu g m^{-3}$ ) during summer, mainly due to decrease of sulfate (30 % on average over the Balkans). The anthropogenic OA control strategy reduces total OA by 15 % during winter and 8 % in the summer. The reduction of total OA is higher in urban areas close to its emissions sources. A slight decrease of OA (8 % in summer and 4 % in winter) is also predicted after a 50 % reduction of VOCs emissions due to the decrease of anthropogenic SOA. The reduction of  $NO_x$  emissions reduces  $PM_{2.5}$  (up to  $3.4 \mu g m^{-3}$ ) during the summer, due a decrease of  $NH_4NO_3$ , causing although an increase of ozone concentration in major urban areas and over Western Europe. Additionally, the  $NO_x$  control strategy actually increases  $PM_{2.5}$  levels during the winter. The increase of temperature results in a decrease of  $PM_{2.5}$  in both periods over Central Europe, mainly due to a decrease of  $NH_4NO_3$  during summer (18 %) and fresh POA during winter (35 %). Significant increases of OA are usually predicted during summer due mainly to the increase of biogenic VOC emissions. On the contrary, OA is predicted to decrease in the winter due to the dominance of fresh POA reduction and the small biogenic SOA contribution to OA. The resulting increase of oxidant levels from the temperature rise lead to an increase of sulfate levels in both periods, mainly over North Europe and the Atlantic

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Ocean. The substantial reduction of PM<sub>2.5</sub> components due to emissions reductions of their precursors in conjunction with significant changes of PM after increasing the temperature indicate that both emissions and temperature need to be of significant concern for improving air quality.

## 1 Introduction

Atmospheric particles have adverse effects on human health and have been implicated in various air quality problems such as the formation of acid rain and acid fogs (Burtraw et al., 2007), visibility reduction (Seinfeld and Pandis, 2006) and changes of the energy balance of the planet. Fine particulate matter less than 2.5 µm in size (PM<sub>2.5</sub>), ozone, and other pollutants are subjected to a complex series of common emissions, meteorological processes and photochemical production pathways. Consequently changes in emissions of one pollutant can lead to changes in the concentrations of other pollutants. In addition, changes in meteorological conditions such as temperature could also influence the concentration and distribution of air pollutants through a variety of direct and indirect processes, including the modification of biogenic emissions (Constable et al., 1999), the change of chemical reaction rates, changes in mixing heights that affect vertical dispersion of pollutants, and modifications of synoptic flow patterns that govern pollutant transport.

Several studies have tried to quantify how the emissions changes of one pollutant can lead to changes in the concentration of others and to estimate these source-receptor relations in Europe (Simpson, 1995; Sutton et al., 2003; Sillman et al., 2003; Erisman et al., 2003; Jonson et al., 2006; Vautard et al., 2006; Berglen et al., 2007; Konovalov et al., 2008; Fagerli et al., 2008). Lövblad et al. (2004) investigated trends of the emissions of sulfur dioxide, nitrogen oxides and ammonia in Europe and the corresponding response of the major inorganic fine particulate components over the past 2 decades. They observed that between 1980 and 2000, SO<sub>2</sub> emissions decreased approximately 70 % while sulfate concentrations decreased around 50 %. Emissions of

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nitrogen oxides and ammonia also decreased 25 % and 20 % respectively with a non-linear response of ammonium nitrate. De Meij et al. (2009) applied a three-dimensional chemical transport model (CTM) over Northern Italy and estimated the impact of 50 % emission reductions of NO<sub>x</sub>, PM<sub>2.5</sub>, SO<sub>2</sub>, VOC and NH<sub>3</sub>, for different source sectors, on O<sub>3</sub> and PM<sub>2.5</sub> concentrations. This study showed that the 50 % reduction of NO<sub>x</sub> and PM<sub>2.5</sub> emissions coming from road transport and non-industrial combustion plants is the most effective control strategy for reducing PM<sub>2.5</sub> levels over Po Valley, leading to an average decrease of 1–6 μg m<sup>-3</sup> and 1–4 μg m<sup>-3</sup> respectively. Jonson et al. (2001) studied the impact on ozone and ozone precursors over Europe due to the combination of global and regional changes in anthropogenic emissions. Their results showed that the expected reductions in the emissions of ozone precursors in Europe from 1996 to 2010 would lead to reductions of ozone, during summer, in southern, central and eastern regions of Europe. However, in Northern and Western Europe ozone levels were predicted to increase. This increase was primarily attributed to reductions in European emissions in areas dominated by high NO<sub>x</sub> levels. Thunis et al. (2007) conducted an intercomparison modeling study at different scales, over several European cities in order to predict the response of O<sub>3</sub> and PM in several emission scenarios for 2010. The authors focused on the importance of fine scale modeling for O<sub>3</sub> and PM related to urban centers. A similar study was carried out by van Loon et al. (2007) covering the whole European continent. Several studies, investigating the response of ozone and fine particulate matter to changes of the major precursor emissions, have focused on different regions of North America (Russell et al., 1986; Jiang et al., 1996; Meng et al., 1997; Tonnesen, 1998; Chock et al., 1999; Stein and Lamb, 2000, 2002; Blanchard et al., 2001, 2007; Pun and Seigneur, 2001; Ngyen and Dabdub, 2002; Mueller et al., 2004; Kleeman et al., 2005; Tsimpidi et al., 2008; Makar et al., 2009). Tsimpidi et al. (2007) applied a three-dimensional CTM, PMCAMx, over the Eastern US to evaluate the response of PM<sub>2.5</sub> mass concentrations to changes in SO<sub>2</sub> and NH<sub>3</sub> emissions for a summer and a winter period. They found that NH<sub>3</sub> emission control during winter is an effective control strategy, while in the summer reductions in SO<sub>2</sub> yield the

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largest reduction of PM<sub>2.5</sub>. Similar results for NH<sub>3</sub> reductions were reported by Pinder et al. (2007) who calculated that the NH<sub>3</sub> control strategy would be particularly cost effective in the winter.

The role of climate change on the concentrations of ozone, particulate matter and other pollutants and the impact of various climate change scenarios on air quality over Europe has been the subject of several studies (Tuovinen et al., 2002; Szopa et al., 2006; Forkel et al., 2007; Giorgi et al., 2007; Jacob et al., 2009; Carvalho et al., 2010). Ordonez et al. (2005) studied the influence of the meteorological variability on the daily maximum ozone concentrations at sites in Switzerland, suggesting that the temperature and the morning solar radiation were the variables that accounted for most of the meteorological variability during summer. A regional CTM was used by Meleux et al. (2007) to investigate the effects of climate change on summer ozone levels over the European region, under different IPCC emissions scenarios (IPCC, 2007). Their study showed a substantial increase of ozone concentrations during summer in future climate conditions, mostly due to higher temperatures and reduced cloudiness and precipitation. They also addressed the importance of temperature-driven increase in biogenic emissions on ozone production. Langner et al. (2005) used a regional CTM to assess the effects of climate change on near-surface ozone concentrations and sulphur and nitrogen deposition over Europe under different greenhouse gas emission scenarios. Their simulations indicated a substantial impact of climate change on both deposition of oxidized nitrogen and concentrations of surface ozone, with a significant increase of ozone over Southern and Central Europe and a decrease in Northern Europe. In addition, Forkel and Knocke (2006) used an online regional coupled atmospheric-chemistry model in order to investigate possible effects of global climate change on the near-surface concentrations of photochemical compounds in Southern Germany. They showed a 10% increase on average daily maximum ozone concentrations during summer mainly due to an increase of temperature and biogenic emissions along with a decrease of cloud water and ice.

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The main objective of this study is to quantify how fine particulate matter ( $PM_{2.5}$ ) responds to emissions changes of its precursors and how a change on temperature would influence its concentrations. For this purpose we apply a three-dimensional CTM (PMCAMx-2008) over Europe, which can accurately and efficiently describe the physical and chemical transformations of gas and aerosol species. The PMCAMx-2008 model includes state-of-the-art organic and inorganic aerosol modules which make it well suited for the purpose of this study. In addition, the model uses newly developed emissions inventories from both anthropogenic and biogenic sources in order to better understand the effectiveness of each control strategy on  $PM_{2.5}$  levels and to predict correctly the respective response. The PMCAMx-2008 performance has already been evaluated (Fountoukis et al., 2011) against high time resolution aerosol mass spectrometer (AMS) ground measurements taken from various sites in Europe as well as airborne measurements from an aircraft field campaign over Europe (Morgan et al., 2010) during the European Aerosol Cloud Climate and Air Quality Interactions (EU-CAARI) intensive periods (Kulmala et al., 2009).

The remainder of this paper is organized as follows. First, there is a brief description of PMCAMx-2008 and the details of its application in the European domain. In the next section, the temporal and spatial characteristics of the effectiveness of  $NH_3$ ,  $SO_2$ ,  $NO_x$ , anthropogenic VOCs and anthropogenic OA emissions reductions on the concentration of the  $PM_{2.5}$  components are discussed. The response of the individual OA components to these emissions scenarios is also analyzed. The effects of temperature change are quantified in the following section. Finally the effectiveness of each emissions reduction scenario as well as the relative significance of the temperature change on  $PM_{2.5}$  levels, for the different periods are discussed.

## 2 The PMCAMx-2008 CTM

### 2.1 Model description

PMCAMx-2008 (Murphy and Pandis, 2009; Tsimpidi et al., 2010; Karydis et al., 2010) uses the framework of the CAMx air quality model (ENVIRON, 2003) which simulates the processes of horizontal and vertical advection, horizontal and vertical dispersion, wet and dry deposition, and gas-phase chemistry. The gas-phase chemistry is described by the SAPRC99 mechanism (Carter, 2000; Environ, 2003) which includes 211 chemical reactions of 56 gases and 18 radicals. Three detailed aerosol modules are used: inorganic aerosol growth (Gaydos et al., 2003; Koo et al., 2003), aqueous phase chemistry (Fahey and Pandis, 2001) and SOA formation and growth (Koo et al., 2003). These modules employ a sectional approach that dynamically models the size evolution of each aerosol constituent across 10 size sections varying from 40 nm to 40  $\mu\text{m}$ .

Three main approaches are available in PMCAMx-2008 for the simulation of inorganic aerosol growth. In the “bulk equilibrium” approach the bulk inorganic aerosol and gas phase are assumed to be always in equilibrium. At a given time step the amount of each species transferred between the gas and aerosol phases is determined by applying the aerosol thermodynamic equilibrium model ISORROPIA (Nenes et al., 1998) and is then distributed over the aerosol size sections by using weighting factors for each size section based on their surface area (Pandis et al., 1993). The advantage of this approach is its speed, simplicity and stability. The second approach (“hybrid” approach) assumes equilibrium for the fine particles ( $<2.5 \mu\text{m}$ ) and solves the mass transfer differential equations for the coarse particles (Capaldo et al., 2000). The most accurate but computationally demanding method is the “dynamic” approach where mass transfer is simulated explicitly for all particles (Pilinis et al., 2000). In this work we use the bulk equilibrium approach. In this approach the coarse mode nitrate chemistry is included (e.g. reaction of NaCl with  $\text{HNO}_3$  forming  $\text{NaNO}_3$ ), but assuming an average PM composition.

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PMCAMx-2008 includes a state-of-the-art organic aerosol module which is based on the volatility basis set framework (Donahue et al., 2006; Stanier et al., 2008). The model simulates the partitioning of primary emissions assuming primary organic aerosol to be semivolatile. Nine surrogate POA species with effective saturation concentrations at 298 K ranging from  $10^{-2}$  to  $10^6 \mu\text{g m}^{-3}$  are used following the approach of Shrivastava et al. (2008). POA is simulated in the model in three types, “fresh” (unoxidized) POA, oxidized POA (OPOA) and any aged organic aerosol transported into the domain from the boundary conditions. SOA consists of organic aerosol of anthropogenic (aSOA) and biogenic (bSOA) origin. The SOA volatility basis-set approach (Lane et al., 2008) used in the current version of the model includes four SOA species for each VOC with 4 volatility bins (1, 10, 100,  $1000 \mu\text{g m}^{-3}$ ). In addition, the model treats all organic species (primary and secondary) as chemically reactive. Chemical aging through gas-phase OH reaction of OA vapors is modeled. The parameters that we used in this study were taken from Murphy and Pandis (2009).

## 2.2 Modeling domain and inputs

PMCAMx-2008 was applied over Europe covering a  $5400 \times 5832 \text{ km}^2$  region with  $36 \times 36 \text{ km}$  grid resolution and 14 vertical layers covering approximately 20 km (Fig. 1). The necessary inputs to the model include horizontal wind components, vertical diffusivity, temperature, pressure, water vapor, clouds and rainfall, all created using the meteorological model WRF (Weather Research and Forecasting) (Skamarock et al., 2005). In addition updated anthropogenic and biogenic hourly emission gridded fields were developed for the European domain for gases and primary particulate matter (Table 1). Anthropogenic gas emissions include land emissions from the GEMS dataset (Visschedijk et al., 2007) as well as international shipping emissions. Anthropogenic particulate matter mass emissions of organic and elemental carbon are based on the Pan-European Carbonaceous Aerosol Inventory that has been developed as part of the EUCAARI activities (Kulmala et al., 2009). Emissions from ecosystems are produced by MEGAN (Model of Emissions of Gases and Aerosols from Nature) (Guenther

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et al., 2006). MEGAN inputs include the leaf area index, the plant functional type and the emission factors while the weather data needed for MEGAN are provided from the WRF model.

## 2.3 Model evaluation

Fountoukis et al. (2011) evaluated PMCAMx-2008 against high time resolution aerosol mass spectrometer (AMS) ground measurements taken at four European measurement stations as well as airborne measurements from an aircraft field campaign over Europe, during May 2008. The comparison of the model predictions with hourly average ground measurements was encouraging. The model reproduced more than 87 % and 70 % of the hourly averaged data within a factor of 2, for PM<sub>1</sub> OA and sulfate respectively. For PM<sub>1</sub> OA the model reproduces more than 94 % of the daily averaged data within a factor of 2. The model performs well in reproducing the high degree of oxidation as well as the average diurnal profile of the organic concentrations observed in the Eastern Mediterranean region. In addition, its capability to reproduce the vertical distribution of sub-micron aerosol chemical composition was evaluated by comparing the model predictions with the airborne AMS data from 15 flights. The model performance against the high time resolution airborne measurements of OA and sulfate at multiple altitudes and locations is as good as its performance against the ground level hourly measurements. Overall organic aerosol was predicted to account for 32 % of total PM<sub>1</sub> mass at ground level, followed by sulfate (30 %), ammonium (13 %), nitrate (7 %), and elemental carbon (4 %).

The model predictions showed that PM<sub>1</sub> sulfate concentrations in the Mediterranean region are much higher than the PM<sub>1</sub> OA during the late spring period, while organic matter is predicted to be the dominant PM<sub>1</sub> species over a large part of continental Europe. For the OA components, oxidized POA and OA from intermediate volatility organic compounds (IVOCs) is predicted to be the dominant OA component, contributing around 50 % to total OA, while biogenic SOA comprises on average almost one third of the total predicted OA over the domain. In addition, the model predicts low levels

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of fresh POA in most areas of the domain, with an exception for urban and suburban areas located mainly in central and Northern Europe. Finally, PMCAMx-2008 tends to predict relatively flat average diurnal profiles for PM<sub>1</sub> OA in many areas, both rural and urban in agreement with observations.

### 3 Emission reduction scenarios

Five control strategies were examined separately, a 50 % reduction of gaseous emissions (SO<sub>2</sub>, NH<sub>3</sub>, NO<sub>x</sub>, anthropogenic VOCs) and a 50 % reduction of anthropogenic primary OA emissions (POA). In the SO<sub>2</sub>, NO<sub>x</sub> and NH<sub>3</sub> emission control simulations, the initial and boundary conditions of SO<sub>2</sub>, NO<sub>x</sub> and NH<sub>3</sub> as well as the initial and boundary conditions of sulfate nitrate and ammonium were also reduced by 50 %. Two simulation periods were used, summer 2008 and winter 2009. These are oversimplified cases exploring mainly the sensitivity of concentrations to emissions. Summer results were based on a hot period (May 2008) while the winter simulation was based on a late winter and early spring period (February/March 2009). The results of these simulations were compared with the base-case results (Fountoukis et al., 2011) in order to examine the effectiveness of these control strategies in the reduction of the major fine particulate matter as well as their effects on other pollutants. The predicted base case averaged concentrations for particulate ammonium, nitrate, sulfate, total OA and total PM<sub>2.5</sub> mass during summer 2008 and winter 2009 are shown in Fig. 2. During the summer the model predicts high nitrate concentrations in Western Europe, with a predicted maximum of 7 µg m<sup>-3</sup> in South England. In the rest of the domain nitrate is generally low, less than 2 µg m<sup>-3</sup> in most areas. PM<sub>2.5</sub> ammonium shows a similar pattern to nitrate in the domain, while elevated ammonium concentrations show strong association with nitrate, evidence of NH<sub>4</sub>NO<sub>3</sub> formation in the specific area. Additionally, the highest predicted concentrations for fine sulfate are predicted over the Mediterranean region while organic matter is predicted to be the dominant PM<sub>2.5</sub> component in Central and Northern Europe, with oxidized POA and biogenic SOA contributing around 50 % and 30 % to total OA respectively.

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During the winter, in most areas, the model predicts lower concentrations for nitrate and ammonium with similar spatial trends. Sulfate is predicted to contribute around 20 % of total  $PM_{2.5}$  in a large fraction of the domain, while the highest predicted concentrations for total OA are predicted over Central and North Europe. Fresh POA is predicted to be the dominant OA component in the winter.

## 4 Results

The major findings from the sensitivity tests assuming a 50 % reduction of gaseous and anthropogenic POA emissions during summer 2008 and winter 2009 are discussed in this section. We focus on the differences between the base case and reduced emission scenario at the ground level.

### 4.1 Reduction of $NH_3$ emissions

#### 4.1.1 Ammonium-Nitrate response

Figure 3 depicts the predicted changes in average ground-level concentrations of ammonium nitrate after a 50 % reduction of  $NH_3$  emissions during summer 2008 and winter 2009. The reduction of  $NH_3$  emissions leads to a significant reduction of ammonium in both periods, especially in areas where the ammonium concentration is high. During summer, the ammonium reduction exceeds 10 % everywhere (22 % on average in the entire domain) with a highest decrease in Western Europe (35 %) whereas the peak reduction occurs in the United Kingdom and is approximately  $1.5 \mu g m^{-3}$  (40 %) (Fig. 3a). Significant decrease of ammonium is also predicted in Southwest Europe (27 % on average) and in the Balkans (25 %). During the winter, the average ammonium reduction is 24 %. The predicted decrease is high in areas where ammonium levels are elevated, while the highest reduction is predicted in Portugal, approximately  $0.7 \mu g m^{-3}$  (40 %) (Fig. 3b). In Western and Central Europe ammonium reduction reaches up to  $0.5 \mu g m^{-3}$  (35 %) while in North Europe up to  $0.4 \mu g m^{-3}$  (31 %) respectively.

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Nitrate has a similar response to  $\text{NH}_3$  reductions as ammonium. During the summer, nitrate is decreased 21 % on average in the entire domain. The highest reduction is predicted in South Wales around  $3.1 \mu\text{g m}^{-3}$  (50 %) (Fig. 3c), while the average reduction of nitrate in Western Europe is 39 %. In other high nitrate areas such as Southwest Europe the reduction of nitrate is 26 %. In winter the average nitrate concentration reduction is 20 %, and the highest reduction is predicted in Southwest (up to  $1.1 \mu\text{g m}^{-3}$  or 52 % in Portugal) (Fig. 3d). In Central Europe nitrate is reduced up to  $0.7 \mu\text{g m}^{-3}$  (43 %) while in the Western and North Europe up to  $0.45 \mu\text{g m}^{-3}$  (31 %) and  $0.65 \mu\text{g m}^{-3}$  (39 %) respectively.  $\text{NH}_3$  is the limiting reagent in the formation of  $\text{NH}_4\text{NO}_3$  during the winter in these areas and it controls PM nitrate concentrations.

### 4.1.2 Sulfate response

$\text{NH}_3$  availability indirectly affects sulfate formation in the atmosphere. Sulfate, even in environments with low  $\text{NH}_3$ , exists in the aerosol phase as ammonium sulfate or in extreme cases as  $\text{H}_2\text{SO}_4$ . Sulfate is formed heterogeneously in cloud and fog droplets via the dissolution of gaseous  $\text{SO}_2$  and its oxidation. The second most important aqueous-phase reaction is the reaction of the dissolved  $\text{SO}_2$  with  $\text{O}_3$  at pH values greater than 5 (Seinfeld and Pandis, 2006). Therefore, the effective cloud  $\text{SO}_2$  oxidation rate depends partially on the presence of species affecting pH, such as  $\text{NH}_3$ .

The reduction of  $\text{NH}_3$  emissions results in a slight decrease of sulfate in most of the model domain, in both periods. In the summer, sulfate is decreased 2 % on average, however locally in areas located in Western and Central Europe, sulfate reduction reaches up to  $0.7 \mu\text{g m}^{-3}$  (22.5 %) and  $0.6 \mu\text{g m}^{-3}$  (19 %) respectively (Fig. 3e). During winter sulfate is decreased by 3.5 % on average in the model domain while in Central Europe its concentration is reduced up to  $0.7 \mu\text{g m}^{-3}$  or 25 % (The Netherlands) and in North Europe up to  $0.6 \mu\text{g m}^{-3}$  (24 %) (Fig. 3f). The response of sulfate is mainly due to the reduction of the cloud pH and the reduction of the rate of in-cloud sulfate production.

### 4.1.3 Organic Aerosol (OA)

The 50 % reduction of  $\text{NH}_3$  emissions does not have a significant effect on OA concentrations. In both periods the predicted changes of total OA are less than  $0.02 \mu\text{g m}^{-3}$ . This very small change is due to changes in the PM size distributions and the corresponding removal rates.

### 4.1.4 $\text{PM}_{2.5}$ response

The reduction of  $\text{NH}_3$  emissions by 50 % significantly reduces  $\text{PM}_{2.5}$  levels in both periods. The reduction of  $\text{PM}_{2.5}$  comes mainly from the reduction of the ammonium nitrate. In summer, the reduction is highest over Western Europe (15 %), where the ammonium concentration was high, with a maximum decrease predicted for South England ( $5.1 \mu\text{g m}^{-3}$  or 22.5 %) (Fig. 3g). Significant decrease is also predicted in Southwest Europe (10 %) whereas the peak reduction occurs in Italy ( $2 \mu\text{g m}^{-3}$  or 18 %) and also in Albania (up to  $1.8 \mu\text{g m}^{-3}$  or 15 %). The average reduction of  $\text{PM}_{2.5}$  in the model domain is 5.5 %.

During winter,  $\text{NH}_3$  reduction is also effective in reducing  $\text{PM}_{2.5}$  levels (4 % average reduction). The highest reduction takes place in Portugal (approximately  $1.8 \mu\text{g m}^{-3}$  or 11 %) (Fig. 3h), while the average reduction of  $\text{PM}_{2.5}$  in Southwest Europe reaches 7 %. Significant decrease is also predicted in Western, Central and North Europe where  $\text{PM}_{2.5}$  is decreased up to  $1.45 \mu\text{g m}^{-3}$  (10 %),  $1.4 \mu\text{g m}^{-3}$  (8.5 %) and  $1.5 \mu\text{g m}^{-3}$  (13 %) respectively. The sensitivity of  $\text{PM}_{2.5}$  levels to  $\text{NH}_3$  reductions during winter is consistent with the conclusions of the modelling study of Aksoyoglu et al. (2011).

## 4.2 Reduction of $\text{NO}_x$ emissions

### 4.2.1 Sulfate response

The main source of sulfate is the oxidation of  $\text{SO}_2$ , which takes place either homogeneously (reaction with OH) or heterogeneously (cloud reactions with dissolved

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hydrogen peroxide or ozone) (Pandis et al., 1989). Thus, the oxidant levels and OH in particular are critical for the formation of sulfate. There is a competition between VOCs and  $\text{NO}_x$  for the OH radical. Under a typical polluted air mix of VOCs, OH reacts with VOCs and  $\text{NO}_2$  at an equal rate when the VOC/ $\text{NO}_x$  concentration ratio is approximately 5.5:1 (Seinfeld and Pandis, 2006). In areas where the VOC/ $\text{NO}_x$  ratio is higher than this value, OH preferentially reacts with VOCs. In these  $\text{NO}_x$ -limited areas, a reduction of  $\text{NO}_x$  levels, decreases the rate of  $\text{O}_3$  formation, leading to lower OH radical concentration. As a result, a reduction of  $\text{NO}_x$  emissions, by reducing OH, can indirectly decrease sulfate concentration levels (Stockwell and Calvert, 1983). On the contrary at a lower ratio of VOC to  $\text{NO}_x$  concentration, the  $\text{NO}_x$  reaction predominates. In these  $\text{NO}_x$ -saturated areas, a reduction of  $\text{NO}_x$  emissions results in an increase of OH and  $\text{O}_3$  and subsequently sulfate concentrations can increase.

During the summer, in most of the model domain the 50 % reduction of  $\text{NO}_x$  emissions results in a decrease of sulfate levels, especially in the Balkans and in Central Europe. In these areas the VOC to  $\text{NO}_x$  concentration ratio is higher than the 5.5:1 threshold value ( $\text{NO}_x$ -limited areas). Therefore, a 50 % reduction of  $\text{NO}_x$  emissions tends to decrease the oxidant levels, resulting in a decrease of sulfate. The highest reduction, of  $0.4 \mu\text{g m}^{-3}$  (12.5%) is predicted in the Eastern Mediterranean (Fig. 4a) where sulfate has the highest concentration during summer. However, over a significant part of Western Europe, the VOC to  $\text{NO}_x$  ratio is lower than the 5.5:1 limit. In these  $\text{NO}_x$ -saturated areas, the 50 %  $\text{NO}_x$  reduction leads to an increase of oxidant levels and consequently to an increase of sulfate. Sulfate is increased in Western Europe (5% on average) with the maximum increase, approximately  $0.6 \mu\text{g m}^{-3}$  (18%) predicted in South Wales (Fig. 4a). An increase of sulfate is also predicted in Portugal (5% on average).

In winter, the VOC to  $\text{NO}_x$  concentration ratio is lower than 5.5:1 in most of the model domain due to lower biogenic emissions. Therefore the 50 % reduction of  $\text{NO}_x$  emissions results in an increase of the oxidant levels and consequently in an increase of sulfate concentration. Sulfate is increased in the entire model domain by 8% on

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average. In North Europe, sulfate is predicted to increase by 10 % on average with a predicted maximum in Russia (around  $0.5 \mu\text{g m}^{-3}$  or 21 %) (Fig. 4b) while in the rest of Europe its concentration increase is also noticeable. In particular, sulfate is increased by 9 % in Central Europe and in the Balkans, 6 % in Southwest and 5 % in Western Europe.

#### 4.2.2 Ammonium-Nitrate

During summer the reduction of  $\text{NO}_x$  along with a decrease of oxidant levels lead to a significant reduction of  $\text{HNO}_3$  formation in most areas of the model domain and to a subsequent decrease of particulate nitrate. Nitrate responds quite linearly to  $\text{NO}_x$  changes, as the 50 %  $\text{NO}_x$  reduction leads to an average 40 % nitrate reduction. The highest reduction, approximately  $2.9 \mu\text{g m}^{-3}$  (47 %) is predicted in Western Europe (Fig. 4c), where nitrate has its highest concentration. Additionally, in Albania and in Italy, where nitrate levels were also elevated during this summer simulation, nitrate is reduced by  $1.2 \mu\text{g m}^{-3}$  (50 %) and  $1 \mu\text{g m}^{-3}$  (45 %) respectively (Fig. 4c).

In winter, the increase of oxidant levels results in a lower response of particulate nitrate to the  $\text{NO}_x$  emissions reduction, compared to the summer period. Nitrate is decreased by 30 % on average with a maximum decrease of  $0.8 \mu\text{g m}^{-3}$  (30 %) in Portugal (Fig. 4d), where nitrate concentration has the highest value ( $2.5 \mu\text{g m}^{-3}$ ). Nitrate reduction is also significant in Central Europe, up to  $0.6 \mu\text{g m}^{-3}$  (33 %) in Western France, and also in North Europe, up to  $0.65 \mu\text{g m}^{-3}$  (36 %) in Russia (Fig. 4d). In these areas nitrate levels were high during winter.

Ammonium is also predicted to decrease after a 50 % reduction of  $\text{NO}_x$  emissions with similar spatial trends as nitrate. During summer the average ammonium concentration reduction is 9 %, while the peak reduction occurs in the northern coast of France ( $0.8 \mu\text{g m}^{-3}$  or 25 %) (Fig. 4e). In Western Europe, a high ammonium concentration area, the predicted reduction reaches up to  $0.75 \mu\text{g m}^{-3}$  (27 %). Significant reduction of ammonium concentration is also predicted in Italy (up to  $0.45 \mu\text{g m}^{-3}$  or 36 %) (Fig. 4e).

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During winter, ammonium decreases in most of the model domain, although its concentration reduction is lower (3 % on average) compared to summertime due to the accompanying increase of sulfate. The highest reduction is predicted in Central Europe (5 %) where ammonium is decreased up to  $0.2 \mu\text{g m}^{-3}$  (17 %) and in South France (Fig. 4f). In the other high ammonium concentration areas such as North Europe and Portugal there is also a reduction of ammonium.

### 4.2.3 Organic Aerosol (OA)

The total OA consists of primary POA and secondary organic aerosol (SOA, anthropogenic and biogenic). Oxidized POA is the result of the chemical aging of primary OA vapours through gas-phase reaction with OH. Anthropogenic condensable gases, which produce the corresponding SOA, are products of the oxidation of toluene, xylene, paraffin, olefins, etc. In addition, monoterpenes, isoprene and sesquiterpenes are the main precursors of the biogenic SOA. The reduction of  $\text{NO}_x$  emissions impacts the oxidant levels and consequently affects aged POA, and anthropogenic and biogenic SOA formation.

During summer, the reduction of oxidant levels in Central and North Europe and in the Balkans, leads to lower oxidized POA and SOA levels, and eventually to a decrease of the total OA concentration by a few percent. The highest reduction of total OA, around  $0.25 \mu\text{g m}^{-3}$  (10%) is predicted in Switzerland (Fig. 4g). In the Balkans and in North Europe total OA is reduced by 5.5 % and 4 % respectively. The predicted OA decrease is mainly attributed to reductions of oxidized POA and the corresponding intermediate volatile organic compounds (IVOCs) (account for 50 % of OA decrease). On the other hand, in Western Europe, the oxidant levels increase with the reduction of  $\text{NO}_x$ , resulting in an increase of total OA with a maximum increase of  $0.5 \mu\text{g m}^{-3}$  (11 %) in United Kingdom (Fig. 4g).

In the winter the decrease of  $\text{NO}_x$  emissions results in an increase of oxidant levels in most of the model domain. Thus, the oxidation of OA precursors is accelerated, leading to an increase of oxidized POA and SOA levels and consequently to an average

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increase of 12 % in the total OA. In North Europe, where OA is high, the model predicts the highest increase, around  $0.5 \mu\text{g m}^{-3}$  (5%) in Russia (Fig. 4h). On average, in North Europe, OA is increased by 11 % with most of the change due to oxidized POA reductions.

#### 5 4.2.4 $\text{PM}_{2.5}$ response

In summer, the  $\text{NO}_x$  emissions reduction results in a net decrease of total  $\text{PM}_{2.5}$  in the entire model domain, mainly because of the significant decrease of ammonium nitrate. The  $\text{NO}_x$  reduction reduces  $\text{PM}_{2.5}$  in Western Europe effectively (8 % on average), with a predicted maximum decrease of  $3.4 \mu\text{g m}^{-3}$  (17 %) (Fig. 4i). In other areas with elevated ammonium nitrate concentrations such as Albania and Italy, the  $\text{PM}_{2.5}$  reduction is also significant, around  $1.8 \mu\text{g m}^{-3}$  (15 %) and  $1.5 \mu\text{g m}^{-3}$  (13 %) respectively (Fig. 4i).

On the contrary, during winter, the response of  $\text{PM}_{2.5}$  is quite different. Sulfate and total OA are predicted to increase with the reduction of  $\text{NO}_x$ , while the relative reduction of ammonium nitrate is not as large as in summer. Consequently, a 50 % reduction of  $\text{NO}_x$  emissions results in an increase of  $\text{PM}_{2.5}$  in areas where sulfate and total OA increase is more significant than ammonium nitrate reduction, and in a decrease in the rest of the model domain. In North Europe  $\text{PM}_{2.5}$  is increased up to  $0.5 \mu\text{g m}^{-3}$  (Fig. 4j) while the highest reductions take place in Spain, Portugal and France (up to  $0.5 \mu\text{g m}^{-3}$ ) (Fig. 4j). The low effectiveness of  $\text{NO}_x$  controls in reducing  $\text{PM}_{2.5}$  levels during winter has been mentioned in other studies for different modeling areas (e.g. Tsimpidi et al., 2008).

#### 4.2.5 Ozone response

During the summer,  $\text{O}_3$  is predicted to decrease in most of the model domain. The reduction is predicted to be highest in the Balkans (14 % on average) with a predicted maximum over the Eastern Mediterranean (8 ppb or 18 %) (Fig. 5a). In Southwest

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in Southwest) indicating that  $\text{SO}_2$  is the limiting reagent for sulfate formation during summer.

During the winter the 50%  $\text{SO}_2$  reduction leads to an average 15% reduction of sulfate. The highest reduction is predicted in Northern France (approximately  $0.7 \mu\text{g m}^{-3}$  or 25.5%) (Fig. 6b), where sulfate concentration is relatively high. Additionally sulfate is significantly reduced in Denmark ( $0.6 \mu\text{g m}^{-3}$  or 20%) and in Russia ( $0.5 \mu\text{g m}^{-3}$  or 18%) (Fig. 6b). The in-cloud formation of sulfate by the reaction of dissolved  $\text{SO}_2$  with  $\text{H}_2\text{O}_2$  is a major pathway. This rate is often limited by  $\text{H}_2\text{O}_2$  during the winter and thus the response of sulfate to  $\text{SO}_2$  reductions is lower compared to summertime.

### 4.3.2 Ammonium-Nitrate response

Gaseous  $\text{NH}_3$  reacts preferentially with  $\text{H}_2\text{SO}_4$ , and, if sufficient  $\text{NH}_3$  is available (free  $\text{NH}_3$ ), it also reacts with  $\text{HNO}_3$  forming particulate nitrate. Thus, a reduction of  $\text{SO}_2$  can lead to an increase of free  $\text{NH}_3$  and consequently more  $\text{HNO}_3$  can be transferred to the particulate phase (electroneutrality effect) (Seinfeld and Pandis, 2006). However the formation of  $\text{NH}_4\text{NO}_3$  depends on its equilibrium vapour pressure product of ammonia and nitric acid,  $K_{\text{AN}}$ , which in general, depends on temperature, RH and sulfate concentration. In the aqueous phase, when sulfate increases,  $K_{\text{AN}}$  decreases due to ion interactions. Consequently the reduction of sulfate levels, increases  $K_{\text{AN}}$ , which may produce a decrease of ammonium nitrate (thermodynamic effect) (Ansari and Pandis, 1998). In areas where the total nitrate is high and the  $\text{NH}_3$  is low, nitrate tends to increase because of the electroneutrality effect, while in areas with high free  $\text{NH}_3$ , nitrate tends to decrease due to the thermodynamic effect.

During summer, the 50% reduction of  $\text{SO}_2$  emissions leads to a significant increase of nitrate (16% on average), in most of the model domain. This response of nitrate to  $\text{SO}_2$  reductions was also shown by Fagerli and Wenche (2008). The increase reaches its maximum in Western Greece (approximately  $0.8 \mu\text{g m}^{-3}$  or 50%) (Fig. 6c).

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Significant increase is also predicted in other high nitrate areas such as Albania (up to  $0.4 \mu\text{g m}^{-3}$  or 20 %) and Italy (up to  $0.3 \mu\text{g m}^{-3}$  or 15 %). However there are areas where nitrate decreases (Bulgaria, Romania, etc.), although the predicted reduction does not exceed  $0.1 \mu\text{g m}^{-3}$ .

5 In winter, nitrate is predicted to increase in most of the model domain but less than during the summer period (8 % on average). The corresponding maximum increase is predicted in Portugal ( $0.3 \mu\text{g m}^{-3}$  or 26 %), where nitrate has the highest concentration (Fig. 6d). In Central Europe, a slight decrease of nitrate is predicted (up to  $0.1 \mu\text{g m}^{-3}$ ), in areas with high gaseous  $\text{NH}_3$ .

10 Ammonium has a different response than nitrate as  $\text{SO}_2$  is reduced, with a predicted decrease in most of the model domain during both periods (Fig. 6e, f). In the summer ammonium is reduced 8 % on average, and the predicted reduction is more significant in areas with high sulfate levels. In the Balkans ammonium is reduced by 18 % (up to  $0.4 \mu\text{g m}^{-3}$  or 35 % in Bulgaria) (Fig. 6e), while in Central and North Europe by 16 % and 13 % respectively.

15 Similar results are predicted during winter, although the greater availability of  $\text{HNO}_3$  (g) after the reduction of  $\text{SO}_2$  led to a lower average decrease of ammonium (4 %). The ammonium reduction is highest in North Europe (up to  $0.2 \mu\text{g m}^{-3}$  or 14 % in Russia) (Fig. 6f).

20 The 50 % reduction of  $\text{SO}_2$  emissions does not have a significant effect on the OA concentration. In both periods the predicted changes of total OA do not exceed  $0.01 \mu\text{g m}^{-3}$ .

### 4.3.3 $\text{PM}_{2.5}$ response

25 The large sensitivity of sulfate to  $\text{SO}_2$  reduction and the accompanying reduction of ammonium produce a decrease of  $\text{PM}_{2.5}$  in both periods. In summer,  $\text{SO}_2$  reduction has a significant effect on  $\text{PM}_{2.5}$  levels over the Balkans (10 % average decrease) with a maximum concentration reduction of  $1.6 \mu\text{g m}^{-3}$  in Bulgaria (Fig. 6g). In Central and

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Western Europe,  $PM_{2.5}$  is reduced up to  $1.2 \mu\text{g m}^{-3}$  (8%) and in North Europe up to  $1 \mu\text{g m}^{-3}$  (13%). In Southwest Europe the  $PM_{2.5}$  reduction is lower (5% on average).

During winter, when sulfate levels are lower, the  $SO_2$  reduction is less effective in reducing  $PM_{2.5}$ . In particular, in Central Europe the peak reduction is  $0.9 \mu\text{g m}^{-3}$  (5.5%), and in North and Western Europe  $0.75 \mu\text{g m}^{-3}$  (4.5% in both areas) (Fig. 6h). The lower response of  $PM_{2.5}$  to  $SO_2$  reductions is primarily attributable to the limited  $H_2O_2$  availability during winter, and secondly to the increase of nitrate.

## 4.4 Reduction of anthropogenic VOCs emissions

### 4.4.1 Sulfate response

When the emissions of VOCs are halved, the oxidant levels ( $O_3$ , OH) either increase ( $NO_x$ -limited areas) or decrease ( $NO_x$ -saturated areas). This variable response, as we have seen, is determined by the VOC/ $NO_x$  ratio and is the key for understanding the response of  $PM_{2.5}$  components after this reduction.

The gas-phase sulfate formation is affected by the competition between VOCs and  $NO_x$  for the OH radical. In areas with high  $NO_x$  concentration levels ( $NO_x$ -saturated areas), the conversion of NO to  $NO_2$  is VOC-limited and by reducing VOCs, ozone is reduced. This leads to lower OH concentrations slowing down the gas phase formation of sulfate. On the contrary in  $NO_x$ -limited areas (high VOC/ $NO_x$  ratio) the decrease of anthropogenic VOC emissions leads to increased OH levels, which reacts with  $SO_2$  forming additional particulate sulfate.

During the summer, in most of the model domain the oxidant levels increase with the VOC control strategy resulting in an increase of sulfate. The predicted increase is quite low and does not exceed  $0.1 \mu\text{g m}^{-3}$ . In the winter the response of sulfate to VOC reduction is different due to the decrease of oxidant levels. Sulfate is predicted to decrease but its concentration reduction is also marginal.

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## 4.4.2 Ammonium-Nitrate

During summer most of the domain is  $\text{NO}_x$ -limited. In these  $\text{NO}_x$ -limited areas the decrease of VOCs emissions increases the oxidant levels and consequently, increase particulate nitrate. Nitrate is predicted to increase up to  $0.15 \mu\text{g m}^{-3}$  (4.5 %) in Central Europe and over  $0.1 \mu\text{g m}^{-3}$  (3 %) in the Balkans. On the other hand in Western Europe where nitrate concentration is high ( $\text{NO}_x$ -saturated area), nitrate is reduced up to  $0.2 \mu\text{g m}^{-3}$  (3 %).

The reduction of anthropogenic VOCs leads to a different response of nitrate during winter when the domain is  $\text{NO}_x$ -saturated. In most of areas nitrate is reduced due to decreasing oxidant levels with the highest reduction approximately  $0.15 \mu\text{g m}^{-3}$  (7.5 %) predicted in North Europe.

The increase of nitrate and sulfate concentrations, after the VOC reduction leads to higher concentrations of ammonium, during the summer. However its predicted increase is small and does not exceed  $0.05 \mu\text{g m}^{-3}$  in Central Europe. In Western Europe the corresponding decrease of oxidant levels, produces a small decrease of ammonium (up to  $0.04 \mu\text{g m}^{-3}$ ). Ammonium responds similarly to nitrate in the winter too. The highest decrease is predicted in North Europe ( $0.06 \mu\text{g m}^{-3}$ ).

## 4.4.3 Organic Aerosol (OA)

The reduction of the anthropogenic VOCs emissions is expected to reduce total OA concentration in both periods. However the increase of oxidant levels in the  $\text{NO}_x$ -limited areas accelerates the VOC oxidation, offsetting some of this reduction.

During summer total OA is predicted to decrease in the whole domain. The predicted decrease is mainly attributed to the linear response (50 % on average) of anthropogenic SOA. Anthropogenic VOCs are precursors of SOA and therefore a 50 % reduction of their emissions leads to decreased aSOA. Total OA is reduced  $0.2 \mu\text{g m}^{-3}$  (9 %) in Western and Central Europe (Fig. 7a), where aSOA has the highest concentration, with a predicted maximum reduction of  $0.4 \mu\text{g m}^{-3}$  (6 %) in Northern France (Fig. 7a).

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On average, total OA is reduced by 8 % with aSOA accounting for almost 90 % of this reduction.

Total OA is also reduced in the winter (4 % on average) mainly due to the reduction of aSOA. The lower response is mainly explained from the lower aSOA levels during winter. The reduction of OA is highest in North Europe (up to  $0.2 \mu\text{g m}^{-3}$  or 2 % in Russia) (Fig. 7b) as well as in Portugal, both areas with high aSOA.

#### 4.4.4 $\text{PM}_{2.5}$ response

The reduction of anthropogenic VOCs emissions does not appear to be significantly effective in reducing  $\text{PM}_{2.5}$ . The VOC control strategy slightly decreases  $\text{PM}_{2.5}$  in both periods mainly due to reductions of OA. In summer, the highest reduction is predicted in Western Europe (up to  $0.5 \mu\text{g m}^{-3}$  or 2 %) (Fig. 7c). The decrease of the oxidant levels ( $\text{NO}_x$ -saturated area) along with the decrease of OA account for this trend. In the rest of Europe  $\text{PM}_{2.5}$  reduction is even lower (less than  $0.2 \mu\text{g m}^{-3}$ ), despite the predicted OA reduction, due to the increase of the oxidant levels and the accompanying increase of inorganic  $\text{PM}_{2.5}$ . Similar to the summer simulation, the highest predicted  $\text{PM}_{2.5}$  reduction is  $0.4 \mu\text{g m}^{-3}$  (1 %) (in Russia) (Fig. 7d) while in the rest of the model domain it does not exceed  $0.2 \mu\text{g m}^{-3}$ . The decrease of total OA and the decrease of the oxidant levels ( $\text{NO}_x$ -saturated domain) explain this response.

### 4.5 Reduction of anthropogenic POA emissions

#### 4.5.1 Organic Aerosol (OA) response

The 50 % reduction of primary OA emissions results in a decrease of total OA in both periods (Fig. 8), and is more effective in areas close to the emissions sources. Total OA is reduced by 8 % on average during summer. The highest reduction, around  $3.6 \mu\text{g m}^{-3}$  (34 %) is predicted in North Europe (Fig. 8a), while in Central and Western Europe, OA is reduced up to  $2 \mu\text{g m}^{-3}$  (32 %) and  $1.2 \mu\text{g m}^{-3}$  (24 %) respectively (Fig. 8a). The predicted response of total OA is mainly explained from the almost linear

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decrease of fresh anthropogenic POA concentration after the POA control strategy. Fresh POA is reduced by 50 % in the whole domain and it accounts for approximately 55 % of OA reduction. The additional decrease of oxidized POA (6 % on average) contributes 38 % to the OA concentration decrease.

5 In the winter the higher levels of fresh POA make the POA control strategy more effective in reducing total OA levels. Total OA is reduced in the entire domain (15 % on average). In areas with high POA emissions the reduction is even higher. In Central Europe, OA is reduced by 25 % on average with a predicted maximum of  $6.7 \mu\text{g m}^{-3}$  (48 %) in Northern France close to Paris (Fig. 8b). The predicted reduction is also  
10 substantial in North Europe (up to  $3.8 \mu\text{g m}^{-3}$  or 40 % in Russia) (Fig. 8b). This OA reduction is primarily due to fresh POA, which contributes 77.5 % to the OA decrease and secondly to the decrease of oxidized POA (18.5 % contribution).

#### 4.5.2 Inorganic $\text{PM}_{2.5}$

The primary OA control strategy does not have a significant effect on the inorganic  
15 PM components. In both periods ammonium-nitrate does not change significantly (up to  $0.02 \mu\text{g m}^{-3}$  in summer and  $0.01 \mu\text{g m}^{-3}$  in winter, respectively). Similar negligible changes are predicted for sulfate.

#### 4.5.3 $\text{PM}_{2.5}$ response

The reduction of primary OA emissions reduces  $\text{PM}_{2.5}$  in both periods, having a significant effect close to the emission sources. The response of  $\text{PM}_{2.5}$  is totally due to  
20 reductions of OA. During the summer, the highest reduction of  $\text{PM}_{2.5}$  is predicted in North Europe (approximately  $3.7 \mu\text{g m}^{-3}$  or 12.5 %) (Fig. 9a). The higher OA response to the POA emissions reduction during winter, leads to a higher reduction of  $\text{PM}_{2.5}$ . In areas where OA decrease is highest such as Paris, Russia the reduction of  $\text{PM}_{2.5}$   
25 reaches  $6.8 \mu\text{g m}^{-3}$  (19 %) and  $3.8 \mu\text{g m}^{-3}$  (9 %) respectively (Fig. 9b). This local effectiveness of primary OA reductions has also been shown in other studies (Odman et al., 2009).

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Table 2 summarizes the emission reduction scenarios and the corresponding response of the major PM<sub>2.5</sub> components during summer 2008 and winter 2009.

## 5 Effects of temperature increase

In order to determine the sensitivity of fine PM to temperature we used two simplified scenarios: a uniform increase of 2.5 and of 5 K over the entire domain. This sensitivity test, quantifies the effect of a temperature increase on PM<sub>2.5</sub> levels keeping the rest of the meteorological parameters constant. We assumed temperature sensitive biogenic emissions using the MEGAN model and the results of these higher temperature scenarios were compared with those of the baseline scenarios for each simulation period (summer 2008 and winter 2009).

Figure 10 shows the predicted changes (base case – increased temperature scenario) in ground-level concentrations of total PM<sub>2.5</sub> after a 2.5 K temperature increase. During summer PM<sub>2.5</sub> is reduced in Central Europe due to a significant decrease of ammonium nitrate in this area (18 % on average). A slight decrease of fresh anthropogenic POA due to evaporation decreases even more PM<sub>2.5</sub>. The highest reduction of approximately 1 µg m<sup>-3</sup> (5 %) is predicted in Germany (Fig. 10a) whereas the respective decrease of ammonium nitrate is 1.1 µg m<sup>-3</sup> (22 %). Significant decrease of PM<sub>2.5</sub> is also predicted in areas where ammonium nitrate concentration is high such as United Kingdom and Italy. However in North Europe and also in areas in Southwest Europe and in the Balkans, the response of PM<sub>2.5</sub> to temperature increase differs. In these areas PM<sub>2.5</sub> is predicted to increase mainly due to increase of sulfate and total OA. The increase of oxidant levels from the temperature rise which favours the oxidation of SO<sub>2</sub>, explain the sulfate response. The increase of total OA is mainly attributed to the increase in biogenic VOC emissions and the corresponding increase of biogenic SOA in association with a slight increase of anthropogenic SOA due to acceleration of its chemical production and aging (Day and Pandis, 2011). The increase of oxidant levels and the corresponding increase of sulfate lead also to an increase of total PM<sub>2.5</sub> over

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the Atlantic. In North Europe  $PM_{2.5}$  is increased up to  $0.5 \mu\text{g m}^{-3}$  (12 %) (Fig. 10a), while sulfate, biogenic and anthropogenic SOA are predicted to increase up to 14 % and 20 % and 7 % respectively.

In the winter, the reduction of fresh anthropogenic POA due to evaporation dominates and along with a reduction of ammonium nitrate result in a decrease of total  $PM_{2.5}$  mostly in areas over Central and North Europe. On a domain average basis anthropogenic POA is reduced by 35 % and ammonium nitrate by 5 %. The highest decrease for  $PM_{2.5}$  is predicted in Paris (approximately  $4.5 \mu\text{g m}^{-3}$  or 12 %) (Fig. 10b) where anthropogenic POA is decreased by  $4.9 \mu\text{g m}^{-3}$  or 37 %. The dominance of fresh POA reduction as temperature increases during winter, in association with the small biogenic SOA contribution to total OA due to lower biogenic emissions lead to a different response of total OA to temperature increase. The wintertime total OA levels are predicted to decrease for warmer conditions with a predicted maximum decrease in Paris ( $4.7 \mu\text{g m}^{-3}$  or 35 %). On the contrary the increase of the oxidant levels affects sulfate levels and lead to an increase of  $PM_{2.5}$  in many areas of Europe. The predicted increase of  $PM_{2.5}$  is highest over North Europe reaching a maximum of  $1.3 \mu\text{g m}^{-3}$  (15 %) (Fig. 10b). In this area sulfate is increased by 24 % on average.

The doubling of temperature increase (from 2.5 to 5 K) during the summer almost doubles the corresponding concentration change of all OA components. This OA response followed by higher concentration changes of inorganic  $PM_{2.5}$  result in even larger changes for total  $PM_{2.5}$  concentration.  $PM_{2.5}$  is predicted to decrease even more in Central Europe (up to  $1.5 \mu\text{g m}^{-3}$  or 8 %) (Fig. 11a), mainly due to the larger decrease of ammonium nitrate (27 % on average) and the doubling of anthropogenic POA decrease. On the contrary the higher increase of sulfate along with the linear response of biogenic and anthropogenic SOA to the temperature change account for the higher  $PM_{2.5}$  increase (up to  $1.2 \mu\text{g m}^{-3}$  or 4.5 %) (Fig. 11a).

Similarly to the summer period, the increase in temperature by 5 K, during winter, leads to a higher corresponding concentration change of total  $PM_{2.5}$ . The larger decrease of anthropogenic POA (40 % on average), due to evaporation, associated with

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a decrease on ammonium nitrate (8 % on average) lead to a decrease of PM<sub>2.5</sub> in Central and North Europe with a predicted maximum decrease of 4.9 µg m<sup>-3</sup> (14 %) in Paris (Fig. 11b). On the other hand the larger increase in sulfate concentration dominates in many areas over Europe, increasing total PM<sub>2.5</sub> (up to 1.6 µg m<sup>-3</sup> or 18 % in North Europe) (Fig. 11b).

Table 3 summarizes the temperature increase scenarios and the corresponding response of the major PM<sub>2.5</sub> components during summer 2008 and winter 2009.

## 6 Conclusions

A detailed three dimensional chemical transport model, PMCAMx-2008, was applied to the European domain to evaluate the response of fine aerosol (PM<sub>2.5</sub>) mass concentration to changes in emissions of precursor gases (SO<sub>2</sub>, NH<sub>3</sub>, NO<sub>x</sub>, VOCs) and anthropogenic primary OA (POA) as well as to changes in temperature.

The reduction of NH<sub>3</sub> emissions by 50 % seems to be the most effective control strategy in reducing PM<sub>2.5</sub>, in both periods mainly due to a significant decrease of ammonium nitrate. Our findings for winter are consistent with other studies (Tsimpidi et al., 2007; Odman et al., 2009; Aksoyoglu et al., 2011). During summer, NH<sub>3</sub> emissions reduction resulted in a decrease of ammonium by 22 % in the entire model domain. Nitrate is reduced by 35 % in Western Europe and by 27 % in Southwest Europe, while the corresponding decrease of total PM<sub>2.5</sub> in these areas was 15 % and 10 % respectively. Similarly in winter, ammonium is decreased by 24 % after a 50 % reduction of NH<sub>3</sub> emissions. This reduction also produces an average of 20 % decrease of nitrate concentration. Overall, ammonium nitrate reduction accounts for almost 80 % of total PM<sub>2.5</sub> reduction in both periods. The reduction of NH<sub>3</sub> produces also a slight decrease of sulfate levels due to the effect of NH<sub>3</sub> on cloud pH and on the rate of in-cloud sulfate production.

The 50 % reduction of SO<sub>2</sub> emissions, during the summer, leads to a significant decrease of sulfate in the entire domain (23 % on average). The SO<sub>2</sub> control strategy is

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more effective over the Balkans where sulfate is reduced by 30 %, while the respective decrease of total  $PM_{2.5}$  was 10 %. Ammonium is also reduced by 8 % on average mainly due to the decrease of ammonium sulfate. During the summer the  $SO_2$  control strategy produces also a significant increase of nitrate in most of the model domain (16 % on average). In winter sulfate is reduced by 15 % on average after a 50 % reduction of  $SO_2$  emissions. The lower decrease of sulfate, because its formation was limited by  $H_2O_2$  availability, as well as the higher increase of nitrate make  $SO_2$  emissions reduction less effective in winter.

The 50 % reduction of anthropogenic VOCs and POA produced a decrease of total OA concentration in both periods with the POA control strategy to be more effective in areas close to emissions sources. By reducing VOCs emissions total OA is predicted to decrease in the whole domain by 8 % during summer and 4 % in winter, mainly due to the linear response of anthropogenic SOA (50 % decrease on average). Anthropogenic POA responded linearly (an average reduction of 50 % in the whole domain) to the 50 % reduction of POA emissions, while the respective average decrease of total OA was 15 % during winter (25 % in Central Europe) and 8 % in the summer. Although, both control strategies produce small (VOCs reduction) or negligible (POA reduction) changes in inorganic PM in both periods.

On the contrary, the  $NO_x$  emissions control strategy seems to be problematic in both periods. During the summer, the 50 % reduction of  $NO_x$  emissions produces a significant decrease of ammonium nitrate in the whole domain (25 % on average), but it also leads to an increase of ozone levels (based to VOC/ $NO_x$  ratio), mainly in the major urban areas such as London, Paris and Madrid, and also in the Western Europe. The ozone increase exceeds 10 % in these urban centers while in Western Europe ozone is predicted to increase by 4 % on average. Because of this increment, sulfate and total OA are predicted to increase in these areas (5 % both). Additionally, in the winter, ammonium nitrate is reduced by 17 %, however the reduction of  $NO_x$  emissions results in an increase of sulfate and total OA by 8 % and 12 % respectively.

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The increase of temperature by 2.5 K results in a decrease of ammonium nitrate and fresh anthropogenic POA in both periods. During summer, ammonium nitrate is reduced by 10 % (18 % in Central Europe), while anthropogenic POA is decreased by 7 % due to evaporation. However, the temperature rise during summer resulted in an increase of sulfate due to an increase of oxidant levels which favor the oxidation of SO<sub>2</sub>. Biogenic SOA is also predicted to increase because of the higher biogenic VOC emissions from the temperature increase, leading to an increase of total OA in most of the model domain. During the winter, total OA is predicted to decrease for warmer conditions. This different response is due to the dominance of anthropogenic POA reduction (35 % decrease in the whole domain) along with the small biogenic SOA contribution to total OA due to lower biogenic emissions. The wintertime ammonium nitrate levels are also decreased, mainly in Central and North Europe (6 % in both areas) while sulfate is predicted to increase due to the increase of oxidant levels. The doubling of temperature increase (from 2.5 K to 5 K) doubles the corresponding concentration change of OA components during summer and leads to even larger concentration changes of inorganic PM<sub>2.5</sub>, in both periods.

The sensitivity of PM<sub>2.5</sub> components to emissions reductions of their precursors reveals the significant role that emission control strategies may play for improving air quality. However the temperature change could also lead to significant changes of PM<sub>2.5</sub> indicating that climate change is also of significant concern for atmospheric PM composition and air quality.

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**Table 1.** Emission mass totals for gaseous and PM<sub>2.5</sub> species (in kttons/month) for the European domain during summer 2008 and winter 2009.

Species		CO	NO <sub>x</sub>	SO <sub>2</sub>	NH <sub>3</sub>	NMVOG	NO <sub>3</sub> <sup>-</sup>	Sulfate	NH <sub>4</sub> <sup>+</sup>	EC	OC	Na <sup>+</sup>	Cl <sup>-</sup>
Summer	Anthropogenic	3682	1461	1675	501	1291	–	–	–	47	68	–	–
	Biogenic	1207	46	3	11	1872	4	146	1	12	81	512	920
Winter	Anthropogenic	5002	1531	1961	474	1334	–	–	–	62	112	–	–
	Biogenic	80	5	59	–	257	–	298	–	–	12	1140	2050

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**Table 2.** Response of the major PM<sub>2.5</sub> components to a 50% reduction of NH<sub>3</sub>, NO<sub>x</sub>, SO<sub>2</sub>, VOCs and POA emissions, and percent average predicted reduction of total PM<sub>2.5</sub>, during summer 2008 and winter 2009.

Control Strategy	Season	Average PM <sub>2.5</sub> Reduction	Change of Component			
			Ammonium	Sulfate	Nitrate	Total OA
-50% NH <sub>3</sub>	Summer	5.5 % *	↓	↓	↓	–
	Winter	4.1 %	↓	↓	↓	–
-50 % NO <sub>x</sub>	Summer	5 %	↓	↓ ↑	↓	↓ ↑
	Winter	0.4 %	↓	↑	↓	↑
-50 % SO <sub>2</sub>	Summer	5.1 %	↓	↓	↑	–
	Winter	2.6%	↓	↓	↑	–
-50 % VOCs	Summer	0.5 %	–	–	↓ ↑	↓
	Winter	0.6 %	–	–	↓	↓
-50 % POA	Summer	1.3%	–	–	–	↓
	Winter	1.6 %	–	–	–	↓

\* A negative value corresponds to an increase.

↓ > 10 % reduction

↑ > 10 % increase

↓ ↑ > 10 % reduction

↑ ↓ > 10 % increase

– Negligible effect.

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**Table 3.** Response of the major PM<sub>2.5</sub> components to a 2.5 and 5 K increase of temperature, and percent average predicted reduction of total PM<sub>2.5</sub>, during summer 2008 and winter 2009.

Control Strategy	Season	Average PM <sub>2.5</sub> Reduction	Change of Component			
			Ammonium	Sulfate	Nitrate	Total OA
+2.5 K	Summer	-0.8% *	↓	↑	↓	↑
	Winter	-1%	↓	↑	↓	↓
+5 K	Summer	-1%	↓	↑	↓	↑
	Winter	-5.7%	↓	↑	↓	↓

\* A negative value corresponds to an increase.

↓ > 10% reduction

↑ > 10% increase

↓ > 10% reduction

↑ > 10% increase

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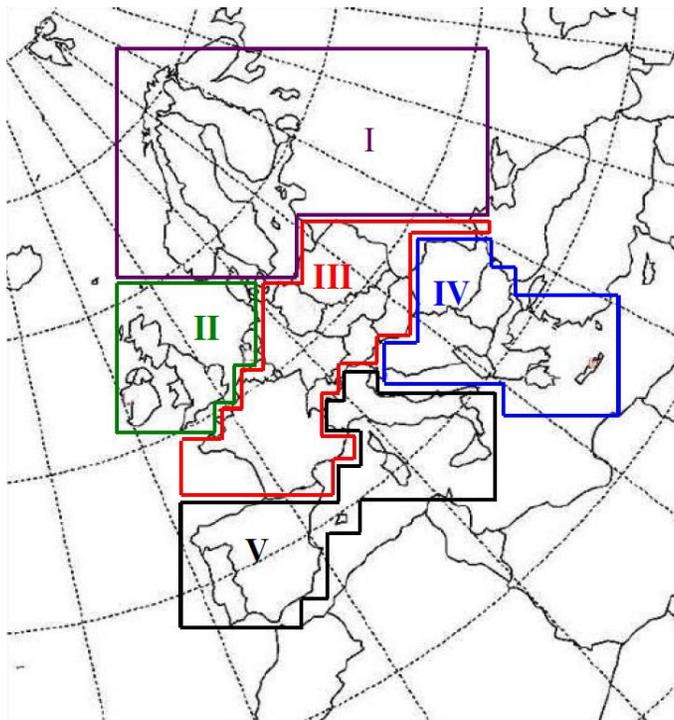
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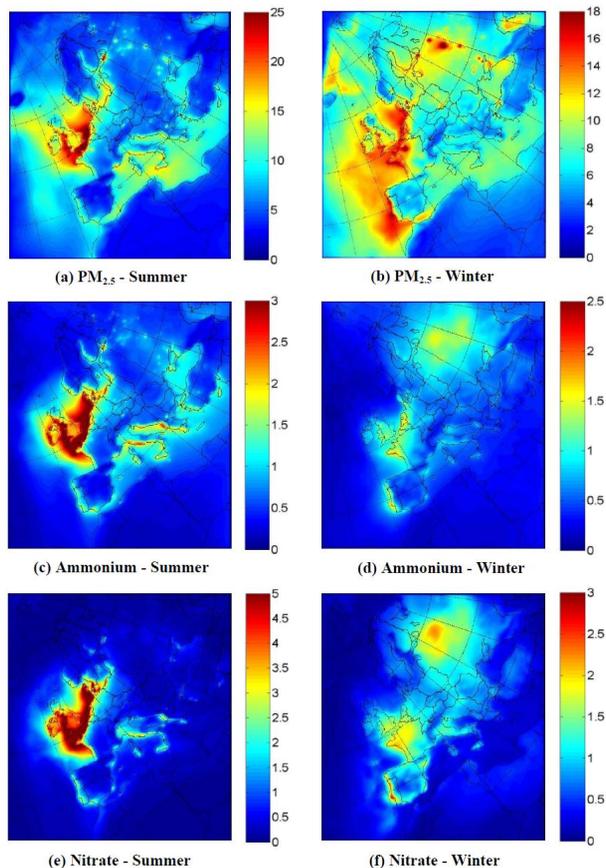
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**Fig. 1.** Modeling domain of PMCAMx-2008 for Europe. The location of the five regions used for the investigation of the spatial dependence of the  $PM_{2.5}$  responses to emissions and temperature changes are also shown (I = North Europe, II = UK and Western Europe, III = Central Europe, IV = Balkans, V = Southwest Europe).

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**Fig. 2a.** Predicted base case ground-level concentrations ( $\mu\text{g m}^{-3}$ ) of **(a–b)**  $PM_{2.5}$ , **(c–d)** ammonium, **(e–f)** nitrate, during summer 2008 and winter 2009. Different concentration scales are used for each graph.

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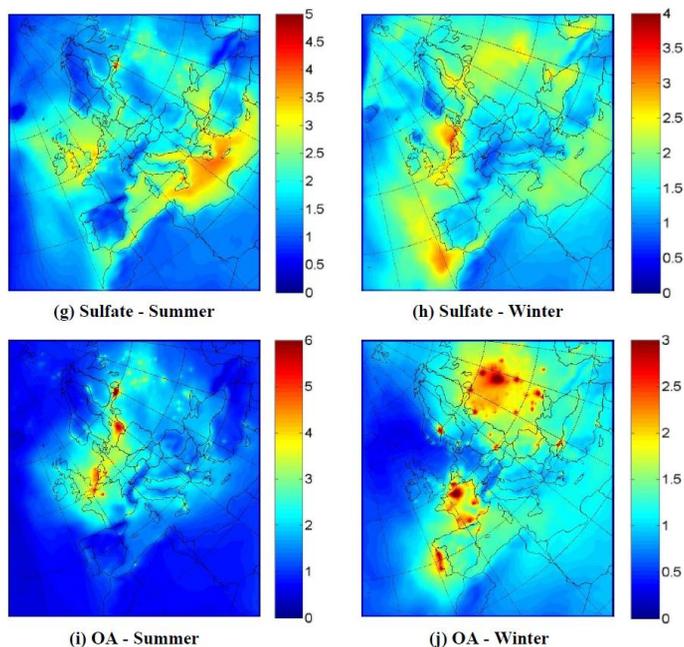
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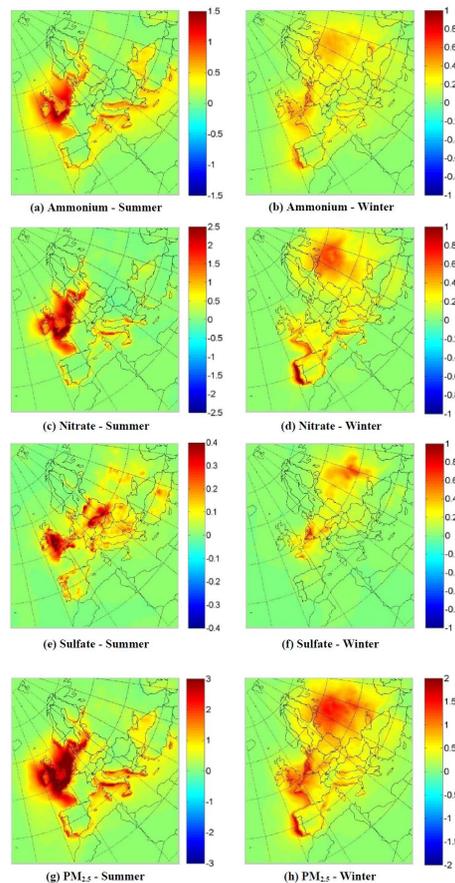


**Fig. 2b.** Predicted base case ground-level concentrations ( $\mu\text{g m}^{-3}$ ) of **(g–h)** sulfate, and **(i–j)** total OA, during summer 2008 and winter 2009. Different concentration scales are used for each graph.

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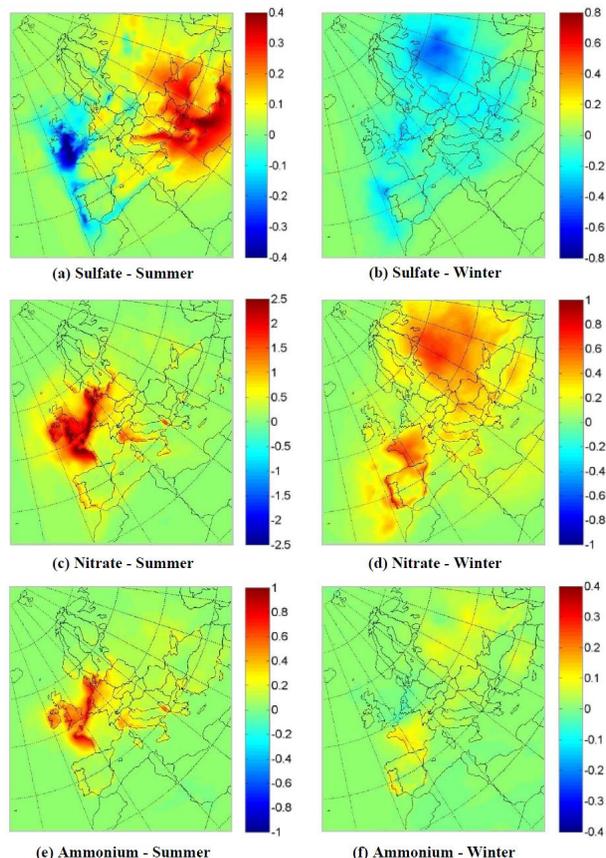


**Fig. 3.** Predicted reduction ( $\mu\text{g m}^{-3}$ ) in ground-level concentrations of **(a–b)** ammonium, **(c–d)** nitrate, **(e–f)** sulfate, and **(g–h)** total  $\text{PM}_{2.5}$  after a 50% reduction of  $\text{NH}_3$  emissions during summer 2008 and winter 2009. A negative value corresponds to an increase.

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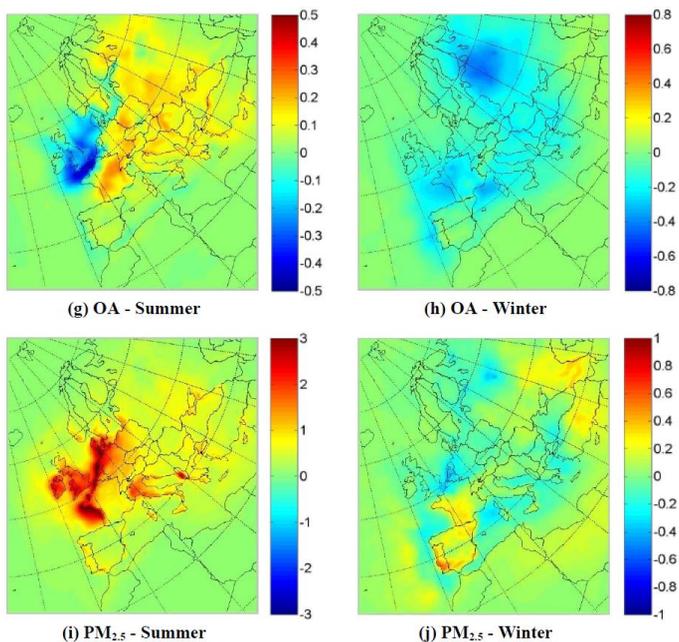


**Fig. 4a.** Predicted reduction ( $\mu\text{g m}^{-3}$ ) in ground-level concentrations of **(a–b)** sulfate, **(c–d)** nitrate, **(e–f)** ammonium, after a 50 % reduction of  $\text{NO}_x$  emissions during summer 2008 and winter 2009. A negative value corresponds to an increase.

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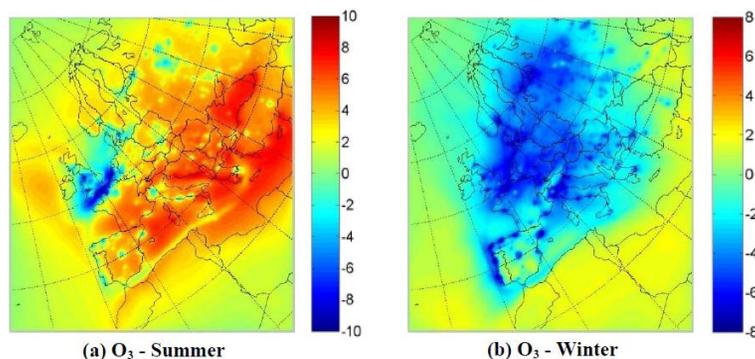


**Fig. 4b.** Predicted reduction ( $\mu\text{g m}^{-3}$ ) in ground-level concentrations of **(g–h)** total OA, and **(i–j)** total PM<sub>2.5</sub> after a 50 % reduction of NO<sub>x</sub> emissions during summer 2008 and winter 2009. A negative value corresponds to an increase.

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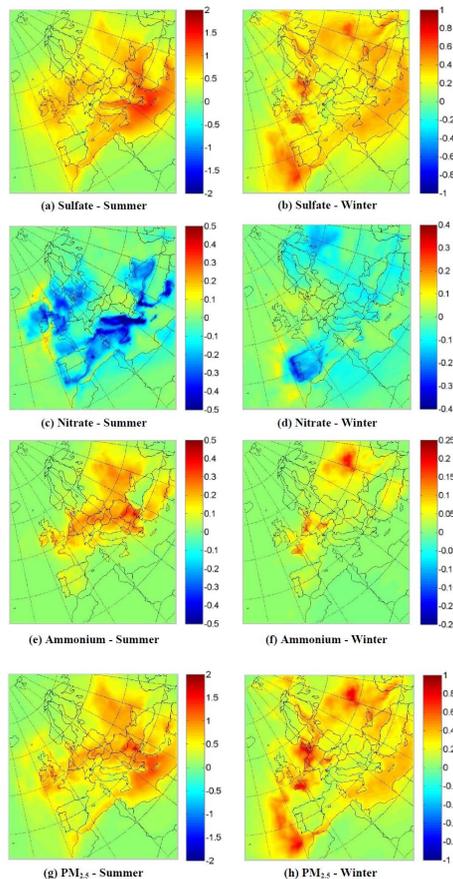
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**Fig. 5.** Predicted reduction (ppb) in ground-level concentrations of O<sub>3</sub> after a 50 % reduction of NO<sub>x</sub> emissions during **(a)** summer 2008 and **(b)** winter 2009. A negative value corresponds to an increase.

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**Fig. 6.** Predicted reduction ( $\mu\text{g m}^{-3}$ ) in ground-level concentrations of **(a–b)** sulfate, **(c–d)** nitrate, **(e–f)** ammonium, and **(g–h)** total  $\text{PM}_{2.5}$  after a 50% reduction of  $\text{SO}_2$  emissions during summer 2008 and winter 2009. A negative value corresponds to an increase.

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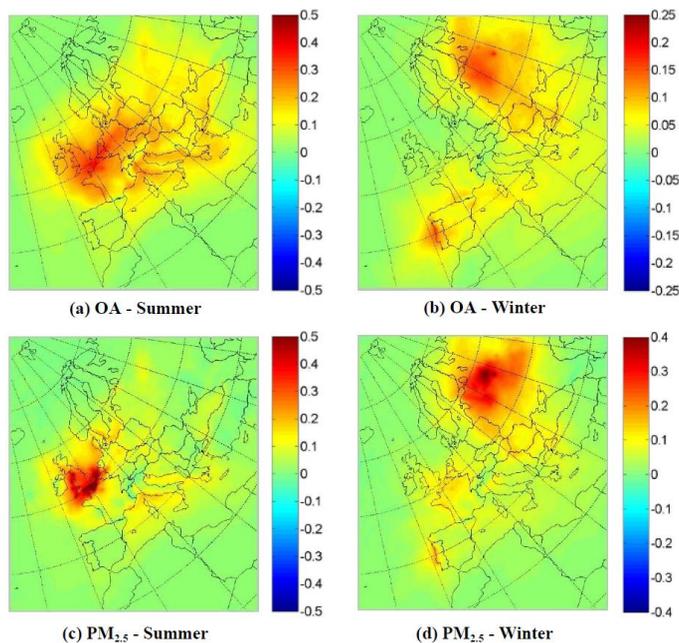
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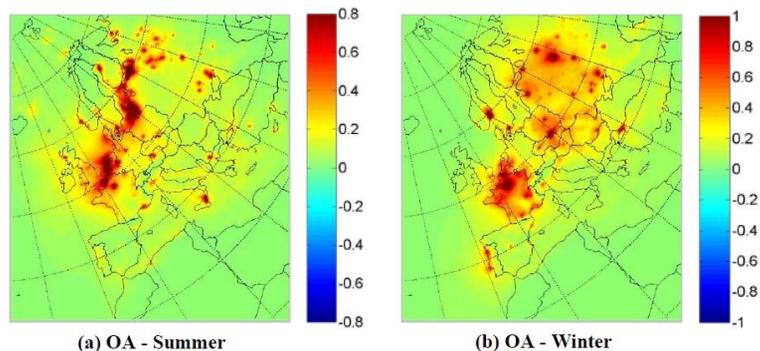


**Fig. 7.** Predicted reduction ( $\mu\text{g m}^{-3}$ ) in ground-level concentrations of **(a–b)** total OA and **(c–d)** total PM<sub>2.5</sub> mass after a 50 % reduction of anthropogenic VOCs emissions during summer 2008 and winter 2009. A negative value corresponds to an increase.

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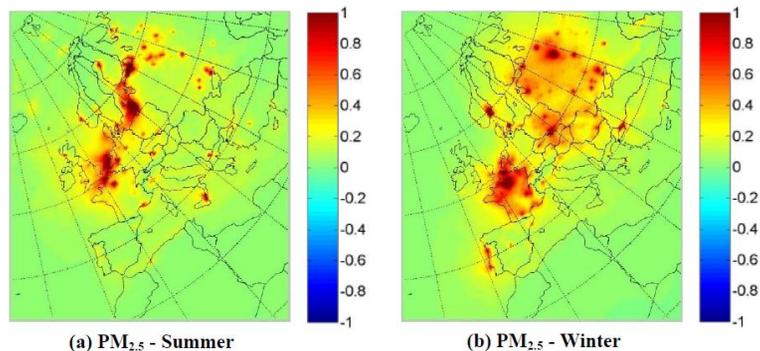


**Fig. 8.** Predicted reduction ( $\mu\text{g m}^{-3}$ ) in ground-level concentrations of total OA after a 50% reduction of anthropogenic POA emissions during (a) summer 2008 and (b) winter 2009. A negative value corresponds to an increase.

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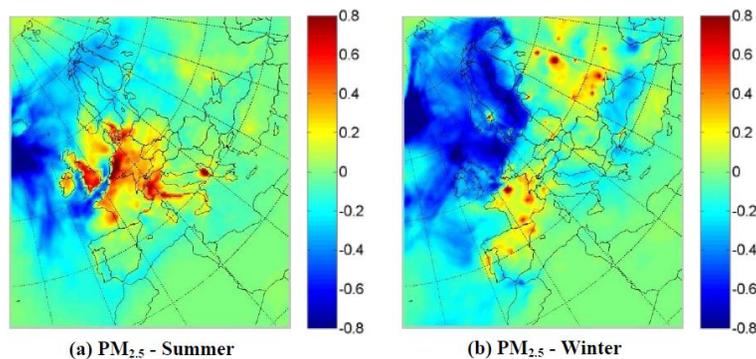


**Fig. 9.** Predicted reduction ( $\mu\text{g m}^{-3}$ ) in ground-level concentrations of total PM<sub>2.5</sub> after a 50 % reduction of anthropogenic POA emissions during **(a)** summer 2008 and **(b)** winter 2009. A negative value corresponds to an increase.

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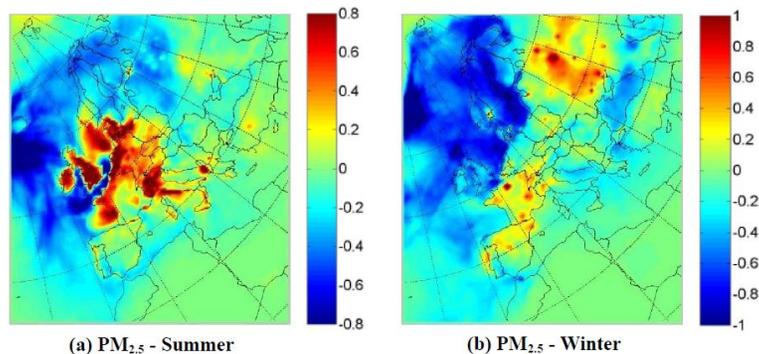


**Fig. 10.** Predicted reduction ( $\mu\text{g m}^{-3}$ ) in ground-level concentrations of total PM<sub>2.5</sub> after a 2.5 K increase of temperature during **(a)** summer 2008 and **(b)** winter 2009. A negative value corresponds to an increase.

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**Fig. 11.** Predicted reduction ( $\mu\text{g m}^{-3}$ ) in ground-level concentrations of total PM<sub>2.5</sub> after a 5K increase of temperature during **(a)** summer 2008 and **(b)** winter 2009. A negative value corresponds to an increase.

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