SIMULATING THE EFFECTS OF CLIMATE CHANGE AND EMISSIONS OF POLLUTANTS ON AIR QUALITY

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Athanasios G. Megaritis

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Αθανάσιο Γ. Μεγαρίτη

Εργαστήριο Μελέτης Ατμοσφαιρικής Ρύπανσης
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Τμήμα Χημικών Μηχανικών Πανεπιστημίου Πατρών

ΕΠΤΑΜΕΛΗΣ ΕΞΕΤΑΣΤΙΚΗ ΕΠΙΤΡΟΠΗ

Σ. ΠΑΝΔΗΣ, Καθηγητής
Τμ. Χημικών Μηχανικών, Παν/μιο Πατρών
Πρόεδρος της εξεταστικής επιτροπής

Κ. ΚΡΑΒΑΡΗΣ, Καθηγητής
Τμ. Χημικών Μηχανικών, Παν/μιο Πατρών

Γ. ΛΥΜΠΕΡΑΤΟΣ, Καθηγητής
Σχολή Χημικών Μηχανικών, ΕΜΠ

Μ. ΚΟΡΝΑΡΟΣ, Επίκουρος Καθηγητής
Τμ. Χημικών Μηχανικών, Παν/μιο Πατρών

Δ. ΜΑΝΤΖΑΒΙΝΟΣ, Καθηγητής
Τμ. Χημικών Μηχανικών, Παν/μιο Πατρών

Χ. ΠΑΡΑΣΚΕΥΑ, Επίκουρος Καθηγητής
Τμ. Χημικών Μηχανικών, Παν/μιο Πατρών

Χ. ΠΗΛΙΝΗΣ, Καθηγητής
Τμ. Περιβάλλοντος, Παν/μιο Αιγαίου
To my parents, Giorgos and Antonia
and my sister Elena
“Ah, recalled moon
standing up there like half comeliness
as a whole opportunity
looking at you to count
how many halves I did not have to leave”

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Abstract

This dissertation is motivated by the challenge of improving air quality and the essential need to enhance our knowledge regarding the potential effects that emissions and climate change could have on the concentration levels of different air pollutants (e.g. particulate matter, ozone, Hg). It is well known that particulate matter (PM), Hg, ozone and other pollutants are subjected to a complex series of common emissions, meteorological processes and photochemical production pathways. Therefore in order to design effective mitigation strategies for improving air quality, it is essential to develop useful quantitative tools, which they can link emissions and meteorology to ambient PM, Hg, etc., concentrations through detailed descriptions of the physics and chemistry of the atmosphere. Chemical Transport models (CTMs) are well suited tools for this purpose.

In the first part of this thesis, a three-dimensional CTM, PMCAMx-2008, is applied over 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 are used, to investigate the seasonal dependence of the PM\(_{2.5}\) response to 50% reductions of sulfur dioxide (SO\(_2\)), ammonia (NH\(_3\)), nitrogen oxides (NO\(_x\)), anthropogenic volatile organic compounds (VOCs) and anthropogenic primary organic aerosol (POA) 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 ammonium nitrate (NH\(_4\)NO\(_3\)) (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 μg m$^{-3}$) during the modeled summer period, mainly due to decrease of sulfate (34% on average over the Balkans). The anthropogenic POA control strategy reduces total OA by 15% during the modeled winter period and 8% in the summer period. The reduction of total OA is higher in urban areas close to its emissions sources. A slight decrease of OA (8% in the modeled summer period and 4% in the modeled winter period) 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 μg m$^{-3}$) during the summer period, due to a decrease of NH$_4$NO$_3$, 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 period, due to more oxidants becoming available to react with SO$_2$ and VOCs. 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$_4$NO$_3$ during summer (18%) and fresh POA during wintertime (35%). Significant increases of OA are predicted during the summer due mainly to the increase of biogenic VOC emissions. On the contrary, OA is predicted to decrease in the modeled winter period 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 Ocean.

Our results regarding the strong sensitivity of PM$_{2.5}$ concentrations to temperature changes support the findings from earlier modeling studies which have concluded that concentrations of PM$_{2.5}$ are strongly influenced by meteorology. However most of these studies have focused on the overall effect of future climate change, and have not tried to quantify the potential effects of changes of individual
meteorological parameters and processes. To address the above issues, we apply PMCAMx-2008 over Europe, trying to examine the effects of various meteorological parameters such as temperature, wind speed, absolute humidity, precipitation, and mixing height on PM$_{2.5}$ concentrations. Our simulations cover three periods, representative of different seasons (summer, winter, and fall). PM$_{2.5}$ appears to be more sensitive to temperature changes compared to the rest meteorological parameters in all seasons. PM$_{2.5}$ generally decreases as temperature increases by 2 K, although the predicted responses vary significantly in space and time, ranging from -700 ng m$^{-3}$ K$^{-1}$ (-8% K$^{-1}$) to 300 ng m$^{-3}$ K$^{-1}$ (7% K$^{-1}$) due to the competing effects on the different PM$_{2.5}$ species. The predicted decreases of PM$_{2.5}$ are mainly due to evaporation of ammonium nitrate (decreases by 15% on average) while the higher biogenic emissions and the accelerated gas-phase reaction rates increase the production of organic aerosol (OA) and sulfate having the opposite effect on PM$_{2.5}$. The predicted responses of PM$_{2.5}$ to absolute humidity are also quite variable, ranging from -130 ng m$^{-3}$ %$^{-1}$ (-1.6% %$^{-1}$) to 160 ng m$^{-3}$ %$^{-1}$ (1.6% %$^{-1}$) dominated mainly by changes in inorganic PM$_{2.5}$ species. An increase in absolute humidity favors the partitioning of nitrate to the aerosol phase and increases average PM$_{2.5}$ during summer and fall. Decreases in sulfate and sea salt levels govern the average PM$_{2.5}$ response to humidity during winter. A decrease of wind speed (keeping constant the emissions), increases all PM$_{2.5}$ species due to changes in dispersion and dry deposition. In all periods, average PM$_{2.5}$ increases by approximately 40 ng m$^{-3}$ %$^{-1}$, while the effects are stronger over the polluted areas of the domain. In addition, the wind speed effects only on sea salt emissions could be significant for PM$_{2.5}$ concentrations over water and in coastal areas (decreases up to 200 ng m$^{-3}$ %$^{-1}$ in the winter). Increases in precipitation have a negative effect on PM$_{2.5}$ (decreases up to 110 ng m$^{-3}$ %$^{-1}$) in all
periods due to increases in wet deposition of PM$_{2.5}$ species and their gas precursors. Changes in mixing height have the smallest effects (up to 35 ng m$^{-3}$ %$^{-1}$) on PM$_{2.5}$. Regarding the relative importance of each of the meteorological parameters in a changed future climate, the projected changes in precipitation are expected to have the largest impact on PM$_{2.5}$ levels during all periods (changes up to 2 μg m$^{-3}$ in the fall). The expected effects in future PM$_{2.5}$ levels due to wind speed changes are similar in all seasons and quite close to those resulting from future precipitation changes (up to 1.4 μg m$^{-3}$). Absolute humidity could potentially lead to large changes in PM$_{2.5}$ levels mainly in the fall (increases up to 2 μg m$^{-3}$) due to the dominance of the increased particulate nitrate levels. In the other two periods the expected PM$_{2.5}$ changes are smaller. Temperature is expected to have a lower impact on future PM$_{2.5}$ levels compared to the rest meteorological parameters in all seasons, while the effects of mixing height are relatively small.

In order to study the overall effect of future climate change on the concentrations of PM$_{2.5}$ and ozone, we use PMCAMx-2008 as part of a global-regional climate-air pollution modeling system (GRE-CAPS). GRE-CAPS consists of three models spanning the global to the regional scale and is applied over Europe, focusing on Greece. Summertime periods are simulated both for the present (2000s) and the future (2050s) assuming constant anthropogenic pollutant emissions. The future time period investigated is the 2050s, using the IPCC (Intergovernmental Panel on Climate Change) A1B scenario which describes a future world of rapid economic growth, rapid introduction of new and more efficient technologies and balance between fossil fuels and other energy sources. Climate change leads to a decrease of average PM$_{2.5}$ concentrations over Greece by 1.1 μg m$^{-3}$ (5%), however the predicted concentration changes are spatially variable and range from -20% to 20% depending on the area.
PM$_{2.5}$ is predicted to decrease in Central Greece, by 1.2 $\mu$g m$^{-3}$ (5.5%) on average, due to the increase in wind speed and the lower absolute humidity, as well as in North Greece and the northern parts of the Aegean. On the contrary, in Crete and the Peloponnese, predicted increases in temperature and absolute humidity lead to higher future PM$_{2.5}$. Decreased precipitation and wind speed also contribute to the changes in these areas. Ozone concentrations over Greece are increased in the future under A1B scenario by 4.5% on average. Highest changes are predicted in Central Greece (8% on average) while in most areas the predicted increases range between 2-3 ppb. The predicted changes in the daily peak O$_3$ concentrations (1-hr maximum and maximum 8-hr average) are higher. The higher future temperatures determine to a large extent the predicted O$_3$ response. Over Europe, climate change significantly affects PM$_{2.5}$ levels, with changes range from -25% to 25%. Changes in several meteorological parameters such as precipitation, temperature, wind speed, and absolute humidity may drive the PM$_{2.5}$ response, having appreciable (and sometimes competing) effects on their concentration levels. Regarding ozone, the model predicts an increase on its concentration in the South Europe (up to 17%) and also in the Balkans, and a decrease in North Europe (up to 10%), with changes in temperature being the dominant factor.

The final objective of this research is to provide useful information regarding the response of atmospheric mercury to future climate change. For the purpose of this study the GRE-CAPS modeling system is applied over the eastern United States in order to study the impact of climate change on the concentration and deposition of atmospheric mercury. Summer and winter periods (300 days for each) are simulated, and the present-day model predictions (2000s) are compared to the future ones (2050s) assuming constant emissions. The future climate period is based on the IPCC A2 scenario which describes a very heterogeneous world, with continuously
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Chapter 1

Introduction
1.1 Air Pollution

A condition of "air pollution" may be defined as a situation in which substances that result from anthropogenic activities are present at concentrations sufficiently high above their normal ambient levels to produce a measurable effect on humans, animals and ecosystems (Seinfeld and Pandis, 2006). Since preindustrial times, the high industrial activities, the rapid growth in urbanization as well as the large demands in energy production and vehicle use, have resulted in significant increases in emissions of gaseous (SO$_2$, NO$_x$, VOCs, etc.) and particulate pollutants as well as in air toxics (e.g., Pb, Cd, Hg), making air pollution one of the most challenging environmental problems, not only locally but also in a global scale.

At the same time, human activities result in emissions of long-lived greenhouse gases (GHG): carbon dioxide (CO$_2$), methane (CH$_4$), nitrous oxide (N$_2$O) and halocarbons (a group of gases containing fluorine, chlorine or bromine). The global emissions of those GHGs have increased markedly since pre-industrial times; only during the last 40 years GHG emissions have increased by 70%. Based on the latest Intergovernmental Panel on Climate Change (IPCC) report (IPCC, 2007), the ongoing increase of GHG emissions since 1750 due to human influences, has warmed the planet resulting in an increase of global surface temperature by approximately 0.7 °C. These GHGs have also contributed to sea level rise and widespread melting of snow and ice (IPCC, 2007). IPCC estimates that global surface temperature is going to increase even more (from 1.1 to 6.4 °C) during the next century.

Despite the fact that for policy purposes air quality and climate are often considered separately, they are inextricably inter-related in their mitigation, their functioning, and their impacts, since the same emitted species are responsible for both (Jacob and Winner, 2009). For example, climate policies imply energy efficiency and
other technical measures that have an impact on a wide range of human activities and, subsequently, on air quality. Reciprocally, air quality mitigation strategies may also have an impact on greenhouse gas emissions. In addition, climate change affects air quality, as it influences the physical and chemical properties of the atmosphere and may lead to more favourable conditions for accumulation of air pollutants. Last, many air pollutants (both gaseous and particulate) have direct and indirect impacts on climate through their radiative forcing (Forster et al., 2007). The combined and sometimes competing linkages among emissions, air quality and climate change indicate that understanding their potential interactions as well as the behavior of air pollutants (e.g., particulate matter, ozone, Hg) is essential for assessing the effectiveness of control strategies.

1.2 Aerosols and their Role in the Atmosphere

Atmospheric aerosols, also referred as particulate matter (PM), are suspended particles (solid or liquid) in a gaseous medium, with diameters ranging from 1 nm to approximately 50 μm. Based on their size, PM is characterized as: coarse (particulate matter with a diameter from 2.5 to 10 μm), fine (particulate matter less than 2.5 μm in size) and ultrafine (less than 0.1 μm). In addition, PM can be classified as primary or secondary, depending on the processes involved during its formation. Primary PM is emitted directly in the particulate phase from various anthropogenic (e.g., industry, transportation, power generation, wood burning) and natural (e.g., dust or sea salt) sources, while secondary PM is formed in the atmosphere through a series of chemical reactions involving different gas-phase precursors such as sulfur dioxide (SO₂), nitrogen oxides (NOₓ), ammonia (NH₃) and volatile organic compounds (VOCs). Usually, PM has a mean residence time from a few days to several weeks,
while it can be removed from the atmosphere via two removal mechanisms: deposition on the Earth’s surface (dry deposition) and incorporation into cloud and rain droplets and then removal by precipitation (wet deposition). Typically, PM consists of a mixture of inorganic and organic chemical species including nitrate, sulfate, ammonium, organic material, elemental carbon, sea salt, crustal species and water.

Atmospheric particles have adverse effects on human health. In particular, fine particulate matter with an aerodynamic diameter less than 2.5 μm (PM$_{2.5}$), in elevated concentrations is associated with increases in morbidity and mortality (Schwartz et al., 1996; Pope et al., 2009). It has been estimated that exposure to PM$_{2.5}$ concentrations in outdoor air leads to about 100,000 deaths (and 725,000 years of life lost) annually in Europe (WHO, 2002). A reduction of the ambient concentration of PM$_{10}$ by 5 micrograms per cubic meter in Europe can “prevent” between 3000 and 8000 early deaths annually (Medina et al., 2004). In addition, several toxicological and epidemiological studies have linked PM concentrations with several cardiovascular and respiratory diseases (Dockery et al., 1996; Gauderman et al., 2000; Bernard et al., 2001). Due to the adverse effects of PM concentrations on human health, the U.S. Environmental Protection Agency and the European Commission have developed legislation which establishes health-based standards for PM. The European air quality limits are currently 25 μg m$^{-3}$ annual concentration for PM$_{2.5}$ and 50 μg m$^{-3}$ 24-hour average concentration for PM$_{10}$ (the European Union has not yet set a 24-hour average concentration limit for PM$_{2.5}$) (EEA, 2013). For comparison, the respective US National Ambient Air Quality Standards (NAAQS) are 35 μg m$^{-3}$ for the 24-hour average concentration and 15 μg m$^{-3}$ annual concentration for PM$_{2.5}$, and 150 μg m$^{-3}$ 24-hour average concentration for PM$_{10}$ (Esworthy, 2013).
Particulate matter has also a significant impact on various physical and chemical processes in the atmosphere, even at low concentrations. PM has a direct effect on the Earth’s radiation balance and climate due to its ability to scatter and absorb light. For example, PM containing elemental carbon (EC) can absorb light and has a warming effect on climate (Hansen et al., 2000). On the contrary, particles composed of a mixture of purely scattering material such as ammonium sulfate have a cooling effect (Seinfeld and Pandis, 2006). As particulate matter contains various components, it often has both absorptive and scattering effects, with the net effect depending on its exact composition, size distribution, the location in the atmosphere, etc.

In addition to the direct effect, particulate matter affects the Earth’s radiation balance and climate indirectly. Particles can act as cloud condensation nuclei (CCN), upon which cloud droplets can form. The number and the size of the cloud droplets for a given supersaturated environment are determined by the size distribution and chemical composition of the aerosol (Lohmann et al., 1999). However, the indirect climate effects of aerosols are more complex and more difficult to assess than direct effects because they depend on a chain of processes that connect aerosol levels to CCN concentrations, CCN levels to cloud droplet number concentrations (and size), and these, in turn, to cloud albedo (defined as the fraction of incident solar radiation that is reflected back into the space) and cloud lifetime (Haywood and Boucher, 2000; Seinfeld and Pandis, 2006).

PM can also reduce the visibility and contribute to the “haze” associated with urban and regional pollution (Seinfeld and Pandis, 2006), while it is often involved in the formation of acid rain and acid fogs (Burtraw et al., 2007).

Due to its detrimental effects on human health and the fact that it has been implicated in various air quality and climate problems, particulate matter has been a
major topic of research during the last decades. A detailed characterization of PM physical and chemical properties, sources, as well as a complete understanding of the major atmospheric processes affecting it is a significant step forward in our efforts to mitigate its negative effects.

1.3 Mercury in the Atmosphere

Mercury (Hg) is an important pollutant due to its high toxicity. Most of the mercury in the atmosphere (>95%) is in the gas phase (Munthe, 1992; Gustin, 2003; Baya and Van Heyst, 2010) and exists in three oxidation states: 0, +1 and +2. Mercury exists predominantly in the gaseous elemental form Hg\textsubscript{0} referred to as gaseous elemental mercury, and in the +2 oxidation state referred to as gaseous oxidized mercury (Hg\textsuperscript{2+}) (Schroeder and Munthe, 1998). Hg\textsubscript{0} is the main component of gaseous Hg, and is around 80% of Hg in the atmosphere (Gbor et al., 2007). Hg\textsubscript{0} is the predominant species because it has a long atmospheric lifetime (0.5-2 yr) (Lindberg et al., 2007) due to its low solubility in water and low chemical reactivity. It is vertically well mixed in the troposphere and can be transported over long distances, making it a persistent global pollutant. On the other hand, Hg\textsuperscript{2+} is highly water soluble, reactive and less volatile than Hg\textsubscript{0}, having a much shorter atmospheric lifetime and is rapidly removed via wet and dry deposition, close to its emissions sources. Another important form of mercury in the atmosphere is particulate mercury (Hg(p)). It is present in the atmosphere as a result of direct emissions from anthropogenic sources (Schroeder and Munthe, 1998) or produced from Hg\textsubscript{0} or Hg\textsuperscript{2+} adsorbed onto particulate matter (Schroeder and Munthe, 1998; Seigneur et al., 2004b). Similar to Hg\textsuperscript{2+}, Hg(p) has a relatively short atmospheric lifetime and deposits closer to emission sources by wet and dry deposition. Hg is released into the
atmosphere from both anthropogenic and natural sources. While anthropogenic Hg is mainly contributed by chloral-alkali production, coal combustion, and waste incineration, there are also natural sources of Hg including volcanoes, soils, forests, lakes, rivers and oceans. Typical Hg$^0$ concentrations are of the order of ng m$^{-3}$, while Hg$^{2+}$ and Hg(p) concentrations are of the order of pg m$^{-3}$.

Despite its low concentration levels in the atmosphere compared to other pollutants (PM, ozone etc.), mercury can cause significant problems to human and ecosystem health. Once deposited through dry or wet removal processes, atmospheric mercury can end up in streams, lakes, or estuaries, where certain microorganisms can change it into a highly toxic form, methylmercury (MeHg). MeHg can accumulate in fish tissues at levels that may harm the fish, other animals that eat them as well as humans, and eventually can influence the total food chain (Satoh, 2000; Weiner et al., 2003). Because Hg is a global pollutant, the concentrations of methylmercury in fish in different waterbodies, are impacted by a combination of local, long-range and global sources. The physical, biological, and chemical properties of different waterbodies and the age, size and types of food the fish eats can also affect fish methylmercury levels.

High levels of methylmercury exposure for humans can cause a variety of negative health effects, including kidney and liver failure, endocrine disruption, reproductive abnormalities, neurodevelopmental delays and compromised cardiovascular health (Clarkson and Magos, 2006; Mergler et al., 2007). A U.S. National Research Council (NRC) committee (NRC, 2000) concluded that the risk of adverse effects from current methylmercury exposures to the majority of the U.S. population is relatively low. However, since the developing human nervous system is sensitive to methylmercury, young children and children of women who consume fish
during pregnancy are at risk (IPCS, 1990; NRC, 2000; Clarkson et al., 2003). Human health data from the United States suggest that 300,000-600,000 U.S. children are born each year with blood MeHg levels exceeding the U.S. Environmental Protection Agency’s (U.S. EPA) reference dose (Mahaffey et al., 2004; Trasande et al., 2005).

Birds and mammals that eat fish are more exposed to methylmercury than any other animals in water ecosystems. Similarly, predators that eat fish-eating animals are at risk. Effects of methylmercury exposure on wildlife can include mortality (death), reduced fertility, slower growth and development, and abnormal behavior that affects survival, depending on the level of exposure.

In order to assess the impact of this highly toxic contaminant on human health and ecosystems we need to improve our knowledge regarding the atmospheric Hg cycle. Despite recent progress, there are still a lot of issues, concerning the transport and chemistry of atmospheric Hg, its major sources and the corresponding concentration levels, as well as the major removal processes, that need to be understood better in order to reduce its negative effects.

1.4 Atmospheric Chemical Transport Models

Particulate matter, Hg, ozone and other pollutants are subjected to a complex series of common emissions, meteorological processes and photochemical production pathways. Thus, in order to design effective control strategies for improving air quality, we need to develop quantitative tools, which can link emissions and meteorology to ambient PM, Hg, etc., concentrations through detailed descriptions of the physics and chemistry of the atmosphere. Chemical Transport models (CTMs) are well suited tools for this purpose. CTMs rely on mathematical representations of the relevant physical and chemical atmospheric processes, which are simulated using
numerical algorithms to obtain pollutant concentrations as a function of space and time for a given set of pollutant emissions and meteorological conditions (Seigneur and Moran, 2004a).

Based on the reference frame employed, CTMs are grouped in two subcategories: Lagrangian (or trajectory) models and Eulerian models. Lagrangian trajectory models use a reference frame that follows the movements of individual air parcels from sources to receptors (Fig. 1.1). Transformations take place within the parcels and the transport processes that are not resolved by the mean advective transport (e.g., vertical turbulent diffusion) may move chemical species between parcels or increase the size of parcels.

**Figure 1.1:** Schematic depiction of a Lagrangian model. A box (left) is used to simulate an air parcel that is moving in the atmosphere. The path is determined by integration of the wind field. Such a path of an air parcel leaving Egypt and arriving in Patras is shown in the map.
Eulerian models use a reference frame that is fixed in space. Their simplest form is the zero-dimensional box model. However, most Eulerian CTMs use a three-dimensional (3-D) grid framework to cover a large area (Fig. 1.2). Chemical and physical transformations are simulated for each grid cell, and transport and diffusion processes move chemical species between grid cells. The height of the grid cells can vary, while the horizontal and vertical size can range from approximately 4 x 4 km to 36 x 36 km or more, depending on the size of the modeling domain and purpose of the model.

Figure 1.2: Schematic depiction of an Eulerian model.
Lagrangian models are usually simpler and less computationally demanding than Eulerian models. However, they are also limited by their simplicity in that they generally do not treat some atmospheric physical processes realistically, including differential advection due to vertical wind shear, and horizontal dispersion (some Lagrangian models try to treat these processes but the computational costs increase accordingly). Therefore the most suitable CTMs for policy and regulatory purposes are the 3-D Eulerian grid models due to the need for realistic representations of all relevant processes.

Before a CTM can be used for a wide range of applications, it is essential to ensure that represents reasonably well all these processes that govern ambient pollutants concentrations in the area and the corresponding simulation periods. As pollutants’ concentrations are a function of meteorology, emissions, and background concentrations, one needs to evaluate the ability of a CTM to predict correctly pollutants concentrations under a wide range of conditions. Pollution in a single geographical area generally does not have sufficient variation to cover all these variables. Therefore, it is recommended to perform comprehensive performance evaluation of the model in multiple regions and during different seasons in order to ensure its applicability (Seigneur and Moran, 2004a).

1.5 Objectives and Motivation

This research was motivated by the challenge of improving air quality by enhancing our knowledge of the potential links among emissions, climate change, and the concentration levels of different air pollutants (e.g. PM, Hg, ozone).

Concentrations of particulate matter, ozone and other air pollutants, emissions and meteorology are strongly linked to each other. For example, a potential change in
emissions of one pollutant can lead to changes (positive or negative) in the concentrations of other pollutants. In addition, changes in meteorological conditions such as a temperature increase also influence the concentration of air pollutants (and subsequently air quality), through a variety of direct and indirect pathways, like the increase of biogenic emissions (Constable et al., 1999), and the accelerated gas-phase chemical production (Dawson et al., 2007). In Chapter 2, we quantify how fine particulate matter (PM$_{2.5}$) concentrations respond to emissions changes of its major gaseous (SO$_2$, NO$_x$, NH$_3$, anthropogenic VOCs) and particulate precursors (anthropogenic primary organic aerosol) as well as how a change on temperature can influence PM concentrations. For this purpose we apply a recently developed and evaluated three-dimensional CTM (PMCAMx-2008) over Europe. PMCAMx-2008 (Fountoukis et al., 2011) is well suited for this scope as it directly links emissions and meteorology to PM$_{2.5}$ concentrations through detailed descriptions of the physics and chemistry of the atmosphere. Two simulation periods are used (summer and winter), representative of each season to estimate also the seasonal dependence of the PM$_{2.5}$ response to emissions and temperature changes.

Our findings from Chapter 2 show the strong sensitivity of PM$_{2.5}$ concentrations to temperature changes. These conclusions are in agreement with earlier studies in the US which found that concentrations of PM are strongly influenced by changes in meteorology (e.g. Dawson et al., 2007; Tsigaridis and Kanakidou, 2007; Jacob and Winner 2009). However most of the earlier studies have focused on the overall effect of future climate change, and have not tried to quantify the potential effects of changes of individual meteorological parameters and processes. In Chapter 3, we conduct a detailed sensitivity analysis, using PMCAMx-2008, trying to quantify how changes in various meteorological variables such as temperature, wind speed, absolute
humidity, precipitation, and mixing height, and their subsequent effects on different processes, can influence fine particulate matter (PM$_{2.5}$) concentrations over Europe. Our simulations cover different periods (summer, winter, and fall), while each of these parameters is studied separately so that the relative importance of each as well as the subsequent response of PM$_{2.5}$ can be quantified.

The results from Chapter 3 provide us useful information regarding the potential effects that meteorology, under a future climate, could have on particulate matter. In Chapter 4 we take a step forward and we try to examine the overall effect of future climate change on PM$_{2.5}$ levels. For the purpose of this study we apply a global-regional climate-air pollution modeling system (GRE-CAPS) over Europe, with a special focus on Greece. GRE-CAPS consists of three models spanning the global to the regional scale: a global CTM with online chemistry, (GISS II GCM) (Racherla and Adams, 2006), the regional meteorological model WRF (Skamarock et al., 2005), and the regional CTM, PMCAMx-2008 (Fountoukis et al., 2011). GRE-CAPS is well suited for this purpose as it links previously evaluated models (for example, PMCAMx-2008 has been extensively evaluated against measurements taken from different types of sites in Greece and also over Europe, as well as during different periods). GRE-CAPS has shown a good performance regarding its ability to capture present-day PM$_{2.5}$ concentrations compared to other coupled modeling systems (Dawson et al., 2008). This study, provide us valuable insights regarding the impacts of future climate change on air quality in Greece, as there has been little work conducted in this area.

In Chapter 5, adding to the above efforts, we use GRE-CAPS to study the impact of future climate change on the concentration and deposition of atmospheric mercury. GRE-CAPS is applied over the eastern United States, simulating summer and winter
periods (300 days for each) to assess also the corresponding spatial and seasonal characteristics.

The conclusions of this work are summarized in Chapter 6 and suggestions for future work are provided.
1.6 References


Chapter 2

Response of Fine Particulate Matter
Concentrations to Changes of Emissions
and Temperature in Europe

This work has been published as:

2.1 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 sulfur dioxide (SO$_2$), ammonia (NH$_3$), nitrogen oxides (NO$_x$), anthropogenic volatile organic compounds (VOCs) and anthropogenic primary organic aerosol (POA) 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 µg m$^{-3}$ and 1.8 µg m$^{-3}$ (5.5% and 4% on average) during summer and winter respectively, mainly due to reduction of ammonium nitrate (NH$_4$NO$_3$) (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 µg m$^{-3}$) during the modeled summer period, mainly due to decrease of sulfate (34% on average over the Balkans). The anthropogenic POA control strategy reduces total OA by 15% during the modeled winter period and 8% in the summer period. The reduction of total OA is higher in urban areas close to its emissions sources. A slight decrease of OA (8% in the modeled summer period and 4% in the modeled winter period) 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 µg m$^{-3}$) during the summer period, due to a decrease of NH$_4$NO$_3$, 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 period, due to more oxidants becoming available to react with SO$_2$ and VOCs.
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$_4$NO$_3$ during summer (18%) and fresh POA during wintertime (35%). Significant increases of OA are predicted during the summer due mainly to the increase of biogenic VOC emissions. On the contrary, OA is predicted to decrease in the modeled winter period 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 Ocean. The substantial reduction of PM$_{2.5}$ components due to emissions reductions of their precursors outlines the importance of emissions for improving air quality, while the sensitivity of PM$_{2.5}$ concentrations to temperature changes indicate that climate interactions need to be considered when predicting future levels of PM, with different net effects in different parts of Europe.

2.2 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$_{2.5}$), 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$_2$ emissions decreased approximately 70% while sulfate concentrations decreased around 50%. Emissions of nitrogen oxides and ammonia also decreased 25% and 20% respectively with a non-linear response of ammonium nitrate. De Meij et al. (2009a) applied a three-dimensional chemical transport model (CTM) over Northern Italy and estimated the impact of 50% emission reductions of NO$_x$, PM$_{2.5}$, SO$_2$, VOC and NH$_3$, for different source sectors, on O$_3$ and PM$_{2.5}$ concentrations. This study showed that the 50% reduction of NO$_x$ and PM$_{2.5}$ emissions coming from road transport and non-industrial combustion plants is the most effective control strategy for reducing PM$_{2.5}$ levels over Po Valley, leading to an average decrease of 1-6 µg m$^{-3}$ and 1-4 µg m$^{-3}$ 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 NOx 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\textsubscript{3} and PM in several emission scenarios for 2010. The authors focused on the importance of fine scale modeling for O\textsubscript{3} 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; Nguyen and Dabdub, 2002; Mueller et al., 2004; Kleeman et al., 2005; Pun et al., 2008; 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\textsubscript{2.5} mass concentrations to changes in SO\textsubscript{2} and NH\textsubscript{3} emissions for a summer and a winter period. They found that NH\textsubscript{3} emission control during winter is an effective control strategy, while in the summer reductions in SO\textsubscript{2} yield the largest reduction of PM\textsubscript{2.5}. Similar results for NH\textsubscript{3} reductions were reported by Pinder et al. (2007) who calculated that the NH\textsubscript{3} 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; Langner et al., 2005; Ordonez et al., 2005; Szopa et al., 2006; Forkel and Knoche, 2007; Giorgi and Meleux, 2007; Jacob and Winner, 2009). Forkel and Knoche (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. 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. In a global study by Heald et al. (2008), the authors used a global atmosphere-land model to investigate the sensitivity of secondary organic aerosol (SOA) concentration to changes in climate and emissions under the year 2100 IPCC A1B scenario. They predicted increases of SOA levels in the future climate, mainly due to increase of biogenic SOA, which were estimated to rise around 35% in Europe. In addition, Carvalho et al. (2010) used downscaled meteorology generated by a global circulation model (GCM) in a regional CTM to study the impact of climate change on the air quality over Europe and Portugal, using the IPCC A2 scenario for the future. Their modeling system predicted that the response of PM$_{10}$ to the future climate varies in space and time with increases of PM$_{10}$ levels predicted mainly over the continental regions.

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. Three-dimensional CTMs are well suited for this purpose because they link emissions and meteorology to PM\textsubscript{2.5} concentrations through descriptions of the physics and chemistry of the atmosphere. 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\textsubscript{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 (EUCAARI) intensive periods (Kulmala et al., 2011).

The remainder of this chapter 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\textsubscript{3}, SO\textsubscript{2}, NO\textsubscript{x}, anthropogenic VOCs and anthropogenic OA emissions reductions on the concentration of the PM\textsubscript{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\textsubscript{2.5} levels, for the different periods are discussed.
2.3 The PMCAMx-2008 CTM

2.3.1 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 (Environ, 2003; Carter, 2013) which includes 211 chemical reactions of 56 gases and 18 free radicals. For the aerosol processes, 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; Murphy and Pandis, 2009). 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 μm.

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 μm) 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 HNO$_3$ forming NaNO$_3$), but assuming an average PM composition.

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 $10^6$ μg m$^{-3}$ are used following the approach of Shrivastava et al. (2008). POA is simulated in the model in two types, “fresh” (unoxidized) POA and oxidized POA (OPOA). For the intermediate VOC (IVOC) emissions we followed the approach of Tsimpidi et al. (2010) and Shrivastava et al. (2008), in which the IVOC emissions are proportional to the emitted primary OA mass. Due to the difficulty in measuring mass in this volatility range (it is emitted and remains largely in the gas phase), emission inventories do not include these compounds. Thus we add an additional 1.5 times the original POA mass emission rate to the intermediate volatility organic gas emission rate following several prior studies (Robinson et al., 2007; Murphy and Pandis, 2009; Hodzic et al., 2010; Tsimpidi et al., 2010). The IVOCs can then be oxidized by OH and may go to lower volatility and condense. SOA consists of organic aerosol of anthropogenic (aSOA) and biogenic (bSOA) origin. The SOA volatility basis-set approach (Lane et al., 2008a) used in the current version of the model includes four SOA species for each VOC with 4 volatility bins ($1, 10, 100, 1000$ μg m$^{-3}$). In addition, the model treats all anthropogenic 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).
For the simulation of wet deposition the model uses a scavenging coefficient approach in which the local rate of concentration change within or below a precipitating cloud is equal to the product of the concentration of a pollutant and the respective scavenging coefficient. The scavenging coefficient is determined differently for gas and aerosol species following Seinfeld and Pandis (2006). For dry deposition, PMCAMx determines a deposition velocity for each land use type, for each given species, particle size, and grid cell, and then linearly combines them according to the fractional distribution of land use. The deposition flux is used as the lower boundary condition in the vertical dispersion algorithm. For the gas phase species, the resistance model of Wesely (1989) is used. The deposition velocity is calculated from three resistances in series: the aerodynamic resistance $r_a$, the quasi-laminar resistance $r_b$, and the surface resistance $r_s$. The surface resistance is further expressed as several more serial and parallel resistances that depend upon the physical and chemical properties of the surface in question. Many of these resistances, such as the stomatal resistance $r_{st}$ vary also with temperature. Over water, the surface resistance is parameterized following Kumar et al. (1996) and Sehmel (1967). For aerosol particles the resistance approach of Slinn and Slinn (1980), as implemented in UAM-AERO (Kumar et al., 1996), has been adopted in PMCAMx.

2.3.2 Modeling domain and inputs

PMCAMx-2008 was applied over Europe covering a 5400 × 5832 km region with 36 × 36 km grid resolution and 14 vertical layers covering approximately 20 km (Fig. 2.1). 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). The performance of WRF for Europe against observed meteorological variables has been the topic of a number of recent studies (Jimenez-Guerrero et al., 2008; de Meij et al., 2009b; Im et al., 2010; Argueso et al., 2011; Garcia-Diez et al., 2012) showing good agreement in comparison with observations. The concentrations of the major PM species used as boundary conditions of the domain in this study were taken from Fountoukis et al. (2011) and are based on measured background concentrations in sites close to the boundaries (e.g., Zhang et al., 2007; Seinfeld and Pandis, 2006).

**Figure 2.1:** 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).
Updated anthropogenic and biogenic hourly emission gridded fields were developed and evaluated for the European domain for gases and primary particulate matter (Table 2.1). Anthropogenic gas emissions include land as well as international shipping emissions and were developed by the TNO team during the EUCAARI project (Denier van der Gon et al., 2010) as a continuation of the work in GEMS and MACC. The major improvement was the development of the Pan-European Carbonaceous Aerosol Inventory improving the emissions estimates of anthropogenic particulate organic and elemental carbon (Kulmala et al., 2011). A detailed description of the emissions temporal variations and NMVOC emissions composition is provided elsewhere (Schaap et al., 2005; Visschedijk et al., 2007). Two different datasets are combined in order to produce the biogenic gridded emissions for the model. Emissions from ecosystems are produced by MEGAN (Model of Emissions of Gases and Aerosols from Nature) (Guenther 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. The sesquiterpene emissions have been set to 30% of the monoterpene emissions (Helmig et al., 2006). For sea salt emissions the marine aerosol emission model developed by O’Dowd et al. (2008) was used, which uses wind speed data from WRF and chlorophyll $\alpha$ concentrations as inputs for the calculations. In addition, for the summer period we also included emissions data from wildfires (Sofiev et al., 2008a, b). The Saharan dust emissions are not modeled explicitly but are included as boundary conditions in the domain. The dust emissions from Europe are included in the corresponding inventories.
Table 2.1: Emission mass totals for gaseous and PM$_{2.5}$ species (in ktons month$^{-1}$) for the European domain during the modelled summer and the modelled winter period.

<table>
<thead>
<tr>
<th>Species</th>
<th>Summer</th>
<th></th>
<th>Winter</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Anthropogenic</td>
<td>Biogenic</td>
<td>Anthropogenic</td>
</tr>
<tr>
<td>CO</td>
<td>3682</td>
<td>1207</td>
<td>5002</td>
</tr>
<tr>
<td>NO$_x$</td>
<td>1461</td>
<td>46</td>
<td>1531</td>
</tr>
<tr>
<td>SO$_2$</td>
<td>1675</td>
<td>3</td>
<td>1961</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>501</td>
<td>11</td>
<td>474</td>
</tr>
<tr>
<td>NMVOC</td>
<td>1291</td>
<td>1872</td>
<td>1334</td>
</tr>
<tr>
<td>NO$_3^-$</td>
<td>-</td>
<td>4</td>
<td>-</td>
</tr>
<tr>
<td>Sulfate</td>
<td>-</td>
<td>146</td>
<td>-</td>
</tr>
<tr>
<td>NH$_4^+$</td>
<td>-</td>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>EC</td>
<td>47</td>
<td>12</td>
<td>62</td>
</tr>
<tr>
<td>OC</td>
<td>68</td>
<td>81</td>
<td>112</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>-</td>
<td>512</td>
<td>-</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>-</td>
<td>920</td>
<td>-</td>
</tr>
</tbody>
</table>

2.3.3 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 (Cabauw, Finokalia, Mace Head and Melpitz), as well as airborne measurements from an aircraft field campaign over Europe, during May 2008. On a domain-average basis, organic aerosol was predicted to account for 32\% of total PM$_1$ mass at ground level, followed by sulfate (30\%), ammonium (13\%), nitrate (7\%), and elemental carbon (4\%). The comparison of the model predictions with hourly average ground measurements was encouraging. The monthly average concentrations for PM$_1$ OA, nitrate, sulfate and ammonium, measured in the four stations were 3.3, 1.7, 2.8 and 1.5 µg m$^{-3}$ respectively compared to the predicted
average values of 3, 2.8, 2.9 and 1.7 μg m\(^{-3}\). The model reproduced more than 87% of
the hourly averaged data within a factor of 2 for PM\(_1\) OA. The mean bias for OA was
-0.4 μg m\(^{-3}\) while the corresponding normalized mean bias (NMB) and normalized
mean error (NME) were 11% (small underprediction) and 30% respectively.
Compared to the daily averaged measurement values, the model performed well for
OA reproducing more than 94% of the hourly data within a factor of 2. In addition,
the model performed 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 while it tended to predict relatively flat average diurnal profiles
for PM\(_1\) OA in many areas, both rural and urban in agreement with observations.

For PM\(_1\) sulfate the model performance was also encouraging reproducing more
than 70% of the hourly data points and more than 82% of the daily averaged data
within a factor of 2. Although, the model predictions for sulfate were subject to
significant scatter (NME=47%, mean error=1.3 μg m\(^{-3}\), fractional error = 0.4). The
NMB in Cabauw, Finokalia and Melpitz was 29% for PM\(_1\) nitrate and to 2% for PM\(_1\)
ammonium and the corresponding mean biases were 0.4 and 0.03 μg m\(^{-3}\) respectively.
Potential explanations for the tendency of the model to overpredict ammonium nitrate
in these areas include overestimation of the ammonia emissions, uncertainties in the
AMS measurements and of course incomplete understanding of the corresponding
production and removal processes. The model predicted significantly higher
concentrations for both nitrate and ammonium in Mace Head, compared to the
measurements. These errors could be partly attributed to the use of the bulk
equilibrium approach for the simulation of the inorganic aerosol growth and the fact
that a significant amount of nitrate over this area is associated with sea salt, which
shifts nitrate and ammonium to the coarse mode (Dall’Osto et al., 2010). Karydis et
al. (2010), found a similar behavior for nitrate, in the high dust concentration area of Mexico City where the bulk equilibrium approach of PMCAMx-2008 was unable to capture this effect. Similarly to our results, they underpredicted concentrations of nitrate and ammonium in the coarse mode and overpredicted them in the fine mode. The prediction skill metrics of PMCAMx-2008 against AMS hourly ground measurements during the EUCAARI summer campaign are summarized in Table 2.4 (in the supplementary material section). The respective skill metrics of the comparison during the EUCAARI winter campaign are summarized in Table 2.6 (see supplementary information).

The model predictions showed that PM$_1$ sulfate concentrations in the Mediterranean region are much higher than the PM$_1$ OA during the late spring period, while organic matter is predicted to be the dominant PM$_1$ species over a large part of continental Europe. Oxidized POA and OA from intermediate volatility organic compounds (IVOCs) were predicted to be the dominant OA components, contributing around 50% to total OA, while biogenic SOA comprised on average almost one third of the total predicted OA over the domain. In addition, the model predicted low levels of fresh POA in most areas of the domain, with an exception for urban and suburban areas located mainly in central and Northern Europe. Compared to a positive matrix factorization analysis of the organic aerosol AMS data at Finokalia (Hildebrandt et al., 2010a), PMCAMx-2008 correctly predicted negligible hydrocarbon-like organic aerosol (HOA) concentrations (~0.02 μg m$^{-3}$) as a result of no strong local sources and rapid conversion of POA to OPOA. On average, both AMS and PMCAMx-2008 give high oxygenated organic aerosol concentrations (more than 98% of total OA in this area). A more detailed comparison between the PMCAMx-2008 predicted concentrations of OA components and the PMF analysis of AMS data from various
European sites, during different periods, is in progress and will be presented in a forthcoming publication.

The capability of PMCAMx-2008 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 was as good as its performance against the ground level hourly measurements. The measured average concentrations for PM$_1$ OA, nitrate, sulfate and ammonium were 2.6, 1.6, 1.6 and 1.2 μg m$^{-3}$ respectively compared to the predicted average values of 2.2, 1.4, 1.6 and 1.3 μg m$^{-3}$. However, compared to the ground measurements the scatter in this comparison was a little larger since the model predictions are compared against each one of the AMS measurements (total of ~7000 points) instead of comparing hourly averages. Overall the model predictions showed small NMB, from 1% (ammonium) to -15% (OA) and larger NME (from 42% for OA to 69% for nitrate), while the model correctly predicted more than 66% and 62% of the observed concentrations within a factor of 2 for OA and sulfate respectively. Table 2.5 in the supplementary information (Section 2.10) gives a summary for the statistical metrics of the comparison between the airborne AMS data and PMCAMx-2008 predictions.

### 2.4 Simulated periods

PMCAMx-2008 was used for the simulation of two month-long periods one during summer and one during the winter. Summer results were based on a hot period (1-29 May 2008) while the winter simulation was based on a cool late winter and early spring period (25 February-23 March 2009). These two periods have been
selected to be representative of each season allowing us to reduce the computational cost of the overall effort. Both periods included a variety of meteorological conditions and pollution levels. For example, the first half of May was characterized by a blocking anticyclone leading to stable meteorological conditions and high pollution levels over Central Europe. Hamburger et al. (2011) have provided an extended analysis of the synoptic and pollution situation over Europe during this period. High temperatures were observed in most of northern and southern Europe (Pikridas et al., 2010; Poulain et al., 2011; Mensah et al., 2012), leading to enhanced photochemical activity, which is characteristic of early summer. The winter period was relatively typical with low temperatures observed in most areas of the domain (Hildebrandt et al., 2010b; Freney et al., 2011; Poulain et al., 2011; Mensah et al., 2012).

The predicted base case averaged concentrations for particulate ammonium, nitrate, sulfate, total OA and total PM$_{2.5}$ mass during the modeled summer and winter periods are shown in Fig. 2.2. During the summer period the model predicts high nitrate concentrations in Western Europe, with a predicted maximum of 7 μg m$^{-3}$ in South England. In the rest of the domain nitrate is lower, less than 2 μg m$^{-3}$ in most areas. PM$_{2.5}$ ammonium shows a similar pattern to nitrate in the domain, while elevated ammonium concentrations show strong association with nitrate, evidence of NH$_4$NO$_3$ formation in the specific area. Additionally, the highest predicted concentrations for fine sulfate are predicted over the Mediterranean while organic matter is predicted to be the dominant PM$_{2.5}$ component in Central and Northern Europe, with oxidized POA and biogenic SOA contributing around 50% and 30% to total OA respectively.

During the winter period, 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.
The high levels of total PM$_{2.5}$ above some sea regions are due to several reasons. During the May period the high PM concentrations in Northern Europe (an area extending from Southern Scandinavia to Western Ireland) were due mainly to high ammonium nitrate concentrations. These predictions are consistent with the extended airborne measurements in the area as well as the measurements in Cabauw and Mace Head (Fountoukis et al., 2011). The high levels over the Mediterranean (central and
eastern) were mainly due to high sulfate levels. These higher sulfate levels over the Mediterranean were due to the transport of sulfur dioxide and the resulting sulfates originating from the Balkans and the industrial areas of eastern Europe (Mihalopoulos et al., 1997; Ganor et al., 2000; Lelieveld et al., 2002; Sciare et al., 2003). Dust (in the Mediterranean), sea-salt as well as DMS from phytoplankton also contributed to these elevated levels over water. The elevated levels in the modeled winter period were due to a combination of high ammonium nitrate, organic aerosol and sea-salt.

The model predicts high nitrate concentrations over most of Europe during the modeled winter period and the levels in the Po Valley are relatively high (Figure 2.2f). However, this simulated period includes periods of accelerated removal (e.g., high rainfall rates); the concentrations during specific episodes are a lot higher. The model predicts also low OA concentrations over Germany, compared to the available observations in Melpitz. The wintertime underestimation of OA levels was due to the fact that the wood-burning emissions in this area are underestimated. Similar underestimation of the emissions has been found also in Sweden and Switzerland and this will be the topic of a forthcoming publication.

2.5 Results

Five control strategies were examined separately, a 50% reduction of gaseous emissions (SO$_2$, NH$_3$, NO$_x$, anthropogenic VOCs) and a 50% reduction of anthropogenic primary OA emissions (POA). In the SO$_2$, NO$_x$ and NH$_3$ emission control simulations, the initial and boundary conditions of SO$_2$, NO$_x$ and NH$_3$ as well as the initial and boundary conditions of sulfate, nitrate, and ammonium were also reduced by 50%. These are oversimplified cases exploring mainly the sensitivity of
concentrations to emissions. We focus on the differences between the base case and reduced emission scenario at the ground level.

2.5.1 Reduction of NH$_3$ emissions

The predicted changes in average ground-level concentrations of the major PM$_{2.5}$ components after a 50% reduction of NH$_3$ emissions during the modeled summer and the modeled winter period are shown in Fig. 2.3 and are summarized in Table 2.2.

The reduction of NH$_3$ emissions significantly reduces PM$_{2.5}$ levels in both periods. The reduction of PM$_{2.5}$ is mainly attributed to decreases of particulate ammonium nitrate levels. In areas where ammonium nitrate concentration is elevated the effect of NH$_3$ emissions on PM$_{2.5}$ levels is even higher.

In addition, NH$_3$ control indirectly affects sulfate formation, resulting on a slight decrease of its levels. Sulfate, even in environments with low NH$_3$, exists in the aerosol phase as ammonium sulfate or bisulfate. Part of this sulfate is formed heterogeneously in cloud droplets via the dissolution of gaseous SO$_2$ and its oxidation. The second most important aqueous-phase reaction is the reaction of the dissolved SO$_2$ with O$_3$ at pH values greater than 5 (Seinfeld and Pandis, 2006). Therefore, the effective cloud SO$_2$ oxidation rate depends partially on the presence of species affecting pH, such as NH$_3$. The respective response of sulfate is mainly due to the reduction of the cloud pH and the reduction of the rate of in-cloud sulfate production.
<table>
<thead>
<tr>
<th>Region</th>
<th>PM$_{2.5}$ Components</th>
<th>Control Strategy</th>
<th>Predicted Change – Summer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>-50% NH$_3$</td>
<td>-50% NO$_x$</td>
</tr>
<tr>
<td>I</td>
<td>Ammonium</td>
<td>0.12 (18%)$^a$</td>
<td>0.07 (10%)</td>
</tr>
<tr>
<td></td>
<td>Sulfate</td>
<td>0.04 (2%)</td>
<td>0.05 (3%)</td>
</tr>
<tr>
<td></td>
<td>Nitrate</td>
<td>0.12 (24%)</td>
<td>0.21 (44%)</td>
</tr>
<tr>
<td></td>
<td>OA</td>
<td>-0.001 (-0.1%)</td>
<td>0.07 (4%)</td>
</tr>
<tr>
<td></td>
<td>Total PM$_{2.5}$</td>
<td>0.3 (4.5%)</td>
<td>0.38 (5.5%)</td>
</tr>
<tr>
<td>II</td>
<td>Ammonium</td>
<td>0.73 (35%)</td>
<td>0.29 (13.5%)</td>
</tr>
<tr>
<td></td>
<td>Sulfate</td>
<td>0.13 (5%)</td>
<td>-0.13 (-5%)</td>
</tr>
<tr>
<td></td>
<td>Nitrate</td>
<td>1.3 (39%)</td>
<td>1.25 (38%)</td>
</tr>
<tr>
<td></td>
<td>OA</td>
<td>0.002 (0.1%)</td>
<td>-0.15 (-6%)</td>
</tr>
<tr>
<td></td>
<td>Total PM$_{2.5}$</td>
<td>2.3 (15%)</td>
<td>1.24 (8%)</td>
</tr>
<tr>
<td>III</td>
<td>Ammonium</td>
<td>0.22 (20%)</td>
<td>0.23 (22%)</td>
</tr>
<tr>
<td></td>
<td>Sulfate</td>
<td>0.12 (6.5%)</td>
<td>0.03 (2%)</td>
</tr>
<tr>
<td></td>
<td>Nitrate</td>
<td>0.43 (28%)</td>
<td>0.75 (49%)</td>
</tr>
<tr>
<td></td>
<td>OA</td>
<td>-0.002 (-0.1%)</td>
<td>0.08 (3.5%)</td>
</tr>
<tr>
<td></td>
<td>Total PM$_{2.5}$</td>
<td>0.8 (9%)</td>
<td>1.1 (12%)</td>
</tr>
<tr>
<td>IV</td>
<td>Ammonium</td>
<td>0.26 (28%)</td>
<td>0.1 (10%)</td>
</tr>
<tr>
<td></td>
<td>Sulfate</td>
<td>0.08 (3%)</td>
<td>0.2 (8%)</td>
</tr>
<tr>
<td></td>
<td>Nitrate</td>
<td>0.1 (22%)</td>
<td>0.2 (43%)</td>
</tr>
<tr>
<td></td>
<td>OA</td>
<td>-0.002 (-0.1%)</td>
<td>0.1 (5.5%)</td>
</tr>
<tr>
<td></td>
<td>Total PM$_{2.5}$</td>
<td>0.51 (6%)</td>
<td>0.6 (7%)</td>
</tr>
<tr>
<td>V</td>
<td>Ammonium</td>
<td>0.29 (30%)</td>
<td>0.1 (10.5%)</td>
</tr>
<tr>
<td></td>
<td>Sulfate</td>
<td>0.06 (3%)</td>
<td>0.03 (1.5%)</td>
</tr>
<tr>
<td></td>
<td>Nitrate</td>
<td>0.33 (32%)</td>
<td>0.4 (40%)</td>
</tr>
<tr>
<td></td>
<td>OA</td>
<td>-0.001 (-0.06%)</td>
<td>0.03 (2.5%)</td>
</tr>
<tr>
<td></td>
<td>Total PM$_{2.5}$</td>
<td>0.75 (10%)</td>
<td>0.53 (6.5%)</td>
</tr>
</tbody>
</table>

$^a$ The location of the five regions used for the analysis is shown in Fig. 2.1
$^b$ A positive value corresponds to a decrease
Table 2.2: (continued)

<table>
<thead>
<tr>
<th>Region</th>
<th>PM$_{2.5}$ Components</th>
<th>-50% NH$_3$</th>
<th>-50% NO$_x$</th>
<th>-50% SO$_2$</th>
<th>-50% VOCs</th>
<th>-50% POA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Control Strategy</td>
<td>Winter</td>
<td>Winter</td>
<td>Winter</td>
<td>Winter</td>
<td>Winter</td>
</tr>
<tr>
<td>I</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ammonium</td>
<td>0.19 (27%)</td>
<td>0.03 (3.5%)</td>
<td>0.04 (4.5%)</td>
<td>0.01 (1.2%)</td>
<td>&lt; -0.001 (-0.01%)</td>
</tr>
<tr>
<td></td>
<td>Sulfate</td>
<td>0.13 (7.5%)</td>
<td>-0.18 (-10%)</td>
<td>0.26 (15%)</td>
<td>0.01 (0.5%)</td>
<td>0.002 (0.1%)</td>
</tr>
<tr>
<td></td>
<td>Nitrate</td>
<td>0.22 (25%)</td>
<td>0.3 (34%)</td>
<td>-0.05 (-6%)</td>
<td>0.04 (4%)</td>
<td>-0.002 (-0.2%)</td>
</tr>
<tr>
<td></td>
<td>OA</td>
<td>0.002 (0.1%)</td>
<td>-0.21 (-11%)</td>
<td>&lt;0.001 (0.05%)</td>
<td>0.07 (4%)</td>
<td>0.3 (18%)</td>
</tr>
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<td>Total PM$_{2.5}$</td>
<td>0.6 (7%)</td>
<td>-0.03 (-0.3%)</td>
<td>0.25 (3%)</td>
<td>0.11 (1.3%)</td>
<td>0.3 (3.5%)</td>
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<td></td>
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<tr>
<td></td>
<td>Ammonium</td>
<td>0.21 (35%)</td>
<td>-0.002 (-0.3%)</td>
<td>0.02 (3.5%)</td>
<td>0.005 (0.8%)</td>
<td>&lt; 0.001 (0.1%)</td>
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<td></td>
<td>Sulfate</td>
<td>0.08 (4%)</td>
<td>-0.1 (-5%)</td>
<td>0.25 (12.5%)</td>
<td>-0.005 (-0.2%)</td>
<td>0.001 (0.05%)</td>
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<td>Nitrate</td>
<td>0.11 (15%)</td>
<td>0.11 (16%)</td>
<td>0.02 (3%)</td>
<td>0.03 (4.5%)</td>
<td>-0.002 (-0.3%)</td>
</tr>
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<td></td>
<td>OA</td>
<td>0.001 (0.15%)</td>
<td>-0.1 (-13%)</td>
<td>&lt;0.001 (0.05%)</td>
<td>0.01 (2%)</td>
<td>0.14 (19%)</td>
</tr>
<tr>
<td></td>
<td>Total PM$_{2.5}$</td>
<td>0.5 (4.5%)</td>
<td>-0.08 (-0.7%)</td>
<td>0.29 (2.5%)</td>
<td>0.04 (0.3%)</td>
<td>0.14 (11%)</td>
</tr>
<tr>
<td>III</td>
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<td></td>
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<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>Ammonium</td>
<td>0.22 (30%)</td>
<td>0.03 (4.5%)</td>
<td>0.04 (5.5%)</td>
<td>0.007 (1%)</td>
<td>-0.001 (-0.1%)</td>
</tr>
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<td></td>
<td>Sulfate</td>
<td>0.17 (11%)</td>
<td>-0.15 (-9%)</td>
<td>0.25 (15%)</td>
<td>-0.001 (-0.05%)</td>
<td>0.002 (0.1%)</td>
</tr>
<tr>
<td></td>
<td>Nitrate</td>
<td>0.2 (18%)</td>
<td>0.29 (26%)</td>
<td>-0.02 (-1.6%)</td>
<td>0.04 (3.5%)</td>
<td>-0.003 (-0.2%)</td>
</tr>
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<td></td>
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<td>-0.18 (-14%)</td>
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<td>0.04 (3%)</td>
<td>0.35 (25%)</td>
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<td>Total PM$_{2.5}$</td>
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<td>0.27 (3%)</td>
<td>0.08 (0.9%)</td>
<td>0.36 (4%)</td>
</tr>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ammonium</td>
<td>0.14 (29%)</td>
<td>0.02 (4%)</td>
<td>0.02 (4%)</td>
<td>0.002 (0.4%)</td>
<td>-0.001 (-0.2%)</td>
</tr>
<tr>
<td></td>
<td>Sulfate</td>
<td>0.06 (4%)</td>
<td>-0.14 (-9%)</td>
<td>0.27 (18%)</td>
<td>0.003 (0.2%)</td>
<td>&lt; -0.001 (-0.02%)</td>
</tr>
<tr>
<td></td>
<td>Nitrate</td>
<td>0.13 (22%)</td>
<td>0.22 (36%)</td>
<td>-0.05 (-8%)</td>
<td>0.01 (1.5%)</td>
<td>-0.001 (-0.2%)</td>
</tr>
<tr>
<td></td>
<td>OA</td>
<td>&lt; 0.001 (0.02%)</td>
<td>-0.15 (-10%)</td>
<td>&lt;0.001 (0.04%)</td>
<td>0.06 (5%)</td>
<td>0.16 (14%)</td>
</tr>
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<td></td>
<td>Total PM$_{2.5}$</td>
<td>0.37 (5.5%)</td>
<td>-0.05 (-0.7%)</td>
<td>0.23 (3.3%)</td>
<td>0.07 (1%)</td>
<td>0.16 (2.3%)</td>
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<tr>
<td></td>
<td>Ammonium</td>
<td>0.18 (30%)</td>
<td>0.03 (4.5%)</td>
<td>0.02 (2.5%)</td>
<td>&lt; -0.001 (-0.06%)</td>
<td>-0.001 (-0.1%)</td>
</tr>
<tr>
<td></td>
<td>Sulfate</td>
<td>0.03 (2%)</td>
<td>-0.1 (-6%)</td>
<td>0.29 (18%)</td>
<td>-0.002 (-0.1%)</td>
<td>&lt; -0.001 (-0.02%)</td>
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<tr>
<td></td>
<td>Nitrate</td>
<td>0.23 (29%)</td>
<td>0.24 (30%)</td>
<td>-0.1 (-12.5%)</td>
<td>0.003 (0.3%)</td>
<td>-0.002 (-0.2%)</td>
</tr>
<tr>
<td></td>
<td>OA</td>
<td>&lt; 0.001 (0.04%)</td>
<td>-0.13 (-10%)</td>
<td>&lt;0.001 (0.04%)</td>
<td>0.06 (4.5%)</td>
<td>0.14 (10%)</td>
</tr>
<tr>
<td></td>
<td>Total PM$_{2.5}$</td>
<td>0.5 (6%)</td>
<td>0.02 (0.2%)</td>
<td>0.18 (2.2%)</td>
<td>0.06 (0.7%)</td>
<td>0.14 (2%)</td>
</tr>
</tbody>
</table>

a The location of the five regions used for the analysis is shown in Fig. 2.1

b A positive value corresponds to a decrease
During the modeled summer period, total PM$_{2.5}$ is predicted to decrease by 5.5% on a domain average basis. The 50% NH$_3$ reduction is more effective in Western Europe (Fig. 2.3g) where total PM$_{2.5}$ is decreased by 2.3 µg m$^{-3}$ (15%) on average, with a maximum decrease predicted in South England (5.1 µg m$^{-3}$ or 22.5%). In this area ammonium nitrate levels show the highest reduction (0.73 µg m$^{-3}$ or 35% and 1.3 µg m$^{-3}$ or 39% respectively) (Fig. 2.3a, c) while sulfate decreases by 4% (Table 2.2). Significant decreases of PM$_{2.5}$ levels are also predicted in Southwest (0.75 µg m$^{-3}$ or 10% on average) and Central Europe (0.8 µg m$^{-3}$ or 9% on average) while in the rest of the domain the reduction of PM$_{2.5}$ is lower (Table 2.2).

During the modeled winter period, the NH$_3$ reduction is also effective in reducing PM$_{2.5}$ levels (4% average). Significant decreases of PM$_{2.5}$ are predicted in Central Europe (up to 1.5 µg m$^{-3}$ or 10% in northern France) (Fig. 2.3h), while the average reduction of PM$_{2.5}$ in this area reaches 0.7 µg m$^{-3}$ (7.5%). The reduction of inorganic PM$_{2.5}$ components exceeds 10% in this area with particulate ammonium and nitrate predicted to decrease by 30% and 18% respectively, and PM$_{2.5}$ sulfate by 11%. In other areas of the domain, total PM$_{2.5}$ is also predicted to decrease and its reduction ranges from 0.37 µg m$^{-3}$ (4.5%) in Western Europe to 0.6 µg m$^{-3}$ (7%) in North Europe.
Figure 2.3: Predicted reduction (base case - emissions reduction scenario) in ground-level concentrations (μg m⁻³) of (a-b) ammonium, (c-d) nitrate, (e-f) sulfate, and (g-h) total PM₂.₅ after a 50% reduction of NH₃ emissions during the modeled summer and the modeled winter period. A positive value corresponds to a decrease.

2.5.2 Reduction of NOₓ emissions

During the modeled summer period, the reduction of NOₓ emissions by 50% results in a net decrease of total PM₂.₅ levels over Europe (5.5% on average). However, its effect on the individual PM₂.₅ components is quite variable spatially. Although the NOₓ reduction results in significant decreases of ammonium nitrate levels in the entire domain (Fig. 2.4c, e) the response of sulfate and total OA to NOₓ emissions changes differs, depending on the respective changes of OH and O₃.

The main source of sulfate is the oxidation of SO₂, which takes place either homogeneously (reaction with OH) or heterogeneously (cloud reactions with dissolved hydrogen peroxide or ozone) (Pandis and Seinfeld, 1989). Thus, the levels of OH are critical for the formation of sulfate. Under typical polluted conditions, OH reacts with VOCs and NO₂ at an equal rate when the VOC/NOₓ concentration ratio is approximately 5.5:1 (Seinfeld and Pandis, 2006). In areas where the VOC/NOₓ ratio
is higher than this value, OH preferentially reacts with VOCs. In these NO\textsubscript{x}-limited areas, a reduction of NO\textsubscript{x} levels decreases the rate of O\textsubscript{3} formation, leading to lower OH radical concentration. As a result, a reduction of NO\textsubscript{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 NO\textsubscript{x} concentration, the NO\textsubscript{x} reaction predominates. In these NO\textsubscript{x}-saturated areas, a reduction of NO\textsubscript{x} emissions results in an increase of OH and O\textsubscript{3} and subsequently sulfate concentrations can increase.

Figure 2.12 in the supplementary material (Section 2.10) shows the predicted base case VOC/NO\textsubscript{x} ratio for each simulation period and the corresponding changes to VOC/NO\textsubscript{x} ratio after the reduction of NO\textsubscript{x} and VOCs emissions. The reduction of NO\textsubscript{x} emissions also impacts the oxidant levels and consequently affects POA aging as well as anthropogenic and biogenic SOA formation.

The lower NO\textsubscript{x} in the summer period has a significant effect on total PM\textsubscript{2.5} levels in Central Europe, reducing them by 1.1 \(\mu\text{g m}^{-3}\) (12\%) (Fig. 2.4i). This reduction is mainly due to the significant decrease of nitrate (0.75 \(\mu\text{g m}^{-3}\) or 49\%), as the reduction of NO\textsubscript{x} leads to a decrease of oxidant levels in this area (the VOC to NO\textsubscript{x} concentration ratio is higher than 5.5:1 threshold value), and eventually less HNO\textsubscript{3} is formed, as well as to a decrease of ammonium (18\% on average). A slight decrease of sulfate and total OA which is mainly attributed to reductions of oxidized POA and the corresponding SOA from intermediate volatile organic compounds (IVOCs) (account for 50\% of OA decrease) contribute also to the net decrease of total PM\textsubscript{2.5} in Central Europe. The NO\textsubscript{x} control has a significant effect on total PM\textsubscript{2.5} levels in Western Europe, reducing them by 1.24 \(\mu\text{g m}^{-3}\) (8\%) due to a reduction of nitrate and ammonium by 38\% and 13.5\% respectively. Over Western Europe the VOC to NO\textsubscript{x} ratio is lower than the 5.5:1 limit. Therefore, in this NO\textsubscript{x}-saturated region, the 50\%
NO$_x$ reduction leads to an increase of oxidant levels and consequently to an increase of sulfate and total OA levels (Table 2.2).
Figure 2.4: Predicted reduction (base case - emissions reduction scenario) in ground-level concentrations (μg m^{-3}) of (a-b) sulfate, (c-d) nitrate, (e-f) ammonium, (g-h) total OA, and (i-j) total PM_{2.5} after a 50% reduction of NO_x emissions during the modeled summer and the modeled winter period. A positive value corresponds to a decrease.

In the modeled winter period, the reduction of NO_x emissions is also effective for reducing nitrate levels over Europe (Fig. 2.4d). Nitrate is predicted to decrease everywhere (30% on average), with its reduction being more significant in North Europe (Table 2.2). However, during wintertime the VOC to NO_x ratio is lower than 5.5:1 in most of the model domain (see Fig. 2.12 in the supplementary material) due
to lower biogenic emissions, thus the NO\textsubscript{x} control results in an increase of the oxidant levels. The increase of oxidant levels increases sulfate concentration in most areas over Europe (Fig. 2.4b), with a highest increase predicted in North and Central Europe (10% and 9% respectively). Additionally, the increase of oxidant levels accelerates the oxidation of OA precursors leading also to higher oxidized POA and SOA levels. In areas were OA is high (North, Central Europe), NO\textsubscript{x} control is predicted to have the highest effect, increasing OA by 11% and 13% respectively. In most areas of the domain, the predicted increases of sulfate and total OA levels are usually higher than the nitrate decreases resulting to a net increase of total PM\textsubscript{2.5} (Table 2.2).

The predicted O\textsubscript{3} response to the decreasing NO\textsubscript{x} was found to vary in time and space (based on the VOC to NO\textsubscript{x} ratio). During the modeled summer period, the NO\textsubscript{x} reduction leads to a decrease of ozone amounts in most of the model domain (Fig. 2.5a), with the highest reduction predicted in the Balkans (14% on average). In Southwest Europe O\textsubscript{3} is reduced by 9% while similar decreases are predicted in Central and North Europe (8% on average). However in major urban areas such as Paris, London, Madrid and Milan the response of O\textsubscript{3} differs. In these NO\textsubscript{x}-saturated areas, O\textsubscript{3} is predicted to increase by several ppb (up to 8 ppb or 43% in London). Increase of O\textsubscript{3} concentration is predicted also in Western Europe (4% on average). During the modeled winter period, O\textsubscript{3} is predicted to increase in most areas of the domain, after the 50% reduction of NO\textsubscript{x} emissions (Fig. 2.5b). The predicted increase of O\textsubscript{3} exceeds 10% especially over Central and North Europe where average O\textsubscript{3} increased by 4.2 ppb (26%) and 3 ppb (17%) respectively.
Figure 2.5: Predicted reduction (base case - emissions reduction scenario) in ground-level concentrations (ppb) of O$_3$ after a 50% reduction of NO$_x$ emissions during (a) the modeled summer period and (b) the modeled winter period. A positive value corresponds to a decrease.

2.5.3 Reduction of SO$_2$ emissions

The predicted changes in average ground-level concentrations of the major PM$_{2.5}$ components after a 50% reduction of SO$_2$ emissions during the modeled summer and winter periods are shown in Fig. 2.6 and are summarized in Table 2.2. The reduction of SO$_2$ emissions is predicted to have different impacts on the different inorganic PM$_{2.5}$ components. Sulfate levels are effectively reduced over Europe in both periods, while the SO$_2$ reduction also causes decreases in particulate ammonium (Table 2.2).

On the contrary the response of nitrate to SO$_2$ reduction is variable depending on the availability of free NH$_3$ and total nitrate in each area. NH$_3$ reacts preferentially with H$_2$SO$_4$, and, if sufficient NH$_3$ is available (free NH$_3$), it also reacts with HNO$_3$ forming particulate nitrate. Thus, a reduction of SO$_2$ can lead to an increase of free NH$_3$ and consequently more HNO$_3$ can be transferred to the particulate phase (electroneutrality effect) (Seinfeld and Pandis, 2006). However the formation of
NH₄NO₃ depends on its equilibrium vapour pressure product of ammonia and nitric acid, K_{AN}, which in general, depends on temperature, RH and sulfate concentration (Stelson and Seinfeld, 1986). In the aqueous particulate phase, when sulfate increases, K_{AN} decreases due to ion interactions. Consequently the reduction of sulfate levels increases K_{AN}, which may cause a decrease of ammonium nitrate (thermodynamic effect) (Ansari and Pandis, 1998). In areas where the total nitrate is high and the NH₃ is low, nitrate tends to increase because of the electroneutrality effect, while in areas with high free NH₃, nitrate tends to decrease due to the thermodynamic effect.

During the modeled summer period the 50% reduction of SO₂ emissions produces an average sulfate decrease of 23% in the entire domain (Fig 2.6a). The SO₂ control strategy is more effective in the Balkans where sulfate is reduced by 0.84 μg m⁻³ (34%) on average, while its reduction reaches up to 1.4 μg m⁻³ (37%) in the Eastern Mediterranean whereas sulfate has the highest concentration. In the other areas, the predicted sulfate decrease is also significant (Table 2.2) indicating that SO₂ is often the limiting reagent for sulfate formation during summer. SO₂ control has also a significant impact on nitrate levels, resulting in an increase of its concentration in most areas of the domain (16% on average) (Fig. 2.6c), with the highest increase predicted over the Balkans (0.13 μg m⁻³ or 29% on average). However, despite the increase of nitrate, the predicted reduction of sulfate after the SO₂ control is higher, and along with the decrease of ammonium (up to 16% in the Balkans) results in a net decrease of total PM₂.₅ levels (Fig. 2.6g) which is ranging from 0.38 μg m⁻³ (5 %) in Southwest Europe to 0.8 μg m⁻³ (10%) in the Balkans.
Figure 2.6: Predicted reduction (base case - emissions reduction scenario) in ground-level concentrations ($\mu$g m$^{-3}$) of (a-b) sulfate, (c-d) nitrate, (e-f) ammonium, and (g-h) total PM$_{2.5}$ after a 50% reduction of SO$_2$ emissions during the modeled summer and the modeled winter period. A positive value corresponds to a decrease.

In the modeled winter period, the SO$_2$ reduction is also effective in reducing sulfate in most areas of the domain (Fig. 2.6b, Table 2.2). However the response of sulfate to SO$_2$ reductions (an approximate reduction of 0.25 $\mu$g m$^{-3}$) is lower compared to summertime, as the in-cloud formation of sulfate by the reaction of dissolved SO$_2$ with H$_2$O$_2$ is often limited by H$_2$O$_2$ availability during winter. Similar to summertime, nitrate levels are also predicted to increase after the reduction of SO$_2$ emissions, with the highest increase predicted in Southwest Europe (0.1 $\mu$g m$^{-3}$ or 12.5%). Nevertheless, the predicted increases of nitrate are once more less than sulfate decreases. Thus, the net impact on PM$_{2.5}$ is a 2-2.5% reduction.
2.5.4 Reduction of anthropogenic VOCs emissions

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. For example, the reduction of anthropogenic VOCs is expected to reduce total OA levels, although in NO$_x$-limited areas the increase of oxidant levels accelerates the VOC oxidation, offsetting some of this reduction. Additionally for sulfate, its gas-phase 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 modeled summer period, the VOC control reduces total OA levels in the whole domain (Fig. 2.7a). The predicted decrease is mainly attributed to the 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. In areas where aSOA levels are predicted to be high (Central and Western Europe) the VOC control is more effective for reducing total OA (0.2 μg m$^{-3}$ or 9% reduction of total OA in these areas) (Table 2.2). On average, aSOA accounts for almost 90% of the OA reduction. However, most of the model domain during summer is NO$_x$-limited. Thus, the expected increase of oxidant levels will lead to increases of sulfate and ammonium nitrate concentration (Table 2.2). The predicted
increases of inorganic PM$_{2.5}$ components are less than the decreases of total OA, therefore the VOC reduction leads to a net reduction of total PM$_{2.5}$ concentration. However, the predicted decrease of total PM$_{2.5}$ is modest, up to 0.2 μg m$^{-3}$ (1.1%) over Western Europe (Fig. 2.7c).

**Figure 2.7:** Predicted reduction (base case - emissions reduction scenario) in ground-level concentrations (μg m$^{-3}$) of (a-b) total OA, and (c-d) total PM$_{2.5}$ after a 50% reduction of anthropogenic VOCs emissions during the modeled summer and the modeled winter period. A positive value corresponds to a decrease.
In the modeled winter period, the VOC reduction leads also to a decrease of total OA levels (Fig. 2.7b), due to the reduction of aSOA. However the response of OA is lower compared to summertime due to the lower aSOA levels during this period. The impact of the VOCs control is relatively uniform in space with the highest decreases of approximately 0.07 μg m$^{-3}$ (4%) predicted in North Europe. In this area aSOA levels were found to be high. In addition, decreases are also predicted in most of the domain, for inorganic PM$_{2.5}$ components (Table 2.2), due to the decrease of oxidant levels. The predicted reductions of inorganic PM$_{2.5}$ are marginal and along with the total OA reduction lead to small decreases of PM$_{2.5}$ levels (Fig. 2.7d, Table 2.2).

2.5.5 Reduction of anthropogenic POA emissions

The 50% reduction of primary OA emissions significantly reduces total OA levels, in both periods, especially in areas close to emissions sources (Fig. 2.8). During the modeled summer period, OA is reduced by 8% on average, with peak reductions in Western and Central Europe, where OA decreases by 0.26 μg m$^{-3}$ (11%) and 0.24 μg m$^{-3}$ (10%) respectively (Table 2.2). The impact on OA levels is also significant in other areas of the domain, while close to emissions sources the OA is reduced even more (e.g., in areas over North and Central Europe the predicted decrease reaches 3.6 μg m$^{-3}$ (34%) and 2 μg m$^{-3}$ (32%) respectively) (Fig. 2.8a). The predicted response of total OA is mainly explained from the almost linear 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. The decrease of primary OA emissions affects also
OH levels through the corresponding reaction of the evaporated organic vapors, and eventually increases the production of nitric and sulphuric acid from NO$_2$ and SO$_2$ oxidation respectively. This can result in higher nitrate and sulfate levels, changes that can be significant during specific periods in major urban areas. During the modeled summer period, increases of nitrate, on an hourly basis, reach as much as 1.5 $\mu$g m$^{-3}$ (25%) while sulfate increases up to 0.6 $\mu$g m$^{-3}$ (15%). However, the corresponding concentration changes are quite small when averaged over the whole simulation period, indicating that the average effect of primary OA emissions on inorganic PM$_{2.5}$ components is on average quite small. (Fig. 2.9a, Table 2.2).

In the modeled winter period the higher levels of fresh POA make the POA control strategy more effective in reducing total OA levels. Total OA is predicted to decrease in the entire domain (15% on average) (Fig. 2.8b), while POA control has the highest impact on its concentrations over Central and North Europe, where total OA is reduced by 0.35 $\mu$g m$^{-3}$ (25%) and 0.3 $\mu$g m$^{-3}$ (18%) respectively. This OA reduction is primarily due to fresh POA, which contributes 78% to the OA decrease and secondly to the decrease of oxidized POA (18% contribution). Similarly to summertime, the decrease of primary OA does increase nitrate and sulfate levels for specific areas and periods by as much as 0.2 $\mu$g m$^{-3}$ (5%) and 0.5 $\mu$g m$^{-3}$ (25%) respectively. However, the monthly average effect of primary OA emissions on inorganic PM$_{2.5}$ components is small and the respective reductions of total PM$_{2.5}$ levels are due almost exclusively to the predicted OA decreases (Fig. 2.9b, Table 2.2).
Figure 2.8: Predicted reduction (base case - emissions reduction scenario) in ground-level concentrations (μg m$^{-3}$) of total OA after a 50% reduction of anthropogenic POA emissions during (a) the modeled summer period and (b) the modeled winter period. A positive value corresponds to a decrease.

Figure 2.9: Predicted reduction (base case - emissions reduction scenario) in ground-level concentrations (μg m$^{-3}$) of total PM$_{2.5}$ after a 50% reduction of anthropogenic POA emissions during (a) the modeled summer period and (b) the modeled winter period. A positive value corresponds to a decrease.
2.6 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$_{2.5}$ levels keeping the rest of the meteorological parameters constant. We assumed temperature sensitive biogenic emissions using the MEGAN model. In addition, dry deposition was simulated assuming temperature dependence for stomatal resistance. The results of these higher temperature scenarios were compared with those of the baseline scenarios for each simulation period (summer and winter).

Figure 2.10 shows the predicted changes (base case – increased temperature scenario) in ground-level concentrations of total PM$_{2.5}$ after a 2.5 K temperature increase. During the modeled summer period PM$_{2.5}$ 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$_{2.5}$. The highest reduction of approximately 1 μg m$^{-3}$ (5%) is predicted in Germany (Fig. 2.10a) where the respective decrease of ammonium nitrate is 1.1 μg m$^{-3}$ (22%). Significant decrease of PM$_{2.5}$ is also predicted in areas where ammonium nitrate concentration is high such as the United Kingdom and Italy. However in North Europe and also in areas in Southwest Europe and in the Balkans, the response of PM$_{2.5}$ to temperature increase differs. In these areas PM$_{2.5}$ 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$_2$, 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$_{2.5}$ over the Atlantic. In North Europe PM$_{2.5}$ is increased up to 0.5 $\mu$g m$^{-3}$ (12%) (Fig. 2.10a), while sulfate, biogenic and anthropogenic SOA are predicted to increase up to 14% and 20% and 7% respectively.

In the modeled winter period, the reduction of fresh anthropogenic POA due to evaporation dominates (35% on average) and along with a reduction of ammonium nitrate (5% on average) result in a decrease of total PM$_{2.5}$ mostly in areas over Central and North Europe. The highest decrease for PM$_{2.5}$ is predicted in Paris (approximately 4.5 $\mu$g m$^{-3}$ or 12%) (Fig. 2.10b) where anthropogenic POA is decreased by 4.9 $\mu$g m$^{-3}$ or 37%. The high OA levels in Paris (consistent with the conclusions of the MEGAPOLI campaigns) (Crippa et al., 2013) as well as in a lot of European major urban centers in the winter, were mainly due to a combination of weak vertical mixing and higher emissions from home heating and residential wood burning. Thus, the significant reduction of fresh POA 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 $\mu$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 $\mu$g m$^{-3}$ (15%) (Fig. 2.10b). In this area sulfate is increased by 24% on average.
**Figure 2.10:** Predicted reduction (base case - increased temperature scenario) in ground-level concentrations (μg m⁻³) of total PM₂.₅ after a 2.5 K increase of temperature during (a) the modeled summer period and (b) the modeled winter period. A positive value corresponds to a decrease.

The doubling of temperature increase (from 2.5 to 5 K) during the modeled summer period almost doubles the corresponding concentration change of all OA components. This OA response followed by higher concentration changes of inorganic PM₂.₅ result in even larger changes for total PM₂.₅ concentration. PM₂.₅ is predicted to decrease even more in Central Europe (up to 1.5 μg m⁻³ or 8%) (Fig. 2.11a), 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 PM₂.₅ increase (up to 1.2 μg m⁻³ or 4.5%) (Fig. 2.11a).

Similarly to the modeled summer period, the increase in temperature by 5 K, during wintertime, 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 a decrease on ammonium nitrate (8% on average) lead to a decrease of PM$_{2.5}$ in Central and North Europe with a predicted maximum decrease of 4.9 µg m$^{-3}$ (14%) in Paris (Fig. 2.11b). On the other hand the larger increase in sulfate concentration dominates in many areas over Europe, increasing total PM$_{2.5}$ (up to 1.6 µg m$^{-3}$ or 18% in North Europe) (Fig. 2.11b). Table 2.3 summarizes the temperature increase scenarios and the corresponding response of the major PM$_{2.5}$ components during the modeled summer and winter periods.

**Figure 2.11:** Predicted reduction (base case - increased temperature scenario) in ground-level concentrations (µg m$^{-3}$) of total PM$_{2.5}$ after a 5 K increase of temperature during (a) the modeled summer period and (b) the modeled winter period. A positive value corresponds to a decrease.
Table 2.3: Response of the major PM$_{2.5}$ components to a 2.5 and 5 K increase of temperature, and percent average predicted reduction of total PM$_{2.5}$, during the modelled summer and the modelled winter period.

<table>
<thead>
<tr>
<th>Increase Scenario</th>
<th>Season</th>
<th>Average PM$_{2.5}$ Reduction</th>
<th>Change of Component</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Ammonium Sulfate Nitrate Total OA</td>
</tr>
<tr>
<td>+2.5 K</td>
<td>Summer</td>
<td>-0.8% *</td>
<td>↓ ↑ ↓ ↑</td>
</tr>
<tr>
<td></td>
<td>Winter</td>
<td>-1%</td>
<td>↓ ↑ ↓ ↓</td>
</tr>
<tr>
<td>+5 K</td>
<td>Summer</td>
<td>-1%</td>
<td>↓ ↑ ↓ ↑</td>
</tr>
<tr>
<td></td>
<td>Winter</td>
<td>-5.7%</td>
<td>↓ ↑ ↓ ↓</td>
</tr>
</tbody>
</table>

* A negative value corresponds to an increase

2.7 Discussion

A recent modelling study from Aksoyoglu et al. (2011) who used a three dimensional CTM over Europe with a focus on Switzerland, showed that in most of European areas the reduction of NH$_3$ emissions by 50% during winter, is more effective in reducing total PM$_{2.5}$ than reductions of other gas precursors. During summer the effect of NH$_3$ emissions on PM$_{2.5}$ concentrations was predicted to be lower mostly due to lower ammonium nitrate concentrations. The wintertime effectiveness of NH$_3$ emissions in reducing PM$_{2.5}$ levels has been reported also in studies conducted in the US (Tsimpidi et al., 2007; Odman, 2009). Our results for
winter are quite consistent with all these previous studies. However our findings suggest these reductions in NH$_3$ could be also efficient during the summer for at least parts of Europe, something that has not been reported in previous studies (Aksoyoglu et al., 2011).

Berglen et al. (2007) quantified the negative trend in sulfate concentrations over Europe during the last two decades as a result of reduced SO$_2$ emissions. The significant expected impact of SO$_2$ control on sulfate levels is also reproduced by our model, showing significant local non-linear effects on sulfate. This non-linear response of sulfate to SO$_2$ reductions was also reported by Lövblad et al. (2004). In addition our model predicts increases of nitrate levels due to SO$_2$ reduction. Similar findings have been reported by other studies (Fagerli et al., 2008; Tsimpidi et al., 2007). These results suggest that SO$_2$ reduction could be effective for improving air quality, by reducing total PM$_{2.5}$, especially in areas where sulfate concentration is high and mainly during summer.

Reduction of the NO$_x$ emissions by 50% during the modeled summer period is predicted to increase average ozone levels in major European cities by several ppb (up to 8 ppb or 43% in London), as well as in Western Europe, while in rest of Europe O$_3$ levels are reduced. The same increases of O$_3$ concentration in urban centers have been reported by Thunis et al. (2007). This summertime response of ozone to NO$_x$ emissions is consistent with the results of Jonson et al. (2001). Thunis et al. (2007) predicted also decreases of total PM concentration after the NO$_x$ reduction, although, without investigating the corresponding impacts that NO$_x$ control has on individual PM components (e.g., our model predicts increases of OA and sulfate over Western Europe, during the modeled summer period). In addition our results are consistent with the conclusions of de Meij et al. (2009a), who showed that the reduction of NO$_x$
emissions along with a reduction of PM$_{2.5}$ emissions leads to significant decrease of total PM$_{2.5}$ levels over PoValley and to increases of O$_3$ in Milan. On the contrary, the predicted net increase of total PM$_{2.5}$ over Europe, due to NO$_x$ reduction in the winter, is not consistent with the conclusions of Aksoyoglu et al. (2011) who reported that NO$_x$ control could reduce total PM$_{2.5}$ levels during winter.

The reduction of primary OA emissions, results in a significant decrease of total OA concentrations and to a consequent reduction of total PM$_{2.5}$ levels. The relative effects of primary OA emissions to PM$_{2.5}$ levels were found to be quite local, having the highest impact in areas close to emissions sources. This local effectiveness of primary OA reduction has also been shown in other studies (Odman et al., 2009). The significant effect that primary OA emissions have on OA levels along with a respective reduction of NH$_3$ emissions, which is effective in reducing inorganic PM$_{2.5}$, could be a favourable control strategy. Generally, a coupled emissions reduction of the major precursors could have better results than individual control strategies. Investigation of these more complex multi-pollutant reductions is outside the scope of this study and will be the topic of future work.

Our results suggest that a temperature increase will lead to lower levels of particulate ammonium nitrate, while biogenic SOA, mainly during summer, will increase due to high biogenic VOCs emissions. The decrease of nitrate levels over the continental Europe, as temperature rises, was also shown by Aksoyoglu et al. (2011), while the predicted increases of biogenic SOA are consistent with other studies (Heald et al. 2008).

There are several issues that need further investigation regarding the system response to emission and temperature changes. These knowledge gaps include uncertainties in emission inventories which could lead to significant discrepancies in
air quality modeling simulations. Uncertainties associated with the modelling of emissions and removal of NH$_4$NO$_3$ precursors, its formation and partitioning to both the fine and coarse particles are still a significant modelling topic. The use of the bulk equilibrium approach in our simulations and the fact that in some areas (e.g., Mace Head) a significant amount of nitrate is associated with sea salt, which shifts nitrate and ammonium to the coarse mode, could lead to significant overpredictions of nitrate concentration in the fine mode. A more detailed but computationally demanding, method, such as the “hybrid” approach could give better estimates for nitrate levels in areas with levels of coarse particles and significant ammonia levels. In addition, the uncertainties inherent in OA modelling are still a challenge. In this work we showed that the reduction of anthropogenic VOCs and primary OA emissions lead to decreases of OA levels, although the predicted changes are quite uncertain. Further investigation based on improved descriptions of the volatility distribution of the primary organic aerosol emissions and better parameterization of the chemical aging of the OA are required to improve the accuracy of the predictions. These uncertainties have been discussed in previous studies (Lane et al., 2008a, b; Murphy et al., 2009, 2010, Tsimpidi et al., 2010, 2011).

2.8 Conclusions

A detailed three dimensional chemical transport model, PMCAMx-2008, was applied to the European domain to evaluate the response of fine aerosol (PM$_{2.5}$) mass concentration to changes in emissions of precursor gases (SO$_2$, NH$_3$, NO$_x$, VOCs) and anthropogenic primary OA (POA) as well as to changes in temperature.
The reduction of NH$_3$ emissions by 50% seems to be the most effective control strategy in reducing PM$_{2.5}$, in both periods mainly due to a significant decrease of ammonium nitrate. During the modeled summer period, NH$_3$ emissions reduction results in a decrease of ammonium by 22% in the entire model domain. Nitrate is reduced by 39% in Western Europe and by 30% in Southwest Europe, while the corresponding decrease of total PM$_{2.5}$ in these areas is 15% and 10% respectively. Similarly in the modeled winter period, the NH$_3$ control produces a significant reduction of ammonium nitrate levels in most areas over Europe. Overall, ammonium nitrate reduction accounts for almost 80% of total PM$_{2.5}$ reduction in both periods. The reduction of NH$_3$ produces also a slight decrease of sulfate levels due to the effect of NH$_3$ on cloud pH and on the rate of in-cloud sulfate production.

The 50% reduction of SO$_2$ emissions, during the modeled summer period, leads to a significant and non-linear decrease of sulfate in the entire domain (23% on average). The SO$_2$ control strategy is more effective over the Balkans where sulfate is reduced by 34%, 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 period the SO$_2$ control strategy produces also a significant increase of nitrate in most of the model domain (16% on average). Nevertheless, the predicted increases of nitrate are less than sulfate decreases; thus, the net impact on total PM$_{2.5}$ levels is a reduction. In the modeled winter period 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$_2$O$_2$ 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 produces 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 summertime and 4% in the modeled winter period, mainly due to the almost linear response of anthropogenic SOA (50% decrease on average). Anthropogenic POA responds 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 is 15% during the modeled winter period (25% in Central Europe) and 8% in the summer period. Both control strategies produce small (VOC reduction) or negligible (POA reduction) changes on monthly average inorganic PM$_{2.5}$ levels, in both periods.

On the contrary, the NO$_x$ emissions control strategy seems to be problematic in both periods. During the modeled summer period, 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% and 6% respectively). Additionally, in the winter period, ammonium nitrate is reduced by 17%, however the reduction of NO$_x$ emissions results in an increase of sulfate and total OA and eventually to a net increase of total PM$_{2.5}$.

The increase of temperature by 2.5 K results in a decrease of ammonium nitrate and fresh anthropogenic POA in both periods. During the modeled summer period, 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 summertime results in an increase of sulfate due to an increase of oxidant levels
which favor the oxidation of SO$_2$. 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 modeled winter period, 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) approximately doubles the corresponding concentration change of OA components during summer and leads to even larger concentration changes of inorganic PM$_{2.5}$, in both periods.

The significant impact that the emissions reductions of the major gaseous and particulate precursors may have on PM$_{2.5}$ levels, as well as the sensitivity of PM$_{2.5}$ concentrations to temperature changes should be of significant concern for atmospheric PM composition and air quality. The above results indicate that the challenge of improving air quality needs understanding the relative effects that emissions and climate change could have on particulate matter.


2.9 References


Pun, B. K., Seigneur, C., Bailey, E. M., Gautney, L. L., Douglas, S. G., Haney, J. L., and Kumar, N.: Response of atmospheric particulate matter to changes in


Stelson, A. W., and Seinfeld, J. H.: Thermodynamic prediction of the water activity, NH$_4$NO$_3$ dissociation constant, density and refractive index for the NH$_4$NO$_3$-(NH$_4$)$_2$SO$_4$-H$_2$O System at 25 °C, Atmos. Environ., 16, 2507-2514, 1986.


2.10 Supplementary material

Table 2.4: Prediction skill metrics of PMCAMx-2008 against AMS hourly ground measurements during the EUCAARI summer campaign*.

<table>
<thead>
<tr>
<th>PM$_i$</th>
<th>Mean Observed (μg m$^{-3}$)</th>
<th>Mean Predicted (μg m$^{-3}$)</th>
<th>MB$^a$ (μg m$^{-3}$)</th>
<th>MAGE (μg m$^{-3}$)</th>
<th>FBIAS</th>
<th>FERROR</th>
<th>Percent within a factor of 2</th>
</tr>
</thead>
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<tr>
<td>Cabauw</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>OA</td>
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<td>1.1</td>
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<td>89</td>
</tr>
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<td>1.1</td>
<td>0.3</td>
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<td>-0.2</td>
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<td></td>
<td></td>
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<td>0.5</td>
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*Number of data points; Cabauw: 640, Finokalia: 490, Mace Head: 330, Melpitz: 160.
Table 2.5: Prediction skill metrics of PMCAMx-2008 against AMS airborne measurements during the EUCAARI-LONGREX summer campaign*.

<table>
<thead>
<tr>
<th>PM$_i$</th>
<th>Mean Observed (μg m$^{-3}$)</th>
<th>Mean Predicted (μg m$^{-3}$)</th>
<th>MB (μg m$^{-3}$)</th>
<th>MAGE (μg m$^{-3}$)</th>
<th>FBIAS</th>
<th>FERROR</th>
<th>Percent within a factor of 2</th>
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* 7010 data points.

# \[ MB = \frac{1}{n} \sum_{i=1}^{n} (P_i - O_i) \]
\[ MAGE = \frac{1}{n} \sum_{i=1}^{n} |P_i - O_i| \]

\[ FBIAS = 2 \frac{\sum_{i=1}^{n} (P_i - O_i)}{n \sum_{i=1}^{n} P_i + O_i} \]
\[ FERROR = 2 \frac{\sum_{i=1}^{n} |P_i - O_i|}{n \sum_{i=1}^{n} (P_i + O_i)} \]
<table>
<thead>
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<th>PM$_i$</th>
<th>Mean Observed (μg m$^{-3}$)</th>
<th>Mean Predicted (μg m$^{-3}$)</th>
<th>MB (μg m$^{-3}$)</th>
<th>MAGE (μg m$^{-3}$)</th>
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Figure 2.12: Predicted base case VOC/NO$_x$ ground-level concentration ratio (a-b), and predicted VOC/NO$_x$ ground-level concentration ratio after a 50% reduction of
NO\textsubscript{x} (c-d), and anthropogenic VOCs emissions (e-f) during the modeled summer and the modeled winter period. The red colour indicates ratio values higher than 5.5:1 (NO\textsubscript{x}-limited areas), whereas the blue colour indicates ratio values lower than 5.5:1 (NO\textsubscript{x}-saturated areas).
Chapter 3

Linking Climate and Air Quality over Europe: Effects of Meteorology on PM$_{2.5}$ Concentrations
3.1 Abstract

The effects of various meteorological parameters such as temperature, wind speed, absolute humidity, precipitation and mixing height on PM$_{2.5}$ concentrations over Europe were examined using a three-dimensional chemical transport model, PMCAMx-2008. Our simulations covered three periods, representative of different seasons (summer, winter, and fall). PM$_{2.5}$ appears to be more sensitive to temperature changes compared to the rest meteorological parameters in all seasons. PM$_{2.5}$ generally decreases as temperature increases by 2 K, although the predicted response varies significantly in space and time, ranging from -700 ng m$^{-3}$ K$^{-1}$ (-8% K$^{-1}$) to 300 ng m$^{-3}$ K$^{-1}$ (7% K$^{-1}$) due to the competing effects on the different PM$_{2.5}$ species. The predicted decreases of PM$_{2.5}$ are mainly due to the evaporation of ammonium nitrate (decreases by 15% on average) while the higher biogenic emissions and the accelerated gas-phase reaction rates increase the production of organic aerosol (OA) and sulfate having the opposite effect on PM$_{2.5}$. The predicted responses of PM$_{2.5}$ to absolute humidity are also quite variable, ranging from -130 ng m$^{-3}$ %$^{-1}$ (-1.6% %$^{-1}$) to 160 ng m$^{-3}$ %$^{-1}$ (1.6% %$^{-1}$) dominated mainly by changes in inorganic PM$_{2.5}$ species. An increase in absolute humidity favors the partitioning of nitrate to the aerosol phase and increases average PM$_{2.5}$ during summer and fall. Decreases in sulfate and sea salt levels govern the average PM$_{2.5}$ response to humidity during winter. A decrease of wind speed (keeping constant the emissions), increases all PM$_{2.5}$ species due to changes in dispersion and dry deposition. In all periods, average PM$_{2.5}$ increases by approximately 40 ng m$^{-3}$ %$^{-1}$, while the effects are stronger over the polluted areas of the domain. In addition, the wind speed effects only on sea salt emissions could be significant for PM$_{2.5}$ concentrations over water and in coastal areas (decreases up to 200 ng m$^{-3}$ %$^{-1}$ in the winter). Increases in precipitation have a negative effect on
PM$_{2.5}$ (decreases up to 110 ng m$^{-3}$ %$^{-1}$) in all periods due to increases in wet deposition of PM$_{2.5}$ species and their gas precursors. Changes in mixing height have the smallest effects (up to 35 ng m$^{-3}$ %$^{-1}$) on PM$_{2.5}$. Regarding the relative importance of each of the meteorological parameters in a changed future climate, the projected changes in precipitation are expected to have the largest impact on PM$_{2.5}$ levels during all periods (changes up to 2 μg m$^{-3}$ in the fall). The expected effects in future PM$_{2.5}$ levels due to wind speed changes are similar in all seasons and quite close to those resulting from future precipitation changes (up to 1.4 μg m$^{-3}$). Absolute humidity could potentially lead to large changes in PM$_{2.5}$ levels mainly in the fall (increases up to 2 μg m$^{-3}$) due to the dominance of the increased particulate nitrate levels. In the other two periods the expected PM$_{2.5}$ changes are smaller. Temperature is expected to have a lower impact on future PM$_{2.5}$ levels compared to the rest meteorological parameters in all seasons, while the effects of mixing height are relatively small.

3.2 Introduction

Over the past decades, increased levels of atmospheric particulate matter (PM) have received considerable attention due to their impact on human health, climate change, and visibility. In particular, fine particulate matter with an aerodynamic diameter less than 2.5 μm (PM$_{2.5}$) has detrimental effects on human health as it is associated with increases in mortality, as well as respiratory and cardiovascular diseases (Schwartz et al., 1996; Bernard et al., 2001; Pope et al., 2009). PM$_{2.5}$ has also been implicated in various air quality problems such as changes of the energy balance of the planet (IPCC, 2007), visibility reduction (Seinfeld and Pandis, 2006), and the formation of acid rain and acid fogs (Burtraw et al., 2007).
Concentrations of PM are strongly influenced by meteorology. For example, increasing temperature can lead to elevated sulfate concentrations due to increased rate of SO$_2$ oxidation (Aw and Kleeman, 2003; Dawson et al., 2007; Jacob and Winner 2009, Lecoeur and Seigneur, 2013). In contrast, particulate nitrate and semi-volatile organic aerosols evaporate as temperature increases (Dawson et al., 2007; Jimenez-Guerrero et al., 2012; Sheehan and Bowman, 2001; Tsigeridis and Kanakidou, 2007). Temperature has also a significant indirect effect on secondary organic aerosol (SOA) concentrations. In a warmer climate, secondary organic aerosol can increase due to increasing biogenic VOC emissions (Heald et al., 2010; Jacob and Winner, 2009). Changes in absolute humidity also affect PM$_{2.5}$ levels. Increases in humidity can favor nitric acid partitioning to the aerosol phase and therefore can lead to nitrate concentration increases (Dawson et al., 2007; Galindo et al., 2011; Lecoeur and Seigneur, 2013). Wet deposition is in most areas the major removal process for PM$_{2.5}$, hence changes in precipitation rate or the area extent of precipitation have a significant impact on aerosol concentrations (Dawson et al., 2007; Lecoeur and Seigneur, 2013). Changes in wind speed lead to changes in dispersion and transport as well as to changes in marine aerosol production and coastal PM$_{2.5}$ levels (Aksoyoglu et al., 2011; Jacob and Winner 2009). Finally mixing height determines to a large extend the dilution of primary and the formation of secondary pollutants (Jimenez-Guerrero et al., 2012; Pay et al., 2012).

Over the next decades, climate is expected to change compared to the present-day conditions and will influence PM$_{2.5}$ concentrations. Based on IPCC projections for Europe (IPCC, 2007), temperature is expected to rise from 1 to 5.5 K over the next century. Emissions of biogenic VOCs are also expected to increase as temperature increases. Forkel and Knoche (2007) predicted a 30% increase (locally up to 50%) of
biogenic VOCs emissions in Europe due to a predicted 1.7 - 2.4 °C temperature increase, under the IPCC IS92a scenario within the next 30 years. Higher temperatures in a future climate, will also lead to increases in absolute humidity (IPCC, 2007). Precipitation is also expected to change over Europe in the future, having large spatial and seasonal variations. Based on the IPCC A2 emission scenario, Raisanen et al. (2004) predicted an increase in mean winter precipitation in northern and central Europe (up to 50%) and a substantial decrease in southern Europe in the next century, while during summer precipitation was projected to decrease throughout central and southern Europe. Similar projections for precipitation were also found by other modeling studies (Giorgi and Meleux, 2007; Hedegaard et al., 2008; Kjellström et al., 2010). In addition, several simulations using general circulation models (GCMs) and regional climate models (RCMs) indicate both changes in rainfall intensity and frequency (Argüeso et al., 2012; Boe et al., 2009; Buonomo et al., 2007; Christensen and Christensen, 2004; Frei et al., 2006). Jacob and Winner (2009) suggested that the critical variable that affects PM concentrations is precipitation frequency rather than precipitation rate. Wind speed is also predicted to change in a future climate. Andersson and Engardt (2010) predicted increases in wind speed over northern Europe, and decreases in the southern regions. Similar projections for wind speed were found in other model studies (Katragkou et al., 2011; Kjellström et al., 2010; Raisanen et al., 2004). Hedegaard et al. (2013) reported increasing mixing height in most of Europe under a future climate (above 100 m in southeastern Europe), but Jimenez-Guerrero et al. (2011) predicted an average decrease for most continental Europe.

The impact of various climate scenarios on air quality over Europe as well as the correlation between meteorology and PM concentrations has been the subject of
several studies (Galindo et al., 2011; Heald et al., 2008; Hedegaard et al., 2008, 2013; Im et al., 2012; Jacob and Winner, 2009; Koch et al., 2003; Manders et al., 2012; Megaritis et al., 2013; Pay et al., 2012; Redington et al., 2009; Roustan et al., 2010). Carvalho et al. (2010) applied a regional CTM, CHIMERE, over Europe with downscaled meteorology generated by a global GCM to study the impact of climate change on ozone and PM$_{10}$ levels, using the IPCC A2 scenario. Their predicted PM$_{10}$ concentration changes showed a strong spatial and temporal variability with increases over the continental regions and decreases over water. Their predicted PM$_{10}$ response was mainly driven by changes in the boundary layer height and wind speed. Jimenez-Guerrero et al. (2012) used a regional modeling system, MM5-CHIMERE, over southwestern Europe in order to study how concentrations of air pollutants respond to a changing climate under the year 2100 IPCC A2 scenario. Their findings suggest that aerosol species are strongly influenced by the higher future temperatures. They predicted an increase of sulfate and secondary organic aerosols (SOA) due to faster reactions and higher emissions of biogenic VOCs, and a decrease of particulate nitrate. In a multi-year simulation (2000-2008), Lecoeur and Seigneur (2013) used a three-dimensional CTM, Polyphemus/Polair3D, to investigate the response of PM$_{2.5}$ species to changes in meteorology. Their results suggest that wind speed and precipitation have a strong negative effect on PM$_{2.5}$ and its components (with sea salt being the only exception, for which a positive correlation with wind speed was predicted), while the response of PM$_{2.5}$ to temperature changes varied significantly among the PM$_{2.5}$ species considered. The negative response of PM$_{2.5}$ to wind speed changes and the variable effects caused by changes in temperature were also reported by Aksoyoglu et al. (2011). Additional work has been conducted in several areas over the world with the majority focused on the United States (Avise et al., 2009; Dawson
et al., 2007, 2009; Day et al., 2011; Hogrefe et al., 2004; Jeong and Park, 2013; Mahmud et al., 2010; Pye et al., 2009; Racherla and Adams, 2006; Singh and Palazoglu, 2012; Tagaris et al., 2007, 2008; Tai et al., 2012; Zhang et al., 2008). The predicted PM$_{2.5}$ changes due to climate are quite variable in space and time, governed mainly by changes in temperature, precipitation, absolute humidity and ventilation (wind speed and mixing height).

So far, most of the earlier modeling studies have focused on the overall effect of future climate on PM$_{2.5}$ concentrations. While this has provided valuable insights, it has often been difficult to quantify the effects of changes of individual meteorological parameters and processes. One of the few available studies has focused on the United States (Dawson et al., 2007). In addition, to our knowledge, there has been little work trying to quantify how individual processes (such as the partitioning of semi-volatile PM components, the marine aerosol production, etc) can be affected by changes in meteorology and eventually, how sensitive PM$_{2.5}$ is to these changes. The goal of this study is to conduct a detailed sensitivity analysis quantifying how changes in temperature, wind speed, absolute humidity, precipitation, and mixing height, and their subsequent effects on different processes, can influence fine particulate matter (PM$_{2.5}$) concentrations over Europe. Each of these parameters is studied separately so that the relative importance of each as well as the subsequent response of PM$_{2.5}$ can be quantified. For this purpose we use a three-dimensional CTM, PMCAMx-2008 over Europe. PMCAMx-2008 implements a state-of-the-art organic module for organic aerosol (OA) modeling based on the volatility basis set framework (VBS) (Donahue et al., 2006), which has not been used in earlier climate-air quality interactions studies, as well as updated inorganic aerosol modules for the simulation of inorganic PM species.
A brief description of the PMCAMx-2008 along with the characteristics of its application in the European domain is given in Section 3.3. The PMCAMx-2008 base-case predictions for PM$_{2.5}$ concentrations and some information regarding the model evaluation are given in Section 3.4. The description of each sensitivity simulation conducted in this study as well as the predicted response of PM$_{2.5}$ to these meteorological perturbations is presented in the next sections. Finally the relative importance of the various meteorological parameters and the main conclusions are presented in Sections 3.11 and 3.12 respectively.

3.3 The PMCAMx-2008 CTM

3.3.1 Model description

PMCAMx-2008 (Fountoukis et al., 2011; Megaritis et al., 2013) uses the framework of the CAMx air quality model (Environ, 2003). The chemical mechanism used in this study to describe the gas-phase chemistry is based on the SAPRC99 mechanism (Environ, 2003; Carter, 2013) and includes 211 reactions of 56 gases and 18 free radicals. For the simulation of the aerosol species, the model uses three detailed modules: inorganic aerosol growth (Gaydos et al., 2003; Koo et al., 2003), aqueous phase chemistry (Fahey and Pandis, 2001) and SOA formation and growth (Murphy and Pandis, 2009). These modules employ a sectional approach using ten aerosol size sections, spanning the diameter range from 40 nm to 40 μm. In this study inorganic aerosol formation was simulated using the “bulk equilibrium approach” where the bulk inorganic aerosol and gas phase are assumed to be always in equilibrium. The organic aerosol treatment in PMCAMx-2008 is based on the volatility basis set framework (Donahue et al., 2006; Stanier et al., 2008).
organic aerosol is assumed to be semivolatile in PMCAMx-2008, while the model treats all anthropogenic organic species (primary and secondary) as chemically reactive. Further details regarding the simulation of inorganic and organic aerosol species in PMCAMx-2008 can be found in Fountoukis et al. (2011).

For the simulation of wet scavenging the model assumes that the scavenging rate within or below a cloud due to precipitation is equal to the product of the concentration of a pollutant and the respective scavenging coefficient (Seinfeld and Pandis, 2006). Dry deposition, for the gas-phase species, is simulated using the resistance model of Wesely (1989), while for aerosol species the PMCAMx-2008 uses the resistance approach of Slinn and Slinn (1980) as implemented in UAM-AERO (Kumar et al., 1996). More information about the simulation of removal processes can be found in Fountoukis et al. (2011) and Megaritis et al. (2013).

### 3.3.2 Model application

PMCAMx-2008 was set to run over Europe covering a 5400×5832 km region with a 36×36 km resolution grid and 14 vertical layers extending up to approximately 6 km altitude. Three month-long periods, representative of different seasons (summer, winter, and fall) were simulated. The summer simulations were based on a hot late spring period (1-29 May 2008), the fall modeled period was from 15 September to 17 October 2008, while the winter period covered a cool late winter and early spring period (25 February - 23 March 2009). The first two days from each period were used as model initialization days and were excluded from the analysis. All three periods showed a variety of meteorological conditions and pollution levels. The summer period was characterized by a blocking anticyclone (especially in the first half of May) leading to stable meteorological conditions and enhanced pollution over Central
Europe. In addition, high temperatures were observed in most of Europe (Hamburger et al., 2011; Mensah et al., 2012; Pikridas et al., 2010; Poulain et al., 2011). Fall represented the transition from summer to winter with a moderate temperature (which was decreasing during this period), less stable atmospheric pressure and frequent precipitation events (EMEP, 2010; Poulain et al., 2011) while the winter period was characterized by low temperatures in most of Europe (Freney et al., 2011; Hildebrandt et al., 2010b; Mensah et al., 2012; Poulain et al., 2011).

The necessary inputs to the model included emissions, meteorological conditions, land use data and initial and boundary conditions of the simulated PM species. Anthropogenic gas emissions included land as well as international shipping emissions and were developed by the TNO team as a continuation of the work in GEMS and MACC (Denier van der Gon et al., 2010; Visschedijk et al., 2007). Anthropogenic particulate organic and elemental carbon emissions were based on the EUCAARI Pan-European Carbonaceous Aerosol Inventory (Kulmala et al., 2011). Biogenic emissions were produced by utilizing the MEGAN (Model of Emissions of Gases and Aerosols from Nature) model (Guenther et al., 2006). Sea salt emissions (O’Dowd et al., 2008) as well as wildfire emissions (Sofiev et al., 2009) were also included. Further details about the emissions data used in this study can be found in Fountoukis et al. (2011). The meteorological input into the model included hourly data of temperature, pressure, water vapor, clouds, rainfall, horizontal wind components and vertical diffusivity, all generated using the meteorological model WRF (Weather Research and Forecasting) (Skamarock et al., 2005). For the boundary conditions of the major PM species we used the same concentrations as Fountoukis et al. (2011). The boundary conditions were chosen on the basis of measurements taken in sites close to the boundaries (e.g., Zhang et al., 2007; Seinfeld and Pandis, 2006).
3.4 Base case simulations and model evaluation

The predicted concentrations of total PM$_{2.5}$ during the three modeled base case periods are presented in Fig. 3.1. During the summer period, the domain-average ground-level concentration of total PM$_{2.5}$ is 7.7 μg m$^{-3}$. Elevated PM$_{2.5}$ concentrations are predicted in most of Western Europe (up to 25 μg m$^{-3}$) (Fig. 3.1a), due mainly to high ammonium nitrate levels in this area (maximum concentration of 11 μg m$^{-3}$). In Central and Northern Europe fine organic matter dominates with biogenic secondary OA and oxidized primary OA (including OA from IVOCs) contributing the most (approximately 60% and 25% respectively). PM$_{2.5}$ concentrations in these areas may exceed 20 μg m$^{-3}$. Sulfate is predicted to be the dominant PM$_{2.5}$ species over the Eastern Mediterranean. The strong photochemical activity in this area favors the conversion of sulfur dioxide to sulfate and can partly explain the relatively high PM$_{2.5}$ levels in this area (up to 15 μg m$^{-3}$).

During the winter period the mean predicted ground-level concentration of total PM$_{2.5}$ over the domain is 7.1 μg m$^{-3}$. Sulfate and organics are predicted to be the major components contributing approximately 25% and 28% of total PM$_{2.5}$ mass. Peak period average concentrations of total PM$_{2.5}$ (mostly over Central and Northern Europe) reach up to 30 μg m$^{-3}$ especially in areas with large industrial activity or large urban emissions (Fig. 3.1b). OA accounts for up to half of total PM$_{2.5}$ in these areas with fresh primary OA being the dominant OA component.

In the fall period the model predicts an average total PM$_{2.5}$ concentration of 8.3 μg m$^{-3}$ over the domain. The elevated PM$_{2.5}$ levels are due to a combination of high ammonium nitrate, sulfate, and organic aerosol. On a domain-average basis organic aerosol and sulfate are predicted to account for 28% of total PM$_{2.5}$ mass each, followed by ammonium (12%), and nitrate (10%). High levels of PM$_{2.5}$ over the
Balkans and the Mediterranean (up to 22 μg m⁻³), are mainly due to high sulfate concentrations while ammonium nitrate dominates over the western parts of the domain (Fig. 3.1c). The largest OA concentrations, with a peak period average of 6.8 μg m⁻³, are predicted in the Po Valley area. High OA levels are also predicted over the Balkans.

**Figure 3.1**: Predicted average base case PM$_{2.5}$ ground-level concentrations (μg m⁻³) during the modeled (a) summer, (b) winter, and (c) fall periods.
Fountoukis et al. (2011) have evaluated the PMCAMx-2008 predictions against high time aerosol mass spectrometer (AMS) measurements during the summer EUCCARI intensive period (May 2008) used here. The observed data included ground measurements taken at four sites in Europe (Cabauw, Finokalia, Mace Head, Melptiz) as well as airborne data from an aircraft campaign (Morgan et al., 2010). PMCAMx-2008 had the most accurate performance for PM$_1$ organic aerosol (monthly average measured concentration: 3.3 $\mu$g m$^{-3}$, PMCAMx-2008: 3 $\mu$g m$^{-3}$), reproducing more than 87% of the hourly averaged data within a factor of 2, showing a normalized mean bias (NMB) of -11% and a normalized mean error (NME) of 30%. The model reproduced more than 94% of the observed daily averaged organic aerosol data within a factor of 2. The monthly average concentration of PM$_1$ sulfate predicted by the model in the four sites was 2.9 $\mu$g m$^{-3}$ compared to the measured value of 2.8 $\mu$g m$^{-3}$. PMCAMx-2008 was able to reproduce more than 70% of the hourly averaged data and more than 82% of the daily averaged points within a factor of 2. The normalized mean error (NME) for PM$_1$ sulfate concentration was 47% and the corresponding mean error and fractional error, 1.3 $\mu$g m$^{-3}$ and 0.4 respectively. The model had also a reasonable performance for PM$_1$ nitrate and PM$_1$ ammonium in Cabauw, Finokalia and Melpitz (the corresponding mean bias and NMB were 0.4 $\mu$g m$^{-3}$ and 29% for PM$_1$ nitrate, and 0.03 $\mu$g m$^{-3}$ and 2% for PM$_1$ ammonium respectively). However in Mace Head, the model significantly overpredicted both nitrate and ammonium concentrations. These errors as suggested by Fountoukis et al. (2011) could be, in some extent, attributed to the assumption of the bulk equilibrium approach that PMCAMx-2008 uses for the inorganic aerosol simulation, and the fact that in Mace Head a significant fraction of nitrate is associated with sea salt and shifts to the coarse mode, an effect that is not well captured by the model.
The comparison of PMCAMx-2008 predictions against the airborne measurements showed also an encouraging agreement. The model predicted average concentrations for PM$_1$ OA, sulfate, nitrate, and ammonium were 2.6, 1.6, 1.6 and 1.2 μg m$^{-3}$ respectively, while the corresponding measured average values were 2.2, 1.6, 1.4 and 1.3 μg m$^{-3}$, respectively. The model did also a good job for OA and sulfate, reproducing more than 66% and 62% of the airborne hourly measured data, while for concentrations higher than 1 μg m$^{-3}$, PMCAMx-2008 was able to capture more than 75% and 77% of the measured OA and sulfate data within a factor of 2. For PM$_1$ nitrate and ammonium, the model had a small normalized mean bias (NMB) (1% and -14% respectively) and a mean absolute gross error (MAGE) of 1.1 and 0.7 μg m$^{-3}$ respectively.

The comparison of PMCAx-2008 predictions against AMS hourly ground measurements during the EUCAARI winter intensive period indicates a reasonable agreement for PM$_1$ OA and sulfate (see supplement of Megaritis et al., 2013). On average the monthly measured concentrations for PM$_1$ OA, nitrate, sulfate and ammonium were 2.3, 2.1, 1.0 and 0.9 μg m$^{-3}$ respectively compared to the predicted average values of 1.1, 1.8, 0.9 and 1.2 μg m$^{-3}$. The underprediction of OA was attributed to underestimation of wood burning emissions. The model reproduced 44% of the hourly averaged PM$_1$ OA data and 42% of the hourly averaged PM$_1$ sulfate data within a factor of 2. The model predictions for OA and sulfate were subject to significant scatter (for OA the fractional bias was -0.3 and the fractional error 0.9, while for sulfate the fractional bias was 0.1 and the fractional error 0.9).

During the fall period, hourly AMS measurements performed at numerous sites over Europe (Hyytiala, K-Puszta, Melpitz, Puy de Dome, Payerne, Puijo, and Vavihill) during an EMEP intensive campaign, were used for the PMCAMx-2008 evaluation.
The model reproduced more than 74% of the hourly averaged OA data within a factor of 2, having a fractional bias of -0.1 and a fractional error of 0.48. Sulfate, ammonium and nitrate were characterized by small to moderate factional bias (0.1 for sulfate, 0.11 for nitrate and 0.29 for ammonium) and larger fractional errors (up to 0.8 for nitrate) than organics. The predicted monthly average concentrations for PM$_{10}$ OA, sulfate, nitrate, and ammonium were 2.5, 1.5, 1.6, and 1.2 μg m$^{-3}$ respectively, relatively close to the measurements, 2.9, 1.4, 1.4, 1.0 μg m$^{-3}$.

### 3.5 Sensitivity to meteorological variables

For each of the three modeled periods, we performed a suite of individual sensitivity simulations by perturbing various meteorological parameters, one at a time. The sensitivity tests included perturbations in temperature, wind speed, absolute humidity, precipitation rate, precipitating area and mixing height. Table 3.1 summarizes the sensitivity simulations imposed in this study and the processes that were perturbed directly in each change.

Sensitivity to temperature was tested by performing four different simulations. The impact of temperature on biogenic emissions and PM$_{2.5}$ levels was examined, using temperature sensitive biogenic emissions, produced by the MEGAN model, based on an increase of 2 K. In this simulation the only change was on the biogenic emissions inventory. The temperatures used by the model (to simulate chemistry, thermodynamics, etc) were those of the base case scenario. The effect of temperature on aerosol thermodynamics was tested in another simulation where we increased temperature by 2 K only for the module of PMCAMx-2008 that simulates the partitioning of semi-volatile inorganic and organic PM$_{2.5}$ species. Similar to the first simulation, temperatures for the other processes in PMCAMx and all the other
meteorological parameters were the same as in the base case simulation. The third test studied the sensitivity of PM$_{2.5}$ to the temperature dependence of the gas-phase reaction rates. The overall temperature effect on PM$_{2.5}$ concentrations (using also temperature-dependent biogenic emissions) was studied in a different simulation where all surface and air temperatures were increased uniformly over the domain by 2 K, keeping all the other meteorological inputs constant.

**Table 3.1: Description of performed sensitivity simulations.**

<table>
<thead>
<tr>
<th>Meteorological Parameter</th>
<th>Change Examined</th>
<th>Directly Affected in Simulation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>+2 K</td>
<td>Biogenic VOC emissions only</td>
</tr>
<tr>
<td></td>
<td>+2 K</td>
<td>Organic and inorganic aerosol thermodynamics only</td>
</tr>
<tr>
<td></td>
<td>+2 K</td>
<td>Gas-phase chemistry only</td>
</tr>
<tr>
<td></td>
<td>+2 K</td>
<td>All temperature-dependent processes (including BVOC emissions)</td>
</tr>
<tr>
<td>Wind Speed</td>
<td>-10%</td>
<td>Turbulent dispersion coefficients, advection, dry deposition. Emissions (including marine) were kept constant</td>
</tr>
<tr>
<td></td>
<td>-10%</td>
<td>Marine aerosol emissions only</td>
</tr>
<tr>
<td>Absolute humidity</td>
<td>+5%</td>
<td>Reaction rates with H$_2$O, aerosol thermodynamics</td>
</tr>
<tr>
<td>Precipitation rate</td>
<td>+10%</td>
<td>Wet deposition</td>
</tr>
<tr>
<td>Precipitation area</td>
<td>+10%</td>
<td>Wet deposition</td>
</tr>
<tr>
<td>Mixing Height</td>
<td>+1 model layer</td>
<td>Vertical dispersion</td>
</tr>
</tbody>
</table>
The effect of wind speed on PM$_{2.5}$ concentrations was studied by two different simulations. We used first a simplified scenario where horizontal wind speed was decreased uniformly over the entire domain by 10% keeping all other inputs constant. The vertical wind components were calculated from the perturbed horizontal wind speeds to ensure mass conservation. In this simulation the only changes were on the dispersion coefficients, as well as the transport (vertical velocity, advection, dilution) and removal processes (dry deposition resistance), while sea-salt emissions were kept constant as in the base case. In the second test, we examined the effect of wind speed on marine aerosol emissions, recalculating the corresponding emissions inventory for wind speeds decreased by 10%. This simulation examines only changes in sea salt emissions, therefore wind speed and all other meteorological data used as input by the model were based on the base case scenario.

The effect of absolute humidity was tested based on a uniform increase of 5% over the entire domain. Precipitation intensity was increased uniformly by 10% to study its effects. Sensitivity to the spatial extent of precipitation was investigated in a simulation where the area undergoing precipitation was increased by +10%. This was done by extending the existing precipitating area into non-precipitating but adjacent cells which were chosen randomly. In addition, the sensitivity of PM$_{2.5}$ to mixing height changes was examined in a simulation where the mixing height was increased by one model layer. This was done by changing the vertical diffusivity in only the layer immediately above the base case mixing height. The corresponding average change was an increase in mixing height by approximately 150 m.

In all tests, initial and boundary conditions of the modeled PM species did not change compared to the baseline scenario. Emissions of all pollutants were also kept constant as in the base case conditions in all tests, except for the two simulations
using temperature sensitive biogenic emissions and new sea salt emissions due to wind speed change.

3.6 Sensitivity to Temperature

3.6.1 Temperature-dependent biogenic emissions

The predicted changes (sensitivity scenario - base case) in average ground-level concentrations of total PM$_{2.5}$ due to higher biogenic emissions (based on a 2 K temperature increase) are shown in Fig. 3.2. During the modeled summer period, PM$_{2.5}$ is predicted to increase by 10 ng m$^{-3}$ K$^{-1}$ (0.13% K$^{-1}$) on a domain average basis, with a maximum increase of 250 ng m$^{-3}$ K$^{-1}$ (2% K$^{-1}$) in France (Fig. 3.2a). This is mainly due to an OA increase of 26 ng m$^{-3}$ K$^{-1}$ (1.5% K$^{-1}$) on average, which reaches up to 200 ng m$^{-3}$ K$^{-1}$ (5% K$^{-1}$). Higher biogenic emissions lead to increases in biogenic SOA concentrations which account for almost 90% of the OA increase. The increased biogenic VOCs, on the other hand result in reductions of OH in several areas. The reduced OH levels, slow down the gas phase formation of sulfate (through SO$_2$ oxidation), and also lead to decreases of ammonium nitrate. On average, sulfate and ammonium nitrate decrease by 10 ng m$^{-3}$ (0.4% K$^{-1}$) and 6.5 ng m$^{-3}$ (0.4% K$^{-1}$) respectively. This negative effect of increased biogenic VOCs on OH levels and hence on inorganics was also noted by Zhang et al. (2008). However, the predicted decreases of inorganic PM$_{2.5}$ components are less than the increases of total OA, thus the net impact is an increase of total PM$_{2.5}$ levels.

Biogenic emissions have also a positive effect on total PM$_{2.5}$ concentrations during the modeled winter and fall period. PM$_{2.5}$ is predicted to increase throughout the domain by 10 ng m$^{-3}$ K$^{-1}$ (0.1% K$^{-1}$) and 20.3 ng m$^{-3}$ K$^{-1}$ (0.25% K$^{-1}$) on average, during the modeled winter and fall period respectively (Fig. 3.2b, c). The predicted
Increases during the winter period can reach up to 130 ng m\(^{-3}\) K\(^{-1}\) (1% K\(^{-1}\)) while during fall are even higher (up to 200 ng m\(^{-3}\) K\(^{-1}\) or 1.5% K\(^{-1}\)). Increases in OA levels dominate the response of total PM\(_{2.5}\), while inorganic PM\(_{2.5}\) is less sensitive to biogenic emissions during these seasons.

**Figure 3.2:** Predicted average change in ground-level concentrations (µg m\(^{-3}\)) of total PM\(_{2.5}\) due to changes on biogenic VOC emissions (based on a 2 K temperature increase) during the modeled (a) summer, (b) winter, and (c) fall periods. A positive value corresponds to an increase.
3.6.2 Temperature effects on gas/aerosol partitioning

Increasing temperature by 2 K only for the partitioning of semi-volatile PM components has a significant effect on total PM$_{2.5}$ levels in all three periods (Fig. 3.3). The predicted response of PM$_{2.5}$ shows a strong spatial variability, as a result of competing changes in inorganic species concentrations and, to a lesser extent, in organic ones. In the modeled summer period, total PM$_{2.5}$ concentrations decrease by 49 ng m$^{-3}$ K$^{-1}$ (1% K$^{-1}$) on average, although its response is quite variable and ranges from -700 ng m$^{-3}$ (-5% K$^{-1}$) to 50 ng m$^{-3}$ (1.5% K$^{-1}$). The predicted PM$_{2.5}$ decrease is largely due to significant decreases of nitrate. Rising temperature leads to increased volatilization of ammonium nitrate, which partitions to the gas-phase (Seinfeld and Pandis, 2006). As a result, less ammonium nitrate exists in the particulate phase (approximately 15% in this simulation), leading to significant decreases of nitrate which reach up to 600 ng m$^{-3}$ K$^{-1}$ (14% K$^{-1}$). Over the domain, the average reduction of nitrate is 40 ng m$^{-3}$ K$^{-1}$ (8% K$^{-1}$). On the contrary, as particulate nitrate decreases the availability of gas-phase NH$_3$ increases, leading to higher cloud pH and accelerated aqueous-phase formation of particulate sulfate. On average, PM$_{2.5}$ sulfate is predicted to increase by 3 ng m$^{-3}$ K$^{-1}$ (0.2% K$^{-1}$), reaching up to a maximum of 30 ng m$^{-3}$ K$^{-1}$ (2% K$^{-1}$). This complex effect of temperature changes on partitioning of semi-volatile inorganic PM$_{2.5}$ is consistent with the results of other studies (e.g., Aksoyoglu et al., 2011; Dawson et al., 2007; Jimenez-Guerrero et al., 2012). OA is also sensitive to temperature mainly due to changes in the levels of secondary OA components and to a lesser extent on primary OA. Higher temperature leads to evaporation of all OA components and subsequently to decreases of their levels. The predicted average decrease of total OA is 13 ng m$^{-3}$ K$^{-1}$ (0.7% K$^{-1}$) while in Central and North Europe exceeds 330 ng m$^{-3}$ K$^{-1}$ (4% K$^{-1}$). The sensitivity of OA to
temperature, as well as the increased gas-phase partitioning as temperature increases have been also noted in earlier studies (Dawson et al., 2007; Megaritis et al. 2013).

![Figure 3.3: Predicted average change in ground-level concentrations (μg m⁻³) of total PM_{2.5} due to changes on gas/aerosol partitioning (based on a 2 K temperature increase) during the modeled (a) summer, (b) winter, and (c) fall periods. A positive value corresponds to an increase.](image)

During the modeled winter period, total PM_{2.5} shows also a negative response to temperature, with an average decrease of 25 ng m⁻³ K⁻¹ (0.4% K⁻¹) (Fig. 3.3b) over the
domain. The predicted decrease of PM$_{2.5}$ is significant in Central Europe and reaches up to 500 ng m$^{-3}$ K$^{-1}$ (2% K$^{-1}$), due largely to decreases in nitrate (up to 150 ng m$^{-3}$ K$^{-1}$ or 8% K$^{-1}$) and in a lesser extent in OA levels. However, in some areas (mainly in North Europe), PM$_{2.5}$ is predicted to increase (up to 100 ng m$^{-3}$ K$^{-1}$ or 1.5% K$^{-1}$), due to higher sulfate levels, which offset the respective decreases of nitrate and organics.

During the modeled fall period, total PM$_{2.5}$ decreases by 88 ng m$^{-3}$ K$^{-1}$ (1% K$^{-1}$) on average over the domain. Significant decreases are predicted mainly over the central and south western areas of the domain, approximately 700 ng m$^{-3}$ K$^{-1}$ (7% K$^{-1}$) and 500 ng m$^{-3}$ K$^{-1}$ (3.5% K$^{-1}$) respectively (Fig. 3.3c). Nitrate is significantly reduced (its predicted decreases may exceed 10% K$^{-1}$), and along with total OA decreases dominate the response of total PM$_{2.5}$, despite the predicted increases in sulfate levels.

3.6.3 Temperature-dependent gas-phase reaction rates

Changes in gas-phase reaction rates, due to temperature changes, could also affect total PM$_{2.5}$ levels (Dawson et al., 2007). At higher temperatures, the temperature-dependent gas-phase rate constants will accelerate the chemical production of aerosol precursors as well as they will increase oxidant levels (Dawson et al., 2007; Day and Pandis, 2011; Im et al., 2011; Jacob and Winner, 2009). In all three modeled periods, PM$_{2.5}$ is predicted to increase due to the combined increases on the individual PM$_{2.5}$ components. In the modeled summer period, PM$_{2.5}$ concentrations are predicted to increase by 26 ng m$^{-3}$ K$^{-1}$ (0.3% K$^{-1}$) on a domain average basis. The effect is stronger over continental Europe, where PM$_{2.5}$ increases by 50 ng m$^{-3}$ K$^{-1}$ (0.8% K$^{-1}$) on average, while in some areas in Western Europe, increases in PM$_{2.5}$ reach up to 400 ng m$^{-3}$ K$^{-1}$ (2% K$^{-1}$) (Fig. 3.4a). The predicted response of total PM$_{2.5}$ is mainly driven by increases of nitrate levels (approximately
45% of total PM$_{2.5}$ increase is due to nitrate), followed by increases in total OA (largely attributed to secondary OA) and sulfate.

**Figure 3.4:** Predicted average change in ground-level concentrations (μg m$^{-3}$) of total PM$_{2.5}$ due to changes on gas-phase reaction rates (based on a 2 K temperature increase) during the modeled (a) summer, (b) winter, and (c) fall periods. A positive value corresponds to an increase.

The lower oxidant availability during the winter leads to a lower increase of PM$_{2.5}$ compared to summertime (13.5 ng m$^{-3}$ K$^{-1}$ or 0.2% K$^{-1}$ on average) (Fig. 3.4b). Over continental Europe, the predicted increases are even higher, up to 120 ng m$^{-3}$ K$^{-1}$.
(1% K\textsuperscript{-1}). Changes in organics and nitrate dominate (each of the components accounts for around 40% of total PM\textsubscript{2.5} increase), while increases in sulfate tend to be rather small.

The effects are quite similar during the modeled fall period (an average increase of 47 ng m\textsuperscript{-3} K\textsuperscript{-1} or 0.6% K\textsuperscript{-1} over the domain). The largest changes are in Central and Western Europe where PM\textsubscript{2.5} increases by approximately 160 ng m\textsuperscript{-3} K\textsuperscript{-1} (1.4% K\textsuperscript{-1}) (Fig. 3.4c). Increases of fine particulate nitrate and organics are driving the PM\textsubscript{2.5} response, while there are moderate increases in sulfate.

### 3.6.4 Overall temperature effects

An increase in temperature by 2 K is predicted to have a negative effect on PM\textsubscript{2.5} concentrations for all three modeled periods. On a domain average basis PM\textsubscript{2.5} decreases by 25 ng m\textsuperscript{-3} K\textsuperscript{-1} (0.3% K\textsuperscript{-1}) in the summer, 7 ng m\textsuperscript{-3} K\textsuperscript{-1} (0.1% K\textsuperscript{-1}) in the winter and 33 ng m\textsuperscript{-3} K\textsuperscript{-1} (0.4% K\textsuperscript{-1}) in the modeled fall period, respectively. However the overall effect of temperature on PM\textsubscript{2.5} levels is quite variable in space and time (Fig. 3.5) due to the different effects among the individual processes as well as the competing responses between the PM\textsubscript{2.5} species. The predicted changes on PM\textsubscript{2.5} concentrations range -720 ng m\textsuperscript{-3} K\textsuperscript{-1} (-8% K\textsuperscript{-1}) to 280 ng m\textsuperscript{-3} K\textsuperscript{-1} (7% K\textsuperscript{-1}). Over continental Europe, PM\textsubscript{2.5} changes are dominated by decreases in nitrate, which reach up to 650 ng m\textsuperscript{-3} K\textsuperscript{-1} (12% K\textsuperscript{-1}) during the modeled summer period. These decreases are mainly arising from the significant effects on the partitioning of nitrate, as approximately 18% less ammonium nitrate exists in the particulate phase. On the contrary in several parts of the domain, the higher biogenic VOC emissions and the increased rate of SO\textsubscript{2} oxidation enhance the production of OA and sulfate respectively. These increases can reach up to 225 ng m\textsuperscript{-3} K\textsuperscript{-1} (7% K\textsuperscript{-1}) for sulfate and up to 190 ng m\textsuperscript{-3} K\textsuperscript{-1} (4% K\textsuperscript{-1}) for OA, and may govern the total PM\textsubscript{2.5} response.
These results support the findings from previous studies that suggest the competing effects of temperature among the different processes and PM$_{2.5}$ species (Dawson et al., 2007; Heald et al., 2010; Jacob and Winner, 2009; Jimenez-Guerrero et al., 2012). Summarizing, the semi-volatile PM$_{2.5}$ evaporation appears to dominate and determine the overall PM$_{2.5}$ response to temperature changes over Europe, during all seasons. The average changes in PM$_{2.5}$ are higher during the fall.

**Figure 3.5:** Predicted average change in ground-level concentrations (μg m$^{-3}$) of total PM$_{2.5}$ due to an overall temperature increase by 2 K during the modeled (a) summer, (b) winter, and (c) fall periods. A positive value corresponds to an increase.
3.7 Wind Speed

Decreasing wind speed by 10%, without any change on sea-salt emissions (as well as on emissions from other sources), affects all PM$_{2.5}$ components, resulting in increases of their levels in all three modeled periods (Fig. 3.6). During summer, total PM$_{2.5}$ is predicted to increase by 41 ng m$^{-3}$ %$^{-1}$ (0.6% %$^{-1}$) on average over the entire domain (Fig. 3.6a). The effects of wind speed were found to be highest in the more polluted and populated areas of the domain. For example, in Western Europe, a high ammonium nitrate area during summer, total PM$_{2.5}$ increases up to 340 ng m$^{-3}$ %$^{-1}$ (1.5% %$^{-1}$), driven mainly by increases of nitrate (up to 156 ng m$^{-3}$ %$^{-1}$ or 2.5% %$^{-1}$).

Decreases in wind speed affect advection, dispersion and mixing as well as lead to changes in dry deposition. A reduction in wind speed by 10% decreases horizontal advection of PM$_{2.5}$ into the domain by approximately 7.5-10% and horizontal advection out of it by 8-11%. In addition, we predict that approximately 7-13% less PM$_{2.5}$ is dry deposited due to the simulated 10% reduction in wind speed.

The effects of wind speed on total PM$_{2.5}$ levels are similar during the other two periods. During winter, PM$_{2.5}$ increases by 36 ng m$^{-3}$ %$^{-1}$ (0.5% %$^{-1}$) on average over the domain. Significant increases are found mainly over North Europe, where PM$_{2.5}$ increases up to 250 ng m$^{-3}$ %$^{-1}$ (0.8% %$^{-1}$), as well as in Central and Southwestern Europe (Fig. 3.6b), mainly due to increases of total OA and sulfate. In the modeled fall period PM$_{2.5}$ shows a similar sensitivity. On a domain average basis, PM$_{2.5}$ increases by 38 ng m$^{-3}$ %$^{-1}$ (0.5% %$^{-1}$). In most continental areas, the predicted increases in PM$_{2.5}$ exceed 70 ng m$^{-3}$ %$^{-1}$, while in Central Europe reach up to 225 ng m$^{-3}$ %$^{-1}$ (0.9% %$^{-1}$) (Fig. 3.6c). The predicted PM$_{2.5}$ response is driven mainly by increases in particulate nitrate (account for approximately 40% of total PM$_{2.5}$ increase) and to a lesser extent in ammonium, sulfate and organics.
Our results, regarding the PM$_{2.5}$ response to wind speed, are consistent with those by Dawson et al. (2007), who found a PM$_{2.5}$ sensitivity to wind equal to 0.77% $\cdot$ $^{-1}$ during summer and 0.56% $\cdot$ $^{-1}$ during winter in the Eastern US. This negative effect of wind speed on PM$_{2.5}$ has been also reported in earlier modeling studies over Europe (Aksoyoglu et al., 2011; Carvalho et al., 2010; Lecoeur and Seigneur, 2013).

**Figure 3.6:** Predicted average change in ground-level concentrations ($\mu$g m$^{-3}$) of total PM$_{2.5}$ due to a 10% decrease in wind speed during the modeled (a) summer, (b) winter and (c) fall periods. A positive value corresponds to an increase.
3.7.1 Wind effects on sea-salt emissions

The predicted changes (sensitivity scenario - base case) in average ground-level concentrations of PM$_{2.5}$ using a new sea salt emissions inventory (based on a 10% decrease of wind speed) are shown in Fig. 3.7.

Figure 3.7: Predicted average change in ground-level concentrations (μg m$^{-3}$) of total PM$_{2.5}$ due to changes on sea salt emissions (based on a 10% decrease in wind speed) during the modeled (a) summer, (b) winter, and (c) fall period. A positive value corresponds to an increase.
As expected, lower sea salt emissions result in lower PM$_{2.5}$ concentrations in all modeled periods, especially over water and in coastal areas. The predicted PM$_{2.5}$ response is not uniform throughout the domain. During the modeled summer period, the predicted PM$_{2.5}$ decrease exceeds 60 ng m$^{-3}$ %$^{-1}$ (or 0.5% %$^{-1}$), and may reach up to 170 ng m$^{-3}$ %$^{-1}$ (0.9% %$^{-1}$), mainly due to decreases in particulate sodium and chloride. The predicted decreases are even larger (up to 200 ng m$^{-3}$ %$^{-1}$ or 2.7% %$^{-1}$) during the winter modeled period, as sea salt emissions and the accompanying concentrations of particulate sodium chloride were higher, while similar results we have obtained during fall. On the contrary, over continental Europe the effects on PM$_{2.5}$ levels due to less marine aerosol production are moderate. PM$_{2.5}$ is also reduced, however the predicted decrease does not exceed 20 ng m$^{-3}$ %$^{-1}$ (0.1% %$^{-1}$) in all three periods.

3.8 Effects of Absolute humidity

Changes in absolute humidity affect total PM$_{2.5}$ concentrations, however its predicted response varies significantly in space (Fig. 3.8) due to the competing changes among PM$_{2.5}$ species. During the modeled summer period, increases of absolute humidity by 5% result to an average increase of total PM$_{2.5}$ by 8 ng m$^{-3}$ %$^{-1}$ (0.2% %$^{-1}$) over the entire domain. This is consistent with the Dawson et al. (2007) study for the Eastern US who reported a 20 ng m$^{-3}$ %$^{-1}$ increase in summer PM$_{2.5}$ levels due to increases in absolute humidity by 5 - 20%. The highest changes are predicted in Western Europe, with PM$_{2.5}$ increases up to 160 ng m$^{-3}$ %$^{-1}$ (1.6% %$^{-1}$) (Fig. 3.8a) as a result of significant increases in nitrate. Increases in relative humidity favor the partitioning of nitrate as they shift the equilibrium of the ammonia-nitric acid system toward the particles (Seinfeld and Pandis, 2006). As absolute humidity
increases by 5%, approximately 15% more HNO$_3$ is predicted to move to the aerosol phase, leading to higher particulate nitrate levels (up to 115 ng m$^{-3}$ %$^{-1}$ or 3% %$^{-1}$). These changes in nitrate, along with increases in ammonium and OA are driving the PM$_{2.5}$ response over land. On the contrary, over the ocean, total PM$_{2.5}$ decreases as humidity increases, due mainly to changes is sulfate and sodium chloride. The negative response of PM$_{2.5}$ in this area (reaching up to a reduction of 140 ng m$^{-3}$ %$^{-1}$ or 1.5% %$^{-1}$) arises from increases in the size of the particles, and accelerated dry deposition (in all modeled periods a 5% increase in absolute humidity resulted in an approximately 9-15% increase in dry deposited mass of sulfate, sodium, and chloride).

Absolute humidity has also a positive effect on PM$_{2.5}$ levels during the modeled fall period. Significant increases are predicted in most areas of continental Europe (up to 130 ng m$^{-3}$ %$^{-1}$ or 1% %$^{-1}$) (Fig. 3.8c), mainly due to significant increases in particulate nitrate (up to 98 ng m$^{-3}$ %$^{-1}$ or 3% %$^{-1}$). Over the ocean, total PM$_{2.5}$ decreases (its predicted reduction can exceed 50 ng m$^{-3}$ %$^{-1}$ or 0.4% %$^{-1}$), however the predicted increases of nitrate along with the increase in ammonium and total OA exceed the decreases in sulfate and sea salt, thus the net impact on total PM$_{2.5}$ is an average increase of 11.5 ng m$^{-3}$ %$^{-1}$ (0.2% %$^{-1}$).

In the modeled winter period, the predicted response of total PM$_{2.5}$ to absolute humidity differs. In spite of the increase in nitrate concentrations (6 ng m$^{-3}$ %$^{-1}$ or 1.5% %$^{-1}$ on average), the predicted decreases in fine particulate sulfate and sea salt aerosol dominate (on average sulfate decreases by 8 ng m$^{-3}$ %$^{-1}$ while sodium chloride decreases by 9.5 ng m$^{-3}$ %$^{-1}$) and determine the response of total PM$_{2.5}$ (Fig. 3.8b). On a domain average basis, the net effect of absolute humidity on PM$_{2.5}$ is a decrease by 7.5 ng m$^{-3}$ %$^{-1}$ (0.2% %$^{-1}$), while the predicted concentration changes range from -130 ng m$^{-3}$ %$^{-1}$ (-1.6% %$^{-1}$) to 44 ng m$^{-3}$ %$^{-1}$ (0.5% %$^{-1}$).
Figure 3.8: Predicted average change in ground-level concentrations (μg m⁻³) of total PM$_{2.5}$ due to a 5% increase in absolute humidity during the modeled (a) summer, (b) winter, and (c) fall periods. A positive value corresponds to an increase.

3.9 Precipitation

3.9.1 Precipitation rate

The effect of the precipitation rate on PM$_{2.5}$ concentrations is similar during all the modeled periods. The predicted response of average-ground level PM$_{2.5}$ concentrations after a 10% increase in precipitation rate (without changing the precipitation area) is shown in Fig. 3.11 (see supplementary material, Section 3.14).
As it is expected, increases in precipitation rate, accelerate the wet removal of PM$_{2.5}$ species and their gas precursors and consequently results in decreases of their concentrations. In this simulation we predict a 2-4% increase in PM$_{2.5}$ wet deposited mass as well as a 5-12% increase in the wet deposition of PM$_{2.5}$ gas precursors due to a 10% increase in precipitation rate.

During the modeled summer period, total PM$_{2.5}$ is predicted to decrease as precipitation increases, by 13 ng m$^{-3}$ %$^{-1}$ (0.2% %$^{-1}$) on average. Precipitation affects all the individual PM$_{2.5}$ species leading to reductions of their levels in most areas of the domain (Fig. 3.11a). Over the western parts of the domain, total PM$_{2.5}$ is reduced up to 110 ng m$^{-3}$ %$^{-1}$ (1.8% %$^{-1}$). However even in areas with little rainfall during this period (e.g eastern Mediterranean) (Fig. 3.12, supplementary material), total PM$_{2.5}$ also decreased indicating that changes due to precipitation in upwind areas can affect the levels of PM$_{2.5}$ over downwind areas. Similar effects are predicted during the other two periods. PM$_{2.5}$ is reduced as precipitation rate increases, having an average decrease of 0.2% %$^{-1}$ in both periods. The predicted effects are strongest in areas receiving moderate or little precipitation with a maximum reduction of 65 ng m$^{-3}$ %$^{-1}$ (1% %$^{-1}$) during the modeled winter period and up to 68 ng m$^{-3}$ %$^{-1}$ (1.2% %$^{-1}$) in the modeled fall period.

This negative correlation has been also pointed in earlier studies (Hedegaard et al., 2008; Jacob and Winner, 2009; Jimenez-Guerrero et al., 2012; Lecoeur and Seigneur, 2013; Manders et al., 2012). Dawson et al. (2007) predicted quite similar sensitivities for total PM$_{2.5}$ during summer (approximately 0.2% %$^{-1}$).
3.9.2 Precipitation area

The predicted reduction of total PM$_{2.5}$ for a 10% increase in the spatial extent of precipitation covers a significant portion of Europe, during all periods (Fig. 3.13, supplementary material). During summer the predicted reduction of PM$_{2.5}$ reaches a maximum of 19 ng m$^{-3}$ %$^{-1}$ (0.3% %$^{-1}$) with an average sensitivity of 8 ng m$^{-3}$ %$^{-1}$ (0.1% %$^{-1}$). The predicted reductions arising mainly from the increases in PM$_{2.5}$ wet deposited mass (approximately 2-5%). The predicted effect is quite similar during the winter period (average reduction of 7.5 ng m$^{-3}$ %$^{-1}$ or 0.1% %$^{-1}$), while in the modeled fall period the predicted response of total PM$_{2.5}$ is a little higher, 13 ng m$^{-3}$ %$^{-1}$ (0.16% %$^{-1}$) on average, and can reach up to 40 ng m$^{-3}$ %$^{-1}$ (0.3% %$^{-1}$) over the Mediterranean region. Our results support the conclusion that not only the precipitation intensity but the area undergoing precipitation as well, can affect total PM$_{2.5}$ concentrations (Lecoeur and Seigneur, 2013).

3.10 Mixing height

During the base case simulations the average predicted mixing height was 550 m in the summer, 380 m in the winter and 440 m in the fall period respectively. The predicted simulation-averaged changes in PM$_{2.5}$ due to an increase in mixing height (by approximately 150 m) are shown in Fig. 3.14 (see supplementary material, Section 3.14).

As expected, increases in mixing height affect all the individual PM$_{2.5}$ components resulting in decreases in their concentrations during all modeled periods. In the summer, the average total PM$_{2.5}$ concentrations decrease by 3.5 ng m$^{-3}$ %$^{-1}$ (or 0.05% %$^{-1}$). Similar effects on PM$_{2.5}$ levels are also predicted for the other two periods, with an average reduction of 1.8 ng m$^{-3}$ %$^{-1}$ (0.03% %$^{-1}$) and 2.2 ng m$^{-3}$ %$^{-1}$
(0.03% %^{-1}) during the modeled winter and fall period, respectively. The effect of mixing height is strongest over polluted areas, where the predicted reduction of total PM$_{2.5}$ can exceed 35 ng m$^{-3}$ %^{-1} (0.8% %^{-1}) (over Western Europe, during the modeled summer period). Our results are consistent with those by Dawson et al. (2007), who predicted a PM$_{2.5}$ sensitivity to mixing height equal to 0.08% %^{-1} during summer and 0.05% %^{-1} during winter in the Eastern US.

3.11 Relative importance of meteorological parameters

In order to evaluate the relative importance of the various meteorological parameters, we estimated the potential effects that each of them may have on total PM$_{2.5}$ concentrations in a future climate. Our estimates were based on the predicted average PM$_{2.5}$ sensitivities to the meteorological perturbations (Fig. 3.9) and the projected future changes for each parameter. The projected meteorological changes are shown in Table 3.2. According to the different emissions IPCC (2007) scenarios, the average temperature in Europe is expected to increase over the next century from 1 to 5.5 K. Projections for wind speed and precipitation in Europe vary significantly in space. Based on the IPPC SRES A2 scenario, wind speed is predicted to change from -10 to 10%, while precipitation could change from -40% to 40%. In our calculations, the changes in precipitating area and intensity were chosen to represent future projections for total precipitation over Europe. For mixing height, a potential range of changes was assumed, based on the estimates of Hedegaard et al. (2013). For this first order estimate, we assumed the same meteorological changes for all seasons.

In all three periods, PM$_{2.5}$ appears to be more sensitive to temperature changes rather than the rest meteorological parameters (Fig. 3.9). On average, PM$_{2.5}$ shows a negative sensitivity to temperature changes, which is higher during fall compared to
the other periods. However, the predicted PM$_{2.5}$ sensitivities to temperature are spatially and temporally variable as a result of the different effects among the individual processes and the different responses of the PM$_{2.5}$ species. During all seasons, the increased volatilization of ammonium nitrate dominates, causing large decreases in PM$_{2.5}$ with increasing temperature. The negative predicted sensitivities reach up to 440 ng m$^{-3}$ %$^{-1}$ in the fall and 310 ng m$^{-3}$ %$^{-1}$ in the summer period (lower during winter) (Fig. 3.9). On the contrary, the increase of temperature lead to higher biogenic VOC emissions and accelerates the gas-phase chemical reactions which can be, in some cases, as significant as the effects on the partitioning of semi-volatile PM$_{2.5}$, resulting in positive PM$_{2.5}$ sensitivities up to 230 ng m$^{-3}$ %$^{-1}$. PM$_{2.5}$ shows also a strong sensitivity to wind speed and its accompanying effects on the marine aerosol production. However the predicted changes are somewhat lower compared to the PM$_{2.5}$ sensitivities to temperature increase (Fig. 3.9). In all periods, wind speed as well as its effects on sea salt emissions influence PM$_{2.5}$ in a similar way, and the predicted sensitivities may range from -115 ng m$^{-3}$ %$^{-1}$ (due to changes in wind speed, without any change in the emissions) to 132 ng m$^{-3}$ %$^{-1}$ (due to the effects of wind speed on sea salt emissions). PM$_{2.5}$ appears to be less sensitive to absolute humidity changes (Fig. 3.9). In all periods, PM$_{2.5}$ concentrations show variable sensitivities to absolute humidity, due to the competing effects between the individual PM$_{2.5}$ species (e.g., increases in nitrate, decreases in sulfate), thus the average sensitivity does not exceed 12 ng m$^{-3}$ %$^{-1}$ and the largest PM$_{2.5}$ sensitivities reach up to 55 ng m$^{-3}$ %$^{-1}$. Changes in precipitation result in negative sensitivities for PM$_{2.5}$ levels which are comparable to those of absolute humidity, while mixing height seems to have a relatively small effect on PM$_{2.5}$.
Figure 3.9: Predicted simulation-average sensitivities of total PM$_{2.5}$ to changes in temperature, wind speed, sea salt emissions, absolute humidity, precipitation rate, precipitating area, and mixing height, during the three modeled periods. Each bar shows the range between the 10th and 90th percentiles. The black line in each bar shows the mean PM$_{2.5}$ sensitivity.

In a future climate, the projected changes in precipitation are expected to have the largest impact on PM$_{2.5}$ levels during all periods (Fig. 3.10). PM$_{2.5}$ concentrations could potentially change by several μg m$^{-3}$ (up to approximately 2 μg m$^{-3}$ during the fall period), with changes in precipitation intensity being rather more important than changes in precipitating area. Wind speed and absolute humidity may also lead to appreciable changes in future PM$_{2.5}$ levels. The expected effects on PM$_{2.5}$ due to changes in wind speed as well as its accompanying effects on the marine aerosol production are similar in all three periods and quite close to those resulting from future precipitation changes (up to 1.4 μg m$^{-3}$). In addition, absolute humidity could
potentially lead to large changes in PM$_{2.5}$ mainly during the fall period (increases up to 2 $\mu$g m$^{-3}$). The increased particulate nitrate levels, as higher absolute humidity favors its partitioning, are dominant during this period causing large increases in PM$_{2.5}$. In the other two periods the expected changes in PM$_{2.5}$ are smaller due to the competing responses among the individual PM$_{2.5}$ species. Temperature is expected to have a lower impact on future PM$_{2.5}$ compared to the rest meteorological parameters, in all seasons. The expected PM$_{2.5}$ concentration changes range from -1.1 $\mu$g m$^{-3}$ to 0.5 $\mu$g m$^{-3}$, driven from the offsetting effects of increased nitrate volatilization, higher biogenic VOC emissions and accelerated gas-phase chemistry. Mixing height is expected to have a relatively small impact on PM$_{2.5}$ levels in a future climate.

![Graph showing predicted PM$_{2.5}$ concentration changes](image)

**Figure 3.10:** Expected PM$_{2.5}$ concentration changes due to projected changes in temperature, wind speed, sea salt emissions, absolute humidity, precipitation rate, precipitating area, and mixing height in the future, during the three modeled periods.
Table 3.2: Summary of expected effects on total PM$_{2.5}$ concentrations due to changes on meteorological parameters during the modelled summer, the modelled winter and the modelled fall period.

<table>
<thead>
<tr>
<th>Meteorological Parameter</th>
<th>Expected Change of Parameter</th>
<th>Process Affected</th>
<th>Predicted Sensitivity Mean (10%, 90%)</th>
<th>Expected Concentration Change (ng m$^{-3}$) Mean (10%, 90%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Summer Period</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature</td>
<td>+1 - 5.5 K$^a$</td>
<td>BVOC emissions</td>
<td>10.2 ng m$^{-3}$ K$^{-1}$ (-13, 44)</td>
<td>10.2 to 56.1 (-71.5 to 242)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Aerosol partitioning</td>
<td>-49 ng m$^{-3}$ K$^{-1}$ (-142, 4.1)</td>
<td>-49 to -270 (-781 to 23)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Reaction rates</td>
<td>26.3 ng m$^{-3}$ K$^{-1}$ (-1.1, 49)</td>
<td>26 to 145 (-6.1 to 270)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Overall</td>
<td>-23.3 ng m$^{-3}$ K$^{-1}$ (-145, 67)</td>
<td>-23 to -128 (-797 to 369)</td>
</tr>
<tr>
<td></td>
<td>-10 to 10%$^b$</td>
<td>Overall</td>
<td>-41.3 ng m$^{-3}$ %$^{-1}$ (-109, 0.7)</td>
<td>-413 to 413 (-1090 to 1090)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sea salt emissions</td>
<td>39.2 ng m$^{-3}$ (-1.3, 107)</td>
<td>-392 to 392 (-1070 to 1070)</td>
</tr>
<tr>
<td>Absolute humidity</td>
<td>+5 to 40%$^c$</td>
<td>Overall</td>
<td>8.2 ng m$^{-3}$ %$^{-1}$ (-13, 27)</td>
<td>41 to 330 (-520 to 1080)</td>
</tr>
<tr>
<td>Precipitation rate</td>
<td>-40 to +40%$^b$</td>
<td>Overall</td>
<td>-12.9 ng m$^{-3}$ %$^{-1}$ (-40, -1.6)</td>
<td>-516 to 516 (-1600 to 1600)</td>
</tr>
<tr>
<td>Precipitation area</td>
<td>-40 to +40%$^b$</td>
<td>Overall</td>
<td>-7.8 ng m$^{-3}$ %$^{-1}$ (-17, -1.1)</td>
<td>-312 to 312 (-680 to 680)</td>
</tr>
<tr>
<td>Mixing Height</td>
<td>-20 to +20%</td>
<td>Overall</td>
<td>-3.5 ng m$^{-3}$ %$^{-1}$ (-9.5, 1)</td>
<td>-70 to 70 (-190 to 190)</td>
</tr>
</tbody>
</table>

$^a$ IPCC, 2007

$^b$ Based on IPCC A2 scenario

$^c$ Based on IPCC temperature projections and predicted base-case average RH during the three modeled periods
<table>
<thead>
<tr>
<th>Meteorological Parameter</th>
<th>Expected Change of Parameter</th>
<th>Process Affected</th>
<th>Predicted Sensitivity Mean (10%, 90%)</th>
<th>Expected Concentration Change (ng m(^{-3})) Mean (10%, 90%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Winter Period</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature</td>
<td>+1 - 5.5 K(^{a})</td>
<td>BVOC emissions</td>
<td>10 ng m(^{-3}) K(^{-1})</td>
<td>10 to 55</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Aerosol</td>
<td>-25 ng m(^{-3}) K(^{-1})</td>
<td>-25 to -138</td>
</tr>
<tr>
<td></td>
<td></td>
<td>partitioning</td>
<td>(-73, 13)</td>
<td>(-402 to 72)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Reaction rates</td>
<td>13.3 ng m(^{-3}) K(^{-1})</td>
<td>13.3 to 73</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(-1.1, 25)</td>
<td>(-6 to 138)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Overall</td>
<td>-6.5 ng m(^{-3}) K(^{-1})</td>
<td>-6.5 to -36</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(-90, 65)</td>
<td>(-495 to 358)</td>
</tr>
<tr>
<td>Wind Speed</td>
<td>-10 to 10%(^{b})</td>
<td>Overall (constant emissions)</td>
<td>-36.4 ng m(^{-3}) %(^{-1})</td>
<td>-364 to 364</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(-83, -4.4)</td>
<td>(-830 to 830)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sea salt</td>
<td>52.5 ng m(^{-3})</td>
<td>-525 to 525</td>
</tr>
<tr>
<td></td>
<td></td>
<td>emissions</td>
<td>(5, 132)</td>
<td>(-1320 to 1320)</td>
</tr>
<tr>
<td>Absolute humidity</td>
<td>+5 to 40%(^{c})</td>
<td>Overall</td>
<td>-7.6 ng m(^{-3}) %(^{-1})</td>
<td>-38 to -304</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(-35, 9)</td>
<td>(-1400 to 360)</td>
</tr>
<tr>
<td>Precipitation rate</td>
<td>-40 to +40%(^{b})</td>
<td>Overall</td>
<td>-12.2 ng m(^{-3}) %(^{-1})</td>
<td>-488 to 488</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(-33, -1.6)</td>
<td>(-1320 to 1320)</td>
</tr>
<tr>
<td>Precipitation area</td>
<td>-40 to +40%(^{b})</td>
<td>Overall</td>
<td>-7.3 ng m(^{-3}) %(^{-1})</td>
<td>-292 to 292</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(-15, -1.5)</td>
<td>(-600 to 600)</td>
</tr>
<tr>
<td>Mixing Height</td>
<td>-20 to +20%</td>
<td>Overall</td>
<td>-1.8 ng m(^{-3}) %(^{-1})</td>
<td>-36 to 36</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(-5, 0.3)</td>
<td>(-100 to 100)</td>
</tr>
</tbody>
</table>

\(^{a}\) IPCC, 2007

\(^{b}\) Based on IPCC A2 scenario

\(^{c}\) Based on IPCC temperature projections and predicted base-case average RH during the three modeled periods.
**Table 3.2: (continued)**

<table>
<thead>
<tr>
<th>Meteorological Parameter</th>
<th>Expected Change of Parameter</th>
<th>Process Affected</th>
<th>Predicted Sensitivity Mean (10%, 90%)</th>
<th>Expected Concentration Change (ng m$^{-3}$) Mean (10%, 90%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fall Period</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature</td>
<td>+1 - 5.5 K$^a$</td>
<td>BVOC emissions</td>
<td>20.3 ng m$^{-3}$ K$^{-1}$</td>
<td>20.3 to 112 (-7.7 to 286)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Aerosol partitioning</td>
<td>-88 ng m$^{-3}$ K$^{-1}$</td>
<td>-88 to -484 (-1570 to 13)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Reaction rates</td>
<td>47.1 ng m$^{-3}$ K$^{-1}$</td>
<td>47.1 to 259 (-0.6 to 633)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Overall</td>
<td>-33 ng m$^{-3}$ K$^{-1}$</td>
<td>-33 to -182 (-1156 to 468)</td>
</tr>
<tr>
<td></td>
<td>-10 to 10%$^b$</td>
<td>Overall (constant emissions)</td>
<td>-38.3 ng m$^{-3}$ %$^{-1}$</td>
<td>-383 to 383 (-1150 to 1150)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sea salt emissions</td>
<td>40 ng m$^{-3}$</td>
<td>-400 to 400 (-1230 to 1230)</td>
</tr>
<tr>
<td>Absolute humidity</td>
<td>+5 to 40%$^c$</td>
<td>Overall</td>
<td>11.5 ng m$^{-3}$ %$^{-1}$</td>
<td>58 to 460 (-840 to 2280)</td>
</tr>
<tr>
<td>Precipitation rate</td>
<td>-40 to +40%$^b$</td>
<td>Overall</td>
<td>-17.7 ng m$^{-3}$ %$^{-1}$</td>
<td>-708 to 708 (-1720 to 1720)</td>
</tr>
<tr>
<td>Precipitation area</td>
<td>-40 to +40%$^b$</td>
<td>Overall</td>
<td>-13.4 ng m$^{-3}$ %$^{-1}$</td>
<td>-536 to 536 (-1320 to 1320)</td>
</tr>
<tr>
<td>Mixing Height</td>
<td>-20 to +20%</td>
<td>Overall</td>
<td>-2.2 ng m$^{-3}$ %$^{-1}$</td>
<td>-44 to 44 (-130 to 130)</td>
</tr>
</tbody>
</table>

$^a$ IPCC, 2007  
$^b$ Based on IPCC A2 scenario  
$^c$ Based on IPCC temperature projections and predicted base-case average RH during the three modeled periods.
3.12 Conclusions

Climate affects air quality through a complex web of interactions starting with changes in the major meteorological variables like temperature, wind speed, absolute humidity, precipitation intensity, precipitation area, mixing height, etc. and progressing through changes in pollutant concentrations, formation and removal rates. In this study, we used a detailed three-dimensional CTM, PMCAMx-2008, to quantify the individual effects of the major meteorological parameters on the concentration and composition of PM$_{2.5}$ over Europe.

Precipitation is expected to have the largest impact on PM$_{2.5}$ concentrations under a changed future climate. In all periods, PM$_{2.5}$ shows a negative sensitivity to precipitation increases by 10%, driven mainly from the accelerated wet deposition of PM$_{2.5}$ species and their gas precursors (increases around 2-5% and 5-10% respectively). The average PM$_{2.5}$ sensitivity is quite similar during all seasons (an approximate decrease of 15 ng m$^{-3}$ %$^{-1}$) and taking also account the significant projected precipitation changes, PM$_{2.5}$ concentrations could potentially change by several μg m$^{-3}$ (up to 2 μg m$^{-3}$ in the fall) in a future climate.

Wind speed can also have appreciable effects on future PM$_{2.5}$ levels which are arising mainly from its effects on dispersion and transport, dry deposition and marine aerosol production. In all three periods, a decrease of wind speed by 10% (without any change on the emissions), affects the dispersion and dry deposition of PM$_{2.5}$ (decreases of 8% and 10% respectively) resulting in an average PM$_{2.5}$ increase of approximately 40 ng m$^{-3}$ %$^{-1}$. On the other hand, the reduced wind speed leads to less sea salt emissions and subsequently reduces PM$_{2.5}$ especially over water and in coastal areas (up to an average decrease of 52 ng m$^{-3}$ %$^{-1}$ in the winter). Thus, the projected
changes in wind speed over Europe in the future are expected to change PM$_{2.5}$ levels up to 1.4 μg m$^{-3}$.

Changes in absolute humidity influence mainly the inorganic PM$_{2.5}$ species, resulting in competing responses. An increase in absolute humidity by 5% favors the partitioning of nitrate to the aerosol phase and leads to higher particulate levels (up to 15%). During the fall period, this effect dominates the overall PM$_{2.5}$ response, and as absolute humidity is expected to rise in the future, could potentially lead to large increases of PM$_{2.5}$ (up to 2 μg m$^{-3}$). On the contrary, the increase in absolute humidity could lead to decreases in sulfate, and sea salt levels due to the increase in the size of the particles and the accelerated dry deposition (around 9-15%). These negative effects may, in some extent, offset the predicted increases in nitrate, thus during summer and winter the expected changes in future PM$_{2.5}$ due to absolute humidity are smaller.

Temperature is expected to have a lower impact on future PM$_{2.5}$ levels compared to the rest meteorological parameters due to the competing effects among the individual processes and the different responses of the PM$_{2.5}$ species. The evaporation of semi-volatile PM$_{2.5}$ species is found to be the dominant process and determines in a large extent the PM$_{2.5}$ response to temperature changes over Europe, during all seasons. Significant effects are predicted mainly on particulate ammonium nitrate, as the increase in temperature reduces its concentration levels up to 15% K$^{-1}$. Especially during fall, the predicted reduction of nitrate drives the overall PM$_{2.5}$ response, and as temperature is expected to rise in a future climate, could potentially lead to decreases in PM$_{2.5}$ levels up to 1.1 μg m$^{-3}$. However as temperature increases, leads to higher biogenic VOC emissions as well as accelerates the gas-phase chemical reactions,
which may cancel in some extent the expected reductions of PM$_{2.5}$, leading to even smaller changes in future PM$_{2.5}$ levels during the summer and winter period.

PM$_{2.5}$ concentrations generally decrease as mixing height increases. However the predicted effects are not as significant as the other parameters.

The main focus of this study has been the quantification of the effects that meteorology can have on PM$_{2.5}$ concentrations. The results show that average PM$_{2.5}$ levels can change by several µg m$^{-3}$ due to changes in various meteorological parameters, having also a strong spatial and temporal behavior. Therefore, the potential effects that meteorology under a future climate could have on particulate matter should be taken into account during long-term air quality strategies.
3.13 References


Hamburger, T., McMeeking, G., Minikin, A., Birmili, W., Dall’Osto, M., O’Dowd, C., Flentje, H., Henzing, B., Junninen, H., Kristensson, A., de Leeuw, G., Stohl,


3.14 Supplementary material

Figure 3.11: Predicted average change in ground-level concentrations (μg m\(^{-3}\)) of total PM\(_{2.5}\) due to a 10% increase in precipitation rate during the modeled (a) summer, (b) winter, and (c) fall periods. A positive value corresponds to an increase.
Figure 3.12: Predicted base case rainfall rate (mm month$^{-1}$) during the modeled (a) summer, (b) winter, and (c) fall periods.
Figure 3.13: Predicted average change in ground-level concentrations (μg m$^{-3}$) of total PM$_{2.5}$ due to a 10% increase in area undergoing precipitation during the modeled (a) summer, (b) winter, and (c) fall periods. A positive value corresponds to an increase.
Figure 3.14: Predicted average change in ground-level concentrations (μg m⁻³) of total PM₂.₅ due to an increase of mixing height by one model layer (approximately 150 m) during the modeled (a) summer, (b) winter, and (c) fall periods. A positive value corresponds to an increase.
Chapter 4

Effects of Climate Change on Air Quality in Greece
4.1 Abstract

The global-regional climate-air pollution modeling system, GRE-CAPS, was used to study the impact of climate change on the concentrations of PM$_{2.5}$ and ozone (O$_3$) over Europe, focusing on Greece. Summertime periods were simulated both for the present (2000s) and the future (2050s) assuming constant anthropogenic pollutant emissions. The future time period investigated was the 2050s, using the IPCC (Intergovernmental Panel on Climate Change) A1B scenario which describes a future world of rapid economic growth, rapid introduction of new and more efficient technologies and balance between fossil fuels and other energy sources. Climate change leads to a decrease of average PM$_{2.5}$ concentrations over Greece by 1.1 µg m$^{-3}$ (5%), however the predicted concentration changes are spatially variable and range from -20% to 20% depending on the area. PM$_{2.5}$ is predicted to decrease in Central Greece, by 1.2 µg m$^{-3}$ (5.5%) on average, due to the increase in wind speed and the lower absolute humidity, as well as in North Greece and the northern parts of the Aegean. On the contrary, in Crete and the Peloponnese, predicted increases in temperature and absolute humidity lead to higher future PM$_{2.5}$. Decreased precipitation and wind speed also contribute to the changes in these areas.

Ozone concentrations over Greece are increased in the future under A1B scenario by 4.5% on average. Highest changes are predicted in Central Greece (8% on average) while in most areas the predicted increases range between 2-3 ppb. The predicted changes in the daily peak O$_3$ concentrations (1-hr maximum and maximum 8-hr average) are higher. The higher future temperatures determine to a large extent the predicted O$_3$ response.
Over Europe, climate change significantly affects PM$_{2.5}$ levels, with changes range from -25% to 25%. Changes in several meteorological parameters such as precipitation, temperature, wind speed, and absolute humidity may drive the PM$_{2.5}$ response, having appreciable (and sometimes competing) effects on their concentration levels. Regarding ozone, the model predicts an increase on its concentration in the South Europe (up to 17%) and also in the Balkans, and a decrease in North Europe (up to 10%), with changes in temperature being the dominant factor.

4.2 Introduction

Atmospheric pollution is a serious problem for human health and global climate. Elevated concentrations of atmospheric particulate matter (PM), especially those with an aerodynamic diameter less than 2.5 μm (PM$_{2.5}$), are a major air quality concern as they are related with increased mortality as well as respiratory and cardiovascular diseases (Bernard et al., 2001; Pope et al., 2009; Wang et al., 2008). PM$_{2.5}$ plays also an important role in climate change, because of its ability to scatter and absorb light and to act as cloud condensation nuclei (CCN), thus modifying the planetary radiative balance (IPCC, 2007). In addition, PM$_{2.5}$ influences visibility (Seinfeld and Pandis, 2006), as well as the formation of acid rain and acid fogs (Burtraw et al., 2007).

Over the past few years, there has been a growing number of modeling studies focused on the links between PM$_{2.5}$ and O$_3$ concentrations with changes in meteorology. Some of these climate-air quality interaction studies, in particular, have tried to quantify how sensitive PM$_{2.5}$ and O$_3$ are to changes in individual meteorological parameters (Aksoyoglu et al., 2011; Dawson et al., 2007a, 2007b; Day and Pandis, 2011; Im et al., 2011, 2012; Lecoeur and Seigneur, 2013; Megaritis et al.,
2013a, 2013b; Tai et al., 2012). Their conclusions suggest that temperature has the largest impact on \( O_3 \), with absolute humidity and precipitation being also important. In addition, \( PM_{2.5} \) concentrations are also strongly influenced by meteorology, and are rather sensitive to changes in temperature, absolute humidity, precipitation intensity and frequency, wind speed as well as mixing height. However the dependence of \( PM_{2.5} \) on the various meteorological variables is quite complex depending on the area, season and \( PM_{2.5} \) composition (Dawson et al., 2007b; Megaritis et al., 2013b). Under a future climate, many of these meteorological parameters are expected to change and they could have significant effects on \( PM_{2.5} \) levels.

The effects of various climate change scenarios on regional air quality across Europe has been the topic of several recent modeling studies (Andersson and Engardt, 2010; Carvalho et al., 2011; Coleman et al., 2013; Colette et al., 2013; Forkel and Knoche, 2007; Hedegaard et al., 2008; Huszar et al., 2011; Juda-Rezler et al., 2012; Katragkou et al., 2011; Tainio et al., 2013). The majority of them focused on the effects of climate change on ozone and PM concentrations. Meleux et al. (2007) used a regional chemical transport model (CTM), CHIMERE, in order to examine the potential effects of climate change on summer ozone levels over Europe, under the IPCC A2 and B2 emissions scenarios. Their study showed a substantial increase of future ozone concentrations, mostly due to higher temperatures and reduced cloudiness and precipitation. Carvalho et al. (2010) used meteorology generated by a global circulation model (GCM), HadAM3P, and downscaled by a regional meteorological model (MM5), to simulate present-day and future climate in the CTM, CHIMERE. Their results showed that changes in climate alone could have a significant effect on future \( PM_{10} \) levels (changes up to 30 \( \mu g \) \( m^{-3} \)) and \( O_3 \) levels (increases up to 25 ppb in Central Europe, during summer). The predicted \( PM_{10} \) and
O₃ concentration changes showed a strong spatial and temporal dependence with increases mainly over continental regions and decreases over water. Manders et al. (2012) performed two long-term climate simulations, a present-day (1989-2009) and a future one (2041-2060), using the one-way coupled system RACMO2-LOTOS-EUROS with downscaled meteorology from two different GCMs, to study the impact of climate change on air quality over Europe, under the IPCC A1B scenario. They predicted a rather small impact of climate on mean PM₁₀ concentrations, with variable changes between different locations and seasons (up to 3 μg m⁻³). The predicted changes in PM₁₀ levels were mainly attributed to changes in temperature and to a lesser extent to changes in precipitation and wind speed. Jimenez-Guerrero et al. (2012) applied the regional modeling system MM5-CHIMERE with downscaled meteorology provided by a global GCM (ECHO-G), to simulate gaseous and aerosol pollutants over Europe in the present day and in 2071-2100 using the IPCC A2 scenario. They predicted appreciable effects on the future secondary organic and inorganic PM levels due to climate change, with increases of sulfate and secondary organic aerosol (SOA) and decreases of nitrate levels. The authors linked the changes in PM concentrations largely to changes in temperature and precipitation. Similar modeling systems have been used to examine the effects of global climate change on regional air quality, in other areas of the world. The majority of them have focused on the United States (Avise et al., 2009; Dawson et al., 2009; Higrefe et al., 2004; Lam et al., 2011; Liao et al., 2009; Mahmud et al., 2010; Tagaris et al., 2007; Zhang et al., 2008) and have shown a profound impact on air quality due to climate change; however the magnitude and spatial distribution of the predicted effects remain highly uncertain since the chosen scenarios as well as the predicted meteorological changes differ among the various studies.
Given that future PM and ozone levels are strongly affected by changes in climate, the Eastern Mediterranean region could be an area of special interest for two reasons: first the Eastern Mediterranean is quite sensitive to climate change (IPCC 2007); in particular it has been characterized as a “hot spot” area in future climate projections (Giorgi, 2006). In addition, from an air quality perspective, both ozone and PM levels often exceed air quality limits in this area, especially during summer (Kanakidou et al., 2011). However, to our knowledge, there has been little work conducted regarding the potential impacts that future climate may have on ozone and PM concentrations in the Eastern Mediterranean. Some of the few available studies either considered Eastern Mediterranean as part of the whole European continent (e.g., Hedegaard et al., 2013; Juda-Rezler et al., 2012; Langner et al., 2012; Manders et al., 2012), or focused their analysis mainly on areas in the Western Mediterranean (Carvalho et al., 2010; Jimenez-Guerrero et al., 2012). The primary goal of this study is to develop a state-of-the-science version of the pre-existing coupled global-regional modeling system, GRE-CAPS (Dawson et al., 2008), in order to examine the response of PM$_{2.5}$ and O$_3$ concentrations to future climate change, focusing on Greece. GRE-CAPS is well suited for this purpose as it combines previously evaluated models (e.g., PMCAMx-2008), while it has shown a good performance regarding its ability to capture present-day ozone and PM$_{2.5}$ concentrations compared to other coupled modeling systems (Dawson et al., 2008) as well as to CTMs used for standard retrospective modeling. GRE-CAPS has been also used in similar studies in the past, focusing on the United States (Dawson et al., 2009, Megaritis et al., 2013c). In addition, the regional CTM (PMCAMx-2008) used in this version of GRE-CAPS, includes state-of-the-art organic and inorganic aerosol modules which have not been used in earlier air quality-climate change studies.
The remainder of the chapter is organized as follows. In Section 4.3, a brief description of GRE-CAPS along with the details of its application over the area of interest is given. Section 4.4 provides information regarding PMCAMx-2008 (used as the regional CTM in GRE-CAPS) and its performance during a traditional retrospective simulation during a summer period. The GRE-CAPS predictions for present-day meteorology, PM$_{2.5}$ and O$_3$ concentrations as well as their comparison with measurements are discussed in Section 4.5. In the next section, the GRE-CAPS projections for future climate as well as the spatial characteristics of the effect of future climate change on the concentration of the individual PM$_{2.5}$ species and O$_3$ are discussed. Finally the major conclusions are presented in Section 4.7.

4.3 The GRE-CAPS Modeling System

4.3.1 Model description

The GRE-CAPS modeling system consists of three models spanning the global to the regional scale: a global CTM with online chemistry, GISS II’ GCM (Racherla and Adams, 2006), the regional meteorological model, WRF (Skamarock et al., 2005), and the regional CTM, PMCAMx-2008 (Fountoukis et al., 2011; Megaritis et al., 2013a). A detailed description of the GRE-CAPS system is provided by Dawson et al. (2008).

The GISS II’ GCM was used to generate the global-scale meteorology and global pollutant concentration fields for both the present-day and 2050s conditions. The future global climate was based on the IPCC (2000) A1B emission scenario for the 2050s. The A1B scenario describes a future world of rapid economic growth, global population that peaks in mid-century and declines thereafter, and the rapid
introduction of new and more efficient technologies. In addition, there is a balance between fossil fuels and other energy sources. The GCM has a horizontal resolution of 4° latitude by 5° longitude with nine vertical layers. It was run using global-anthropogenic emissions which correspond to present day and climate sensitive biogenic emissions. Both the present and future climate predictions in the GCM were driven by ocean boundary conditions as described by Racherla and Adams (2006). Previous studies (e.g., Cess et al., 1990) have shown that GISS II’ GCM is at the higher end of GCM-predicted climate sensitivities.

The global-scale meteorology generated by GISS II’ was downscaled to the regional scale using the WRF meteorological model (Skamarock et al., 2005). Meteorological conditions from the GISS II’ predictions for the outer edge of the European modeling domain were used as boundary conditions for the WRF simulations. WRF was run using a 36-km resolution grid over the European domain. The WRF runs were periodically reinitialized, every 3 days using the GISS II’ predictions, to ensure consistency with the global field in the corresponding meteorological fields that are used as inputs from the regional CTM.

The regional CTM used in GRE-CAPS is PMCAMx-2008 (Fountoukis et al., 2011; Megaritis et al., 2013a). PMCAMx-2008 uses the framework of the CAMx air quality model (Environ, 2003) describing the processes of emissions, horizontal and vertical advection, horizontal and vertical dispersion, wet and dry deposition and gas-phase chemistry. The SAPRC99 mechanism (Carter, 2000; Environ, 2003), including 211 reactions of 56 gas-phase and 18 radical species is used for gas-phase chemistry simulations. For the aerosol processes, PMCAMx-2008 uses three detailed modules: inorganic aerosol growth (Gaydos et al., 2003; Koo et al., 2003), aqueous phase chemistry (Fahey and Pandis, 2001) and SOA formation and growth (Murphy and
Pandis, 2009). These modules employ a sectional approach using ten aerosol size sections, spanning the diameter range from 40 nm to 40 μm. For the simulation of inorganic aerosol formation the “bulk equilibrium approach” was assumed. For the organic aerosol (OA) treatment, PMCAMx-2008 uses a state-of-the-art module based on the volatility basis set (VBS) framework (Donahue et al., 2006; Stanier et al., 2008). Primary OA in PMCAMx-2008 is assumed to be semivolatile (Shrivastava et al., 2008) while this version treats all organic species (primary and secondary) as chemically reactive. More details about the simulation of inorganic and organic aerosol species in PMCAMx-2008 can be found in Fountoukis et al. (2011).

Dry deposition, for the gas-phase species, is simulated based on the resistance-in-series scheme of Wesely (1989), while for aerosol species the model uses the resistance approach of Slinn and Slinn (1980) as implemented in UAM-AERO (Kumar et al., 1996). For the simulation of wet deposition PMCAMx-2008 assumes that the scavenging rate within or below a precipitating cloud is equal to the product of the concentration of a pollutant and the respective scavenging coefficient (Seinfeld and Pandis, 2006). Further information is given in Megaritis et al. (2013a).

4.3.2 Model application

In our simulations, PMCAMx-2008 is used with a two-way nested grid structure which allows the model to run with coarse grid (spacing over a wide regional domain) and a fine grid (nest in a specific area of interest). PMCAMx-2008 was set to run with coarse grid spacing (36×36 km) over the wide European domain, covering a 5400×5832 km region. A fine grid nest was applied over Greece with a higher resolution (9×9 km) covering an area of 1008×900 km (Fig. 4.1).
The necessary inputs to the model included meteorology, emissions, land use data and initial and boundary conditions of the simulated PM species. The meteorological inputs included hourly data of temperature, pressure, water vapor, clouds, rainfall, horizontal wind components and vertical diffusivities, all taken from the downscaled meteorology using WRF. The model interpolates all the meteorological data from the parent (Europe) to the nested grid (Greece). Anthropogenic gas emissions included land emissions from the GEMS dataset (Visschedijk et al., 2007) as well as international shipping emissions. Anthropogenic particulate organic and elemental carbon emissions were based on the EUCAARI Pan-European Carbonaceous Aerosol Inventory (Kulmala et al., 2011). Three different datasets are combined in order to produce biogenic gridded emissions for the model. Emissions from ecosystems were produced by MEGAN (Model of Emissions of Gases and Aerosols from Nature) model (Guenther et al., 2006). Sea salt emissions were estimated using the marine aerosol model developed by O’Dowd et al. (2008). Emissions from wildfires were also included (Sofiev et al., 2009). For the Greek nested domain, high resolution emissions are used. The boundary conditions were chosen on the basis of measurements taken in sites close to the boundaries (e.g., Seinfeld and Pandis, 2006; Zhang et al., 2007). For the concentrations of the major PM species at the boundaries of the domain, we used the same values as Fountoukis et al. (2011).
Figure 4.1: The two modeling domains used in our simulations. Also shown, the location of the four regions used for the investigation of the spatial dependence of the PM$_{2.5}$ and O$_3$ responses to climate change in Greece: I = North Greece, II = Central Greece, III = Peloponnese, IV = Crete.

In our simulations, a set of two, one-month long, summer periods were used. The future climate period studied was based on the IPCC A1B scenario for the 2050s (IPCC, 2007). In order to examine only the climate change effects on PM$_{2.5}$ concentrations, the anthropogenic emissions were kept constant at present-day levels. Emissions from wildfires were based on historical data during July 2008 and were also kept constant as there is not any available data for the future. On the contrary, climate sensitive biogenic and sea salt emissions were used for present-day and future climate simulations. In addition, in order to separate the effects from global scale transport, the same chemical boundary conditions were used during the future (2050s) simulations as in the present-day simulations. The nested model domain (Greece) was
divided in four sub-regions (North Greece, Central Greece, Peloponnese, and Crete) to quantify how pollutant concentrations respond to climate change in different areas. The locations of the four regions are shown in Figure 4.1.

**4.4 Evaluation of PMCAMx-2008**

Before its application as part of GRE-CAPS, PMCAMx-2008 was configured to simulate air quality over Europe with a fine grid nest over Greece, during a typical summer period (June-July 2012). An intensive field campaign took place during that period in various locations in the Eastern Mediterranean (including Greece, Italy), and also in Europe, as part of the Pan-European Gas Aerosols Climate Interactions project (PEGASOS, 2011). The predicted average ground-level concentrations of total PM$_{2.5}$ over Europe and Greece in particular, during this summer period are presented in Figure 4.2. Over Europe, the model predicts an average PM$_{2.5}$ concentration of 8.2 μg m$^{-3}$. Sulfate is predicted to account for 33% of total PM$_{2.5}$ at ground level averaged over the entire European domain, followed by OA (31%), ammonium (12%), nitrate (5%) and finally EC (4%). The remaining 15% is crustal material, sea-salt and metal oxides. Elevated PM$_{2.5}$ concentrations are predicted mainly over the Mediterranean region (up to 40 μg m$^{-3}$ in the eastern coast of Spain) (Fig. 4.2a), as a result of significant sulfate and OA levels (up to 10 μg m$^{-3}$ and 12 μg m$^{-3}$ respectively) due to significant emissions sources (e.g., wildfires) and the strong photochemical activity in this area which favors the formation of sulfate and OA aerosols. High ammonium nitrate levels are predicted mainly over Western Europe (maximum concentration of 6 μg m$^{-3}$), while in the rest of the domain are generally low (do not exceed 2.5 μg m$^{-3}$). In Central and Northern Europe fine organic matter dominates with biogenic
secondary OA and oxidized primary OA (including OA from IVOCs) contributing the most (approximately 50% and 33% respectively).

Figure 4.2: Average predicted ground-level concentrations of total PM$_{2.5}$ ($\mu$g m$^{-3}$) over (a) Europe and (b) Greece, during the PEGASOS summer (June-July) 2012 campaign.

Over Greece, the predicted average ground-level concentration of total PM$_{2.5}$ is 16.4 $\mu$g m$^{-3}$. Sulfate and organics are predicted to be the major components contributing approximately 40% and 30% of total PM$_{2.5}$ mass respectively. The highest predicted PM$_{2.5}$ concentrations are over Central Greece (up to 25 $\mu$g m$^{-3}$ close to Athens) (Fig. 4.2b), where sulfate and OA show the highest levels, 7 and 8 $\mu$m$^{-3}$ respectively. Average PM$_{2.5}$ concentrations are predicted to range from 13.4 $\mu$g m$^{-3}$ (Peloponnese) to 17.5 $\mu$g m$^{-3}$ (Crete). Ammonium nitrate levels are quite low in most areas and do not exceed 3 $\mu$g m$^{-3}$, while sea-salt levels are predicted to be significant over the Aegean Sea (up to 5 $\mu$g m$^{-3}$). Overall, ammonium nitrate accounts for 14% of total PM$_{2.5}$ while the respective contribution of fine sea salt is 12%.
PMCAMx-2008 predictions can be compared against high time aerosol mass spectrometer (AMS) measurements taken at four ground-level sites in Eastern Mediterranean, two located in Greece (Patras, Finokalia) and two in Italy (Bologna, San Pietro Capofiume). The model predictions show a reasonable agreement with the AMS measurements. In the four stations, the model predicted average concentrations for PM$_1$ OA, sulfate, ammonium, and nitrate were 4.6, 4.1, 1.6 and 0.6 $\mu$g m$^{-3}$ respectively, while the corresponding measured average values were relatively close to the predictions, 4.5, 3.2, 1.1 and 0.6 $\mu$g m$^{-3}$. PMCAMx-2008 had the best performance for PM$_1$ organic aerosol, reproducing more than 60% of the hourly averaged data within a factor of 2, showing a normalized mean bias (NMB) of less than 0.1% and a normalized mean error (NME) of 55%. In Bologna, 80% of the hourly measured PM$_1$ OA and 85% of the observed daily averaged data were reproduced by the model within a factor of 2. PMCAMx does also a good job for sulfate, reproducing 52% of the measured data within a factor of 2. Especially in Patras, the model reproduced 78% of the PM$_1$ sulfate measurements within a factor of 2. The normalized mean error (NME) for PM$_1$ sulfate concentration was 60% and the corresponding mean error and fractional error, 1.8 $\mu$g m$^{-3}$ and 0.55 respectively. The model predictions for ammonium and nitrate were subject to significant scatter. For PM$_1$ ammonium, the model showed a normalized mean bias (NMB) of 69%, and a mean absolute gross error (MAGE) and fractional error of 0.83 $\mu$g m$^{-3}$ and 0.6 respectively. For PM$_1$ nitrate, the model showed a small NMB (2%), and a mean absolute gross error (MAGE) of 0.58 $\mu$g m$^{-3}$. The prediction skill metrics of PMCAMx-2008 against AMS hourly ground measurements during the PEGASOS summer campaign are summarized in Table 4.1.
Table 4.1: Prediction skill metrics of PMCAMx-2008 against AMS hourly ground measurements during the PEGASOS summer campaign*.

<table>
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<th>PM$_1$</th>
<th>Mean Observed (μg m$^{-3}$)</th>
<th>Mean Predicted (μg m$^{-3}$)</th>
<th>MB$^a$ (μg m$^{-3}$)</th>
<th>MAGE (μg m$^{-3}$)</th>
<th>FBIAS</th>
<th>FERROR</th>
<th>Percent within a factor of 2</th>
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<td>-0.9</td>
<td>1.3</td>
<td>23</td>
</tr>
<tr>
<td>Ammonium</td>
<td>1.1</td>
<td>1.6</td>
<td>0.6</td>
<td>0.8</td>
<td>0.6</td>
<td>0.6</td>
<td>42</td>
</tr>
</tbody>
</table>


$$MB = \frac{1}{n} \sum_{i=1}^{n} (P_i - O_i)$$

$$MAGE = \frac{1}{n} \sum_{i=1}^{n} |P_i - O_i|$$

$$FBIAS = \frac{2}{n} \sum_{i=1}^{n} \frac{(P_i - O_i)}{(P_i + O_i)}$$

$$FERROR = \frac{2}{n} \sum_{i=1}^{n} \frac{|P_i - O_i|}{(P_i + O_i)}$$
Figure 4.3: Comparison of predicted vs. observed PM$_1$ organic aerosol (OA) and sulfate concentrations (μg m$^{-3}$) from the 4 measurement sites during the PEGASOS summer 2012 campaign. Each point corresponds to a 1-h average value. Also shown the 1:1, 2:1 and 1:2 lines. Observed data represents AMS measurements.
4.5 Present-day Simulations

4.5.1 Meteorology

The present-day meteorology generated by downscaling the GCM predictions, shows higher temperatures over the southern parts of Europe compared to the rest of the domain, with an average temperature of 26.3 °C and 24.5 °C predicted over the Balkans and South Europe respectively. Over Greece, the predicted average temperature is 25.9 °C, having a small spatial variability ranging from 25.4 °C in Peloponnese to 26.8 °C in North Greece. This spatial trend for temperature predicted by GRE-CAPS is in agreement with earlier modeling studies which use downscaled meteorology from GCMs (Raisanen et al., 2004; Carvalho et al., 2010; Nikulin et al., 2011, Menut et al., 2012). The GRE-CAPS temperature predictions were compared with observed data from 20 different areas located in Greece (e.g., Athens, Heraklion, Larissa) and Europe as well (e.g., Paris, Milan, Madrid, Helsinki). The observed data were taken from the European Climate Assessment and Dataset (ECA&D) and covered a 2-year period (2007-2008). The comparison showed that temperature predicted by GRE-CAPS agrees reasonably well with the observations. On average, the GRE-CAPS predicted temperature in the measurement sites is 23.6 ± 3.6 °C, compared to an observed value of 24.9 ± 4.4 °C. We conclude that the downscaled meteorology used by GRE-CAPS is realistic and quite representative of the temperature spatial patterns over Europe.

The model-predicted amounts of precipitation show a much higher spatial variability compared to temperature. GRE-CAPS predicts high precipitation rates mainly over the ocean and also in Western and Central Europe (average precipitation exceeds 18 mm month^-1 in these areas), while significant amounts of precipitation are also predicted in some areas in Northern Europe (up to 15 mm month^-1). In the
Balkans the predicted precipitation rate is quite lower and does not exceed 4 mm month$^{-1}$. The predicted monthly total precipitation is quite close to the measurements, with a tendency towards overprediction, having also a higher variability. Based on measurements taken from the observed stations used for temperature comparison, the measured monthly total precipitation is $65.5 \pm 48.9$, while GRE-CAPS predicts an average monthly total precipitation of $89.5 \pm 67.3$ mm. This overprediction of the precipitation rates was also found in earlier modeling studies which use WRF to downscale the predicted meteorology from GCMs (Menut et al., 2012).

4.5.2 PM$_{2.5}$ and O$_3$ concentrations

The GRE-CAPS predictions for total PM$_{2.5}$ concentrations over Greece, for present climate conditions are shown in Figure 4.4. On a domain-average basis, the predicted concentration of PM$_{2.5}$ is approximately $23.5$ μg m$^{-3}$, with sulfate and OA being the dominant components contributing approximately 35% and 40%. Ammonium nitrate has low levels in most of Greece (up to 3 μg m$^{-3}$ in Peloponnese), sea salt is significant mainly over the sea, while EC is predicted to be highest over urban areas (e.g., up to 6 μg m$^{-3}$ in Athens) and also in areas with significant emissions sources (e.g., wildfires in Rhodes). The model predicts an average PM$_{2.5}$ concentration of 24 μg m$^{-3}$ in Central Greece, with a maximum concentration of 42 μg m$^{-3}$ in Athens due mainly to high OA levels in this area (approximately 55% of total PM$_{2.5}$). In Peloponnese, the elevated sulfate levels (7.6 μg m$^{-3}$ on average), along with the high secondary OA and oxidized primary OA levels (4.5 μg m$^{-3}$ and 6.5 μg m$^{-3}$ respectively) result in an average PM$_{2.5}$ concentration of approximately 24.5 μg m$^{-3}$. In Crete, the average predicted PM$_{2.5}$ levels are quite close to those in Central Greece (23.3 μg m$^{-3}$), while in North Greece are somewhat lower (21.5 μg m$^{-3}$ on average).
The model predicts also significant PM$_{2.5}$ concentrations in Rhodes, which reach a maximum of $45 \, \mu g \, m^{-3}$ due to significant emissions from wildfires.

![Figure 4.4: Average predicted ground-level concentrations of total PM$_{2.5}$ ($\mu g \, m^{-3}$) in Greece under present-day summer climate conditions.](image)

The ability of GRE-CAPS to reproduce the measured PM$_{2.5}$ concentrations has been analyzed, comparing the model predictions against filter measurements taken throughout Greece (e.g., Athens, Thessaloniki, Patra, Penteli, ICEHT, and Finokalia) and also in Italy (Bologna, San Pietro), during the PEGASOS summer campaign. The comparison was based on monthly average data and the measurement sites were chosen to represent both urban and rural areas. The results showed that there is reasonable agreement between GRE-CAPS average predictions and measurements. In general, the GRE-CAPS predicted PM$_{2.5}$ levels are a little higher compared to the measurements, with more variability (in all sites the GRE-CAPS predicted average PM$_{2.5}$ concentration is $19.7 \pm 4.9 \, \mu g \, m^{-3}$ compared to a measured average of $17.1 \pm 2.9 \, \mu g \, m^{-3}$). These concentrations are also quite close to the PMCAMx-2008
predictions from the standard retrospective episode modeling (June-July 2012) discussed in the previous section. In all sites, the predicted PM$_{2.5}$ from the PMCAMx-2008 retrospective simulation was 16.3 ± 2.4 μg m$^{-3}$ compared to 19.7 ± 4.9 μg m$^{-3}$ here.

The present-day averaged concentrations of ozone in Greece, predicted by GRECAPS are shown in Figure 4.5. Over Greece, on a domain-average basis, the predicted concentration of O$_3$ is approximately 52.5 ppb. The highest concentrations are predicted mainly in the southern parts of the domain with Peloponnese and Crete showing an average concentration of 58 and 55 ppb respectively. The predicted O$_3$ levels in Central Greece are quite close to those in the South (53 ppb on average), while in North Greece are somewhat lower (48 ppb on average). In addition, the GRE-CAPS predictions for O$_3$ agree reasonably well with observations from 10 sites in Greece (EEA, 2013), during a 5-year period (2008-2012). In particular, the GRE-CAPS predicted O$_3$ concentration is 47.1 ± 4.9 ppb compared to a measured average of 39.6 ± 9.6 ppb.

**Figure 4.5:** Average predicted ground-level concentrations of O$_3$ (ppb) in Greece under present-day summer climate conditions.
Over Europe, high PM$_{2.5}$ concentrations are predicted mainly over Ukraine and Russia, where PM$_{2.5}$ reaches up to a maximum concentration of 55 µg m$^{-3}$, mainly due to high OA, and sulfate levels in this area (up to 19 µg m$^{-3}$ and 11.5 µg m$^{-3}$ respectively) (Fig. 4.6a). Elevated PM$_{2.5}$ concentrations are also predicted in South Europe (up to 53 µg m$^{-3}$ in Sicily), while in the rest of Europe, the predicted PM$_{2.5}$ levels do not exceed 25 µg m$^{-3}$. On a domain-average basis the predicted PM$_{2.5}$ concentrations is approximately 11.5 µg m$^{-3}$. For O$_3$, elevated concentrations are predicted mainly in South Europe (55 ppb on average) as well as in some areas in Central Europe, while in northern areas the predicted O$_3$ concentrations are lower (35 ppb on average) (Fig. 4.6b).

**Figure 4.6:** Average predicted ground-level concentrations of (a) PM$_{2.5}$ (µg m$^{-3}$) and (b) O$_3$ (ppb) over Europe under present-day summer climate conditions.
4.6 Future Climate

4.6.1 Meteorology projections

The GRE-CAPS projections for the future climate period show an increase in temperature over Greece, by 0.35 °C on a domain-average basis. Central Greece, Peloponnese and North Greece are predicted to experience the highest increase, approximately 0.5 °C, while in Crete the temperature increase is lower (around 0.3 °C). These spatial patterns for the future temperature in Greece were also found in earlier modeling studies for the same scenario (e.g., Tolika et al., 2012). The future temperature projections over Europe (an average increase of 0.5 °C) are consistent with the predictions of other models suggesting that temperature changes will be small during the 2050s (mostly below 1 °C) and more pronounced by the end of the century (Kjellström et al., 2010; Katragkou et al., 2011; Langner et al., 2012).

Significant changes are also predicted for precipitation in the future climate. Over Greece, precipitation is predicted to decrease by 12% on average, in agreement with previous studies which generally estimate a drier future climate in Greece (Kjellström et al., 2010; Langner et al., 2012; Tolika et al., 2012). However, the predicted precipitation changes show strong variability. Over Central Greece, Peloponnese, and Crete, precipitation is significantly reduced (up to 58% in Crete), while North Greece has an opposite trend with an average increase of 34%. Increases of precipitation are also predicted in the northern Aegean (up to 80% in some areas). Over Europe, the predicted future precipitation shows significant spatial variability with changes ranging from -28% (South Europe) to 20% (Central Europe). The predicted regional changes in several meteorological variables over the different regions in Greece, between the present and future are shown in Table 4.2.
Table 4.2: Regional changes (future – present) in model-predicted meteorological parameters in Greece.

<table>
<thead>
<tr>
<th>Meteorological Parameter</th>
<th>North Greece</th>
<th>Central Greece</th>
<th>Peloponnese</th>
<th>Crete</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>+0.45 K</td>
<td>+0.48 K</td>
<td>+0.5 K</td>
<td>+0.33 K</td>
</tr>
<tr>
<td>Precipitation</td>
<td>+34%</td>
<td>-37%</td>
<td>-55%</td>
<td>-58%</td>
</tr>
<tr>
<td>Wind Speed</td>
<td>-2%</td>
<td>+7%</td>
<td>-4%</td>
<td>+2%</td>
</tr>
<tr>
<td>Absolute Humidity</td>
<td>+1%</td>
<td>-2%</td>
<td>+1%</td>
<td>+5%</td>
</tr>
</tbody>
</table>

4.6.2 Effect on PM$_{2.5}$ and O$_3$ concentrations

The predicted concentration changes in average PM$_{2.5}$ over Greece due to climate change (under the A1B scenario) are shown in Figure 4.7. On a domain-average basis, future PM$_{2.5}$ is predicted to decrease in Greece by 1.1 μg m$^{-3}$ (5%), however the predicted changes vary significantly in space. In Central Greece, average PM$_{2.5}$ is predicted to decrease by 1.2 μg m$^{-3}$ (5.5%). Despite the increases in OA levels in the western part of Central Greece (as a result of higher temperatures), the increase in wind speed (7% on average) as well as the lower absolute humidity dominate the overall response of PM$_{2.5}$ leading to lower concentrations in the future. Average PM$_{2.5}$ decreases also in North Greece by 1 μg m$^{-3}$ (5%) while over the northern parts of the Aegean the predicted reduction of PM$_{2.5}$ may reach up to 6 μg m$^{-3}$ (16%). On the contrary, in Peloponnese and Crete, PM$_{2.5}$ concentrations are predicted to increase. In Crete, PM$_{2.5}$ increases by approximately 0.2 μg m$^{-3}$ (1%) on average, mainly due to increases in nitrate. The higher predicted absolute humidity in this area (5%) favors the partitioning of nitrate to the aerosol phase leading to increase of its concentration.
by 0.15 μg m$^{-3}$ or 18% on average. The predicted increase in nitrate along with an increase in OA (0.1 μg m$^{-3}$), attributed mainly to higher biogenic SOA (65% of the total OA increase) explain the overall PM$_{2.5}$ response. PM$_{2.5}$ also increases in Peloponnese by 0.7 μg m$^{-3}$ (3%) on average. The higher biogenic VOC emissions as a result of temperature rise along with the corresponding effects on oxidant levels are the dominant factors in this region leading to increases in OA levels (0.6 μg m$^{-3}$ or 5% on average). In addition, decreases of wet deposition, due to precipitation, and wind speed (mainly in the western parts) also contribute to the changes. The predicted average reduction of PM$_{2.5}$ levels in Greece under a future climate is consistent with the results from earlier modeling studies which also use the A1B scenario for the future global-regional climate projections (e.g., Hedegaard et al., 2013; Juda-Rezler et al., 2012; Manders et al., 2012). Table 4.3 summarizes the predicted changes in average ground-level concentrations of the major PM$_{2.5}$ components due to climate change.

![Figure 4.7: Predicted changes (future - present climate) in ground-level concentrations of total PM$_{2.5}$ (μg m$^{-3}$) in Greece under A1B scenario. A positive value corresponds to an increase.](image)
Table 4.3: Regional changes (future - present) in average ground-level concentrations (μg m⁻³) of the major PM₂.₅ components in Greece.

<table>
<thead>
<tr>
<th>PM₂.₅ Component</th>
<th>North Greece</th>
<th>Central Greece</th>
<th>Peloponnesse</th>
<th>Crete</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>A1B</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ammonium</td>
<td>-0.15 (-6.5%)</td>
<td>-0.35 (-12%)</td>
<td>+0.03 (+1.1%)</td>
<td>+0.01 (+0.4%)</td>
</tr>
<tr>
<td>Sulfate</td>
<td>-0.4 (-6%)</td>
<td>-0.7 (-9%)</td>
<td>-0.1 (-1.5%)</td>
<td>-0.2 (-3%)</td>
</tr>
<tr>
<td>Nitrate</td>
<td>-0.03 (-13%)</td>
<td>-0.15 (-24%)</td>
<td>+0.03 (+7%)</td>
<td>+0.15 (+18%)</td>
</tr>
<tr>
<td>OA</td>
<td>-0.4 (-4%)</td>
<td>+0.1 (+1%)</td>
<td>+0.6 (+5.5%)</td>
<td>+0.1 (+1%)</td>
</tr>
<tr>
<td>Total PM₂.₅</td>
<td>-1 (-5%)</td>
<td>-1.2 (-5.5%)</td>
<td>+0.7 (+3%)</td>
<td>+0.2 (+1%)</td>
</tr>
</tbody>
</table>

The model predicts also a significant change on O₃ concentrations in Greece. O₃ levels are predicted to be higher in a future climate under the A1B scenario, with an average predicted increase of 2.5 ppb (4.5%) over Greece (Fig. 4.8). The highest increase in O₃ is predicted in Central Greece (approximately 4 ppb, or 8%), while the predicted increases in the other regions are quite similar and range between 2-3 ppb. In Athens, higher O₃ levels of approximately 3 ppb (8%) are predicted for the future, while in other major urban areas (e.g., Thessaloniki, Patras) the predicted changes are similar (average increases of 7-8%). Significant changes are also predicted for the daily 1-hr maximum O₃ concentrations. The predicted increases on the daily 1-hr maximum O₃ levels are somewhat higher than the average O₃ increases, approximately 3 ppb (5.5%) on a Greece-average basis and up to 8 ppb (10%) in Central Greece areas, showing although similar spatial patterns (see Fig. 4.9 in the supplementary material section). Similar results we obtain also for the daily maximum
8-hr average (MDA8) O₃, which increases by 2.6 ppb (6%) on average over Greece (Fig. 4.10, supplementary). The rise of future temperature is the main factor that determines the predicted O₃ response. In addition, changes in wind speed in several areas also contribute to the overall O₃ change. These results are consistent with earlier studies (Juda-Rezler et al., 2012; Langner et al., 2012; Manders et al., 2012; Hedegaard et al., 2013) which have found a substantial increase of O₃ over Greece which ranges from 2-5 ppb.

![Figure 4.8](image)

**Figure 4.8:** Predicted changes (future - present climate) in ground-level concentrations of O₃ (ppb) in Greece under A1B scenario. A positive value corresponds to an increase.

Over Europe, climate change has also a significant impact on PM₂.₅, although the predicted concentration changes are quite variable in space. Changes in several meteorological parameters, especially precipitation, wind speed, temperature and absolute humidity have appreciable and sometimes competing effects on PM₂.₅ concentrations. Significant increases are predicted in Ukraine (reaching up to a
maximum of 11 \( \mu g \ m^{-3} \) or 22\%\) and in the Balkans (up to 8 \( \mu g \ m^{-3} \) or 25\%) driven largely by lower precipitation (30\% on average) and higher temperature (Fig. 4.11a). In Central and North Europe, PM\(_{2.5}\) is predicted to decrease in the future by 1 \( \mu g \ m^{-3} \) (7\%) and 0.6 \( \mu g \ m^{-3} \) (5.5\%). The predicted changes in average \( O_3 \) concentrations are higher in most areas in the south (up to 9 ppb or 15\% in Italy), while in North and Central Europe, average \( O_3 \) is predicted to decrease in the future by 2.5\% on average (Fig. 4.11b). The results for the daily peak \( O_3 \) concentrations show a similar spatial trend compared to the average \( O_3 \) changes, although the absolute values are higher. The daily 1-hr maximum \( O_3 \) is predicted to increase in the South (up to 14 ppb or 17\% in Italy), while the highest decreases are predicted in North Europe (up to 8 ppb or 16\%). The predicted changes for the MDA8 \( O_3 \) concentrations are quite similar and range from -15\% (North Europe) to 15\% (South Europe). The above results agree with the findings of Juda-Rezler et al. (2012) and Langner et al. (2012), although the predicted \( O_3 \) changes in Central Europe are in contrast to the results of Manders et al. (2012) (in their study \( O_3 \) will increase in Central Europe) as they predicted larger increases in temperature (approximately 2 \(^\circ\)C compared to 0.8 \(^\circ\)C in our study) and decreases in wind speed (in our study wind speed increases in Central Europe by 10\% on average).

### 4.7 Conclusions

The global-regional climate-air pollution modeling system, GRE-CAPS, was used in order to investigate the effects of climate change on the concentrations of PM\(_{2.5}\) and ozone in Greece (as well as over the broader area of Europe) under the IPCC A1B scenario. The modeling system uses a global GCM/CTM (GISS II’) to generate meteorology and simulate intercontinental chemical transport. Meteorology
was downscaled using a regional meteorological model (WRF), and air quality was simulated using a regional CTM (PMCAMx-2008). The GRE-CAPS system was able to reproduce the measured PM$_{2.5}$ and ozone concentrations for the present-day climate rather well.

Our results suggest that regional climate change will generally decrease PM$_{2.5}$ levels in Greece by 1.1 µg m$^{-3}$ (5%) on average. However the predicted changes are quite variable in space and range from -20% to 20% depending on the area. The highest PM$_{2.5}$ decrease is predicted in Central Greece, 1.2 µg m$^{-3}$ (5.5%) on average and up to 5 µg m$^{-3}$ (Athens), due to the increase in wind speed and the lower absolute humidity which dominate the overall PM$_{2.5}$ change, offsetting the predicted increases of OA (due to higher temperature). Decreases of PM$_{2.5}$ levels are also predicted in North Greece (5% on average) as well as over the northern parts of the Aegean (up to 15%). On the contrary, future PM$_{2.5}$ levels are higher in Peloponnese and Crete. Average PM$_{2.5}$ is predicted to increase by 3% in Peloponnese and 1% in Crete respectively due mainly to increases in OA and nitrate levels. The higher future temperatures (and the accompanying effects on biogenic VOC emissions and oxidant levels) as well as the increases in absolute humidity are the dominant factors, while decreases of wet deposition, due to precipitation, and wind speed also contribute to the changes.

Ozone concentrations are also predicted to change in a future climate. Higher levels of O$_3$ are predicted in the future over Greece. On average, O$_3$ will increase by 2.5 ppb (4.5%), with Central Greece experiencing the highest changes (8% on average). Significant increases are also predicted in the major urban areas (e.g., Athens), approximately 7-8%. The predicted changes on the daily peak O$_3$ concentrations (1-hr maximum and maximum 8-hr average) are even larger (up to 8
ppb or 10%) showing a similar spatial trend. The higher temperature in the future appears to be the governing factor that determines the O\textsubscript{3} response, while the wind speed in several areas also contributes.

Over Europe, the model predicts variable responses of PM\textsubscript{2.5} concentrations to climate change. The predicted changes range from -25% to 25%, with decreases in North and Central Europe and increases in the Balkans, indicating that changes in several meteorological parameters, especially precipitation, temperature, wind speed, and absolute humidity may have appreciable (and sometimes competing) effects on PM\textsubscript{2.5} concentrations in several areas. Regarding O\textsubscript{3}, the results show a general trend to increase in the future in the South Europe (up to 17%) and also in the Balkans, and to decrease in North Europe, with changes in temperature being the dominant factors.

The above results indicate a significant and variable pattern of changes for future PM\textsubscript{2.5} and ozone concentrations in Greece as well as over Europe. As the various PM\textsubscript{2.5} species respond differently to meteorological changes in the future, the magnitude of the predicted change in each of the meteorological variables (e.g., temperature, precipitation, wind speed, absolute humidity), its spatial characteristics, as well as the PM\textsubscript{2.5} composition in each area, will determine which of those parameters dominate the overall PM\textsubscript{2.5} response. However the future projections for regional-scale changes in meteorology as predicted by climate models indicate that there is not the same degree of robustness, among the variables, and changes in precipitation are still characterized by a relatively high level of uncertainty. The predicted changes in the pollutant concentrations should be, therefore, viewed as trend indicators and interpreted with care.
4.8 References


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the AWMA Specialty Conference on Computing in Environmental Resource Management, Research Triangle Park, NC, 2–4 December, 1996.


4.9 Supplementary material

**Figure 4.9:** Average predicted ground-level daily 1-hr maximum $O_3$ concentrations (ppb) in Greece (a) and (b) predicted concentration changes (future - present climate) due to climate change under A1B scenario (a positive value corresponds to an increase).

**Figure 4.10:** Average predicted ground-level MDA8 $O_3$ concentrations (ppb) in Greece (a) and (b) predicted concentration changes (future - present climate) due to climate change under A1B scenario (a positive value corresponds to an increase).
Figure 4.11: Predicted changes (future - present climate) in ground-level concentrations of (a) total PM$_{2.5}$ (μg m$^{-3}$) and (b) O$_3$ (ppb) over Europe, under A1B scenario. A positive value corresponds to an increase.
Chapter 5

Impact of Climate Change on Mercury Concentrations and Deposition in the Eastern United States

This work has been under review in Science of the Total Environment, as:

5.1 Abstract

The global-regional climate-air pollution modeling system (GRE-CAPS) was applied over the eastern United States to study the impact of climate change on the concentration and deposition of atmospheric mercury. Summer and winter periods (300 days for each) were simulated, and the present-day model predictions (2000s) were compared to the future ones (2050s) assuming constant emissions. The future time period investigated was the 2050s, using the IPCC A2 scenario which describes a very heterogeneous world, with continuously increasing population, self-reliance and preservation of local identities. Climate change affects Hg$^{2+}$ concentrations in both periods. On average, atmospheric Hg$^{2+}$ levels are predicted to increase in the future by 3% in the summer and 5% in winter respectively due to accelerated formation and slower removal. However, the predicted concentration change of Hg$^{2+}$ was found to vary significantly in space due to regional-scale changes in precipitation, ranging from -30% to 30% during summer and -20% to 40% during winter. Particulate mercury, Hg(p) has a similar spatial response to climate change as Hg$^{2+}$, while Hg$^0$ levels are not predicted to change significantly. In both periods, the response of mercury deposition to climate change varies spatially with an average predicted increase of 6% during summer and 4% during winter. During summer, deposition increases are predicted mostly in the western parts of the domain while mercury deposition is predicted to decrease in the Northeast and also in many areas in the Midwest and Southeast. During winter mercury deposition is predicted to change from -30% to 50% mainly due to the changes in rainfall and the corresponding changes in wet deposition.
5.2 Introduction

Mercury (Hg) can accumulate in the food chain in the form of methylmercury, a neurotoxin to living organisms and human beings (Satoh, 2000). Significant amounts of mercury have been found in fish even in remote water bodies (Stephens, 1995), indicating the importance of long-range transport of mercury to locations far from its emission sources. Most of the mercury in the atmosphere (>95%) is in the gas phase (Baya and Van Heyst, 2010) as elemental mercury (Hg\textsubscript{0}). Smaller amounts are present in the +2 oxidation state referred to as gaseous oxidized mercury (Hg\textsuperscript{2+}). Another important form of mercury in the atmosphere is particulate mercury (Hg(p)). Particulate mercury is either emitted directly from anthropogenic sources (Schroeder and Munthe, 1998) or produced from Hg\textsubscript{0} or Hg\textsuperscript{2+} adsorbed onto particulate matter (PM) (Schroeder and Munthe, 1998; Seigneur et al., 2004a). Elemental mercury is the predominant species because it has a long atmospheric lifetime (0.5-2 yr) (Lindberg et al., 2007) due to its low solubility in water and low chemical reactivity. It is vertically well mixed in the troposphere and can be transported over long distances. On the other hand, Hg\textsuperscript{2+} is highly water soluble, reactive and less volatile than Hg\textsubscript{0}, having a much shorter atmospheric lifetime and is rapidly removed via wet and dry deposition. Particulate mercury, Hg(p), is mostly present in fine particulate matter (PM\textsubscript{2.5}), although some Hg(p) may be present in coarse PM (Landis and Keeler, 2002). Similar to Hg\textsuperscript{2+}, Hg(p) has a relatively short atmospheric lifetime and deposits closer to emission sources by wet and dry deposition.

Numerous modeling studies have been conducted to understand the transport, chemistry and deposition of atmospheric mercury at regional (Baker and Bash, 2012; Bash et al., 2010; Bullock and Brehme, 2002; Bullock et al., 2009, 2008; Cohen et al.,
Xu et al. (2000a) applied a three-dimensional chemical transport model (CTM) over an area of the northeastern United States, for a summer and a winter week to study the atmospheric transport and transformation of mercury. Their model predictions were evaluated against measurements from eight monitoring stations in Connecticut and the model was able to capture the spatial variation of total gaseous mercury (TGM, $\text{Hg}^0 + \text{Hg}^{2+}$) concentrations. $\text{Hg}(p)$ levels were overpredicted suggesting an overestimation of $\text{Hg}(p)$ emissions from point sources or an underestimation of dry deposition. Vijayaraghavan et al. (2008) applied a plume-in-grid model to selected power plants in the continental United States. Their results showed an improved model performance with the inclusion of the advanced plume treatment, in comparison with mercury wet deposition data from the MDN sites, especially in Pennsylvania. A recent study in the same area was performed by Holloway et al. (2012) who employed a three-dimensional CTM to examine how local emissions, meteorology, atmospheric chemistry, and deposition affect mercury concentration and deposition over the Great Lakes region. Their model underpredicted $\text{Hg}^0$ by 6% at a rural site and 36% at an urban site in Wisconsin and overpredicted reactive mercury ($\text{RHg} = \text{Hg}^{2+} + \text{Hg}(p)$) concentrations with annual average biases >250%. In addition, the modelled Hg wet deposition agreed reasonably
well against measurements from the Mercury Deposition Network (MDN) sites (National Atmospheric Deposition Program, 2003) in this region, with an underprediction of 21% on an annual basis.

Seigneur et al. (2004a) used a multiscale modeling system consisting of a global chemical transport model (CTM) and a nested continental CTM to simulate the global atmospheric fate and transport of mercury and its deposition over United States. Their model reproduced observed TGM concentrations within 0.1 ng m$^{-3}$ in the eastern US but there were overpredictions in the midwest and northwest. In addition, they estimated that North American anthropogenic sources contribute only 25 to 32% to the total mercury deposition over the continental US. Selin et al. (2007) used a global CTM to interpret worldwide observations of TGM. The mean annual TGM concentration observed at 22 land-based sites ($1.58 \pm 0.19$ ng m$^{-3}$) was reproduced by their model with little mean bias ($1.63 \pm 0.10$ ng m$^{-3}$), while the model accounted for 51% of the spatial variance in the measurements. In addition, the model reproduced the magnitude of annual wet deposition over the US within 10%.

These modeling studies have greatly advanced our understanding on the behaviour of mercury in the atmosphere; however the simulation of the fate, transport and deposition of mercury remains a challenging issue. A fundamental limitation of current models is the uncertainty in the atmospheric chemistry of mercury (Ariya et al., 2009, 2008; Lin et al., 2006; Subir et al., 2011). In many modeling studies, the gas-phase oxidation of Hg$^0$ by OH and ozone has been assumed to be the major pathway for Hg$^{2+}$ formation (Bergan and Rodhe, 2001; Cohen et al., 2004; Holloway et al., 2012; Seigneur et al., 2006). Aqueous-phase reduction of Hg$^{2+}$ to Hg$^0$, mainly via reaction with hydroperoxyl radicals (HO$_2$), competes with deposition as a sink for Hg$^{2+}$ (Holloway et al., 2012; Lin et al., 2006; Seigneur et al., 2006, 2004a; Selin et al.,
2007). However, recent studies suggest that these gas-phase oxidation reactions may not be the dominant pathways (Calver and Lindberg, 2005; Goodsite et al., 2004; Hynes et al., 2009), while the aqueous-phase reduction of \( \text{Hg}^{2+} \) to \( \text{Hg}^{0} \) remains uncertain with no accepted kinetics or mechanism (Ariya et al., 2009; Gardfeldt and Johnson, 2003; Goodsite et al., 2004; Hynes et al., 2009). Several studies have focused on the role of bromine in the atmospheric mercury cycle. Holmes et al. (2010, 2006) has demonstrated that gas-phase Br atoms might be an important oxidant of \( \text{Hg}^{0} \) on a global scale. Their conclusions are supported from several pieces of evidence (Goodiste et al., 2004; Holmes et al., 2009; Sinnhuber et al., 2005; Steffen et al., 2008). A large range of kinetics has been reported in the literature for the reaction of \( \text{Hg}^{0} \) with bromine (Ariya et al., 2008; Hynes et al., 2009), while several models have included this oxidation pathway of \( \text{Hg}^{0} \) in their chemistry modules (Dastoor et al., 2008; Seigneur and Lohman, 2008; Zhang et al., 2012b).

The emission rates of mercury from anthropogenic sources are continuously revised and improved (Pacyna et al., 2010, 2006; Seigneur et al., 2004a). Nevertheless, significant uncertainties still remain in these estimates, regarding the emission speciation of mercury, the lack or inaccuracy in reported emission data and stack measurements of Hg (Lin et al., 2006). Emissions of mercury from natural sources, have been overlooked or estimated as a certain fraction of the deposited mercury in previous modeling studies (Bergan and Rodhe, 2001; Bullock and Brehme, 2002; Seigneur et al., 2004a). In order to reduce this uncertainty, there have been several modeling efforts estimating mercury emissions from various natural sources (vegetation, soil, water surfaces, etc.) (Bash et al., 2004; Gbor et al., 2007; Lin et al., 2005), indicating that natural mercury emissions can be comparable to those from anthropogenic sources, especially during warm months.
Mercury deposition processes and their simulation are additional sources of uncertainty. For example, the dry deposition velocity of Hg\(^0\) is often neglected (Bergan and Rodhe, 2001; Bullock and Brehme, 2002), assigned a very small rate (Lee et al., 2001), or calculated using a detailed treatment on the air-surface exchange of Hg\(^0\) (Lin and Tao, 2003). Uncertainties in the atmospheric chemistry of mercury, the emission rates and the mercury deposition processes have been the focus of a number of review studies (Ariya et al., 2009, 2008; Lin et al., 2007, 2006; Pongprueksa et al., 2008; Subir et al., 2011) aiming to improve models simulating atmospheric mercury.

The impact of climate change on mercury concentration and deposition has received relatively little attention. Despite the fact that there have been several studies of how climate change may influence regional and global air quality (Avise et al., 2009; Chen et al., 2009; Dawson et al., 2009, 2007; Forkel and Knoche, 2006; Giorgi and Meleux, 2007; Heald et al., 2008; Hogrefe et al., 2004; Jacob and Winner, 2009; Jiang et al., 2010; Kunkel et al., 2008; Lam et al., 2011; Leung and Gustafson, 2005; Liao et al., 2006; Mahmud et al., 2010; Meleux et al., 2007; Mickley et al., 2004; Murazaki and Hess, 2006; Nolte et al., 2008; Prather et al., 2003; Pye et al., 2009; Racherla and Adams, 2009, 2008, 2006; Steiner et al., 2006; Tagaris et al., 2009, 2008, 2007; Tsigaridis and Kanakidou, 2007; Wu et al., 2008; Zeng et al., 2008; Zhang et al., 2008), the majority of them focused on the effects of climate change on ozone and particulate matter (PM) concentrations.

In this study, we use a coupled modelling system, GRE-CAPS, to study the spatial and seasonal response of mercury concentration and deposition, to future climate change, with a focus on the eastern United States. GRE-CAPS is well suited for this purpose since it has been used in similar studies in the past (Dawson et al.,
2008) and reproduced present ozone and PM as well as CTMs driven by assimilated meteorology, for PM and ozone concentrations.

The remainder of this chapter is organized as follows. First, there is a brief description of GRE-CAPS and the details of its application in the eastern United States domain. In the next section, the temporal and spatial characteristics of the effect of future climate change on the concentration of the individual mercury species are discussed. The impact of climate change on mercury deposition is analyzed in the next section. A discussion of how uncertain parameters and processes could impact mercury concentration and deposition predicted by the model along with the results from a number of sensitivity simulations are also presented.

5.3 The GRE-CAPS Modeling System

5.3.1 Model description

The GRE-CAPS modeling system, described in detail by Dawson et al. (2008), consists of three models spanning the global to the regional scale: the GISS II’ GCM global CTM with online chemistry (Racherla and Adams, 2006), the MM5 regional meteorological model (Grell et al., 1995), and the PMCAMx regional CTM (Gaydos et al., 2007; Karydis et al., 2007) which was extended in order to simulate atmospheric mercury.

Climate and chemical concentration fields were generated for the present-day and 2050s conditions at the global scale by GISS II’ GCM. The future global meteorology was based on the IPCC (2007) A2 scenario for the 2050s. The A2 scenario describes a very heterogeneous world. The underlying theme is self-reliance and preservation of local identities. Fertility patterns across regions converge very slowly, which results
in continuously increasing population. Economic development is primarily regionally oriented and per capita economic growth and technological change more fragmented and slower than other storylines. The GCM was run using present-day anthropogenic emissions and climate sensitive biogenic emissions. Both the present and future climate predictions in the GCM were driven by ocean boundary conditions as described by Racherla and Adams (2006). The meteorology generated by GISS II’ was downscaled by providing boundary conditions, updated every 4 h, to the regional scale using the MM5 meteorological model (Grell et al., 1995). Meteorological conditions on the outer edge of the entire US modeling domain were used as boundary conditions for the MM5 simulations. MM5 simulations used a 108-km resolution grid over the entire USA and a 36-km resolution nested grid over the Eastern USA. The regional CTM used in GRE-CAPS is PMCAMx. The development and evaluation of the PMCAMx model has been described by Gaydos et al. (2007) and Karydis et al. (2007). PMCAMx uses the framework of CAMx (Environ, 2003), which models the processes of emissions, horizontal and vertical advection, horizontal and vertical dispersion, wet and dry deposition, and gas phase chemistry. In addition, 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 secondary organic aerosol formation and growth (Koo et al., 2003). In order to study the effect of climate change on mercury concentration and deposition, PMCAMx was modified to treat atmospheric mercury processes. These modifications are described in the next section.
5.3.2 Mercury module in PMCAMx

The mercury chemistry module implemented in PMCAMx is an extension of the module developed and evaluated by Seigneur et al. (2004b, 2001). Three mercury species are simulated: elemental gaseous mercury (Hg$^0$), gaseous oxidized mercury (Hg$^{2+}$) and primary particulate mercury (Hg(p)). The mercury transformation processes include the gas-phase oxidation of Hg$^0$ to Hg$^{2+}$, the aqueous phase oxidation of Hg$^0$ to Hg$^{2+}$, the aqueous-phase reduction of Hg$^{2+}$ to Hg$^0$, various aqueous phase equilibria of Hg$^{2+}$ and the adsorption of Hg$^{2+}$ on PM. Oxidation reactions of Hg$^0$ by Br and BrO have been added to the original module. The gas-phase oxidation of Hg$^0$ by atomic bromine is simulated based on the mechanism of Goodsite et al. (2004). The unstable product, HgBr, may either dissociate or react with Br or OH to form Hg$^{2+}$. The kinetic coefficients used in this mechanism were taken from Donohoue et al. (2006), Goodsite et al. (2004), and Balabanov et al. (2005). These coefficients are at the low end of the published range (Ariya et al., 2008). For the oxidation of Hg$^0$ by BrO, a wide range of reaction rates have been reported (Raofie and Ariya, 2004) and here we use the lower limit of the reported values. Other, gas-phase transformations in the mercury chemistry module include the oxidation of Hg$^0$ to Hg$^{2+}$ by hydroxyl radical (OH) (Sommar et al., 2001), ozone (O$_3$) (Hall, 1995), HCl (Hall and Bloom, 1993), hydrogen peroxide (H$_2$O$_2$), (Tokos et al., 1998) and molecular chlorine (Cl$_2$) (Ariya et al., 2002). The aqueous-phase chemistry includes the oxidation of Hg$^0$ to Hg$^{2+}$ by dissolved OH (Lin and Pehkonen, 1997), O$_3$ (Munthe, 1992) and Cl$_2$ (Lin and Pehkonen, 1998) as well as the reduction of Hg$^{2+}$ to Hg$^0$ via reaction with hydroperoxyl radicals (HO$_2$) (Pehkonen and Lin, 1998) and by the formation of the sulfite complexes, HgSO$_3$ and Hg(SO$_3$)$_2$$^{2-}$ (van Loon et al., 2000).
Adsorption of Hg\(^{2+}\) species on atmospheric particulate matter (PM) is simulated, using an adsorption coefficient \(K = 34 \text{ L g}^{-1}\) recommended by Seigneur et al. (1998).

The concentrations of most of the species reacting with mercury are available from PMCAMx. However Br, BrO and Cl\(_2\) are not explicitly simulated and vertical profiles for their concentrations are specified. For Br and BrO, vertical profiles over land and ocean are prescribed, with higher values over ocean than over land. For Br vertical concentrations, during daytime, constant values of 0.03 ppt over the ocean and \(5 \times 10^{-3}\) ppt over the land are assumed for every height (Environ, 2013). The respective values for daytime BrO vertical concentrations are 0.3 ppt over the ocean and 0.05 ppt over land. During nighttime Br and BrO concentrations are assumed to be zero (Holmes et al., 2010). The Cl\(_2\) concentrations are prescribed to be non-zero over the ocean and zero elsewhere. Its vertical concentrations during daytime are approximately two orders of magnitude lower (~\(10^{-6}\) ppm) than nighttime values to account for the photolysis of Cl\(_2\) during the day. The aqueous concentrations of OH and HO\(_2\) are calculated from the gas-phase concentrations using their temperature-dependent Henry’s law constants (Jacobson, 1999). However, since there is not an explicit treatment for the cloud chemistry of OH and HO\(_2\) radicals and due to the fact that the concentrations of these radicals can be reduced by their heterogeneous chemistry within clouds (Jacob, 2000; Jaegle et al., 2001), in the PMCAMx implementation the gas-phase concentrations of OH and HO\(_2\) within clouds are reduced by factors of 2 and 10 respectively.

PMCAMx simulates both dry and wet deposition for mercury. Dry deposition is simulated using the resistance model of Wesely (1989) while the change in concentration within or below a cloud due to precipitation is parameterized using a scavenging coefficient. For Hg\(^0\), its dry deposition is simulated by assuming a
Henry’s law constant equal to 0.1 M atm\(^{-1}\) at 298 K. The sensitivity of the model predictions to the parameterization of the Hg\(^0\) deposition is discussed in Section 5.5. The Henry’s Law constant of Hg\(^{2+}\) is assumed to be similar to that of HNO\(_3\) (Environ, 2003). No temperature dependence is assumed for the Hg\(^{2+}\) Henry’s law constant (Environ, 2003). Additionally, the reactivity parameter of Hg\(^{2+}\) is set to unity so that surface resistance will be calculated based on the Henry’s Law constant using Wesely’s module.

5.3.3 Modeling domain and inputs

PMCAMx was applied over the eastern United States covering a 3492 × 3240 km region with 36 × 36 km grid resolution and 14 vertical layers (Fig. 5.1). The necessary meteorological inputs to the model include horizontal wind components, vertical diffusivities, temperature, pressure, water vapor, clouds and rainfall, all taken from the downscaled meteorology using MM5. The chemical mechanism used in the gas-phase chemistry is based on the CB-IV mechanism (Gery et al., 1989), modified to include Hg\(^0\) and Hg\(^{2+}\). The version of CB-IV used here includes 100 reactions of 36 gas (including Hg\(^0\) and Hg\(^{2+}\)) and 12 radical species. Hourly anthropogenic emission gridded fields for mercury were prepared, based on the CAMR inventory for 2001 (US EPA, 2005). Three different representative days were used: an average weekday, Saturday, and Sunday, while the same emission data were used for the summer and winter simulations. The sensitivity of the model predictions to the emissions from natural sources is discussed in a subsequent section. For the non-mercury species, the emission inventory was the Midwest Regional Planning Organization’s Base E inventory (Lake Michigan Air Directors Consortium, 2003), including BIOME3 biogenics (Wilkinson and Janssen, 2001). All emissions for non-mercury species were
for July 2001 and January 2002. Boundary conditions for mercury were based on those used by Yarwood et al. (2003). The sensitivity of the model predictions on those boundary conditions is discussed also in Section 5.5. For non-mercury species, boundary conditions were chosen on the basis of measurements taken in sites close to the boundaries of the model domain by the IMPROVE and STN monitoring networks (Karydis et al., 2007).

**Figure 5.1:** The eastern United States modeling domain. The five regions used for the analysis of the model predictions are also shown.

The ability of PMCAMx to reproduce the measured PM$_{2.5}$ levels in the region has been analyzed by Karydis et al. (2007), who compared the model predictions against daily average PM$_{2.5}$ measurements taken throughout the eastern United States by the IMPROVE and STN monitoring networks and the EPA Supersites programme. During summertime (July 2001), PMCAMx showed little bias for the concentration of
most PM$_{2.5}$ species (fractional bias for sulfate and ammonium was -0.04 and 0.15 respectively). The only exception was nitrate whose small levels were significantly underpredicted by the model. For the total PM$_{2.5}$ levels, PMCAMx reproduced 67% of the measured daily average concentrations with an error of less than 50%, showing a fractional bias of -0.18. During winter (January 2002) nitrate was slightly underpredicted (fractional bias of -0.06) while it had little bias (0.03 μg m$^{-3}$) for ammonium and overpredicted the concentration of organic PM by 0.71 μg m$^{-3}$. For the total PM$_{2.5}$ levels, the model predictions were within 50% of the measurements for 51% of the data points, showing a tendency to overpredict their levels (fractional bias of 0.51).

In addition, we compared the summertime (July 2001) and wintertime (January 2002) model predictions for mercury wet deposition against measurements from 50 sites of the Mercury Deposition Network (MDN). During summer the model predicted average total wet deposition of mercury was 938 ± 681 ng m$^{-2}$ compared to 1003 ± 797 ng m$^{-2}$ from the observations. The mean bias was -65.3 ng m$^{-2}$ while the corresponding normalized mean bias (NMB) and fractional bias (FBIAS) were -6.5% and -0.07 respectively. The model predictions for mercury wet deposition had a normalized mean error of 36%, mean error = 368 ng m$^{-2}$, fractional error of 0.45, and an R$^2$ value at 0.52.

In the winter period, the monthly total predicted mercury wet deposition was 323 ± 319 ng m$^{-2}$ compared to a measured value of 289 ± 253 ng m$^{-2}$. The normalized mean bias (NMB) for mercury wet deposition was 12% and the corresponding mean bias and fractional bias, 33.8 ng m$^{-2}$ and -0.38 respectively. During winter the model had a mean error of 142 ng m$^{-2}$, and larger normalized mean error and fractional error

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compared to summertime (49% and 0.85 respectively). In addition, the $R^2$ value for the winter comparison was 0.59.

PMCAMx show similar or better skill in reproducing mercury wet deposition as previous modeling studies (Baker and Bash, 2012; Bash et al., 2010; Bullock et al., 2009; Holloway et al., 2012; Lin et al., 2007; Vijayaraghavan et al., 2008; Zhang et al., 2012b). Some of the prior modelling studies, covering different seasons and simulation periods, have shown low biases for modelled mercury wet deposition, e.g., 3.4% in Zhang et al. (2012b) (based on annual data), 2% (Vijayaraghavan et al., 2008, during summer 2001), although there are severe modeling studies in which modelled mercury wet deposition has been found to be biased high, e.g., 26-32% (summer) and 70% (winter) in Holloway et al. (2012), 60% (summer) in Bash et al. (2010) (69% during July). The bias that we have found for mercury wet deposition in our study, is towards the low end of the reported values in the literature. In addition, our seasonal values of $R^2$ (0.52 during July, 0.59 during January) compare well with those reported from earlier modelling studies (Bash et al., 2010; Bullock et al., 2009; Gbor et al., 2007; Holloway et al., 2012; Lin et al., 2007; Vijayaraghavan et al., 2008; Zhang et al., 2012b).

Predicted Hg$^{2+}$ dry deposition velocities are within the range of experimental data: PMCAMx lower and upper quartile estimates are 0.6 and 2.8 cm s$^{-1}$ compared to the measured range 0.5 to 6 cm s$^{-1}$. The predicted terrestrial Hg$^0$ dry deposition velocities appear to be lower by a factor of 2-10 compared to the limited available experimental data (0.1-0.4 cm s$^{-1}$) (Zhang et al., 2009). The sensitivity of the model predictions to the dry deposition rates will be investigated in a subsequent section.

For mercury surface concentrations, on a domain-average basis, the mean monthly Hg$^0$ concentration predicted by the model was $1.35 \pm 0.1$ ng m$^{-3}$ during
summer and 1.43 ± 0.05 ng m⁻³ during winter respectively. The Hg⁰ spatial distribution pattern was similar to the spatial distribution of anthropogenic Hg emissions used by the model. Highest Hg⁰ concentrations were predicted mostly over the Midwest (1.8 - 1.9 ng m⁻³) and Northeast (1.6 - 1.7 ng m⁻³) where a large number of power plants and waste incinerators are located, as well as in areas with significant emissions sources of Hg⁰ (e.g., Texas, Florida). For Hg²⁺ and Hg(p), the predicted concentrations displayed a stronger spatial variability compared to Hg⁰, due to their much shorter lifetimes. On a domain-average basis, the mean monthly predicted Hg²⁺ concentration was 18.6 ± 10.6 pg m⁻³ during summer and 13.2 ± 9.8 pg m⁻³ during winter respectively. Following the anthropogenic emission pattern, Hg²⁺ levels were enhanced over the Midwest and Northeast areas (over 40 pg m⁻³ during summer). For Hg(p), its mean monthly predicted concentration was 8.6 ± 5.1 pg m⁻³ during summer and 12.2 ± 6.9 pg m⁻³ during winter with the highest concentrations predicted in areas close to emissions sources (up to 30 pg m⁻³ during July and 40 pg m⁻³ during January).

These predicted values for mercury species concentrations lie within the range of earlier modeling studies in the same region (Baker and Bash, 2012; Bash et al., 2010; Gbor et al., 2007; Holloway et al., 2012; Lin et al., 2012, 2007; Gbor et al., 2007; Selin et al., 2007; Vijayaraghavan et al., 2008; Zhang et al., 2012b). Several of these studies have compared their model predictions against available measurement data from various sites over US and Canada (AMNet, 2009; CAMNet, 2011). In general, for Hg⁰ concentrations, the models tend to show less variability than the measurements, e.g., Lin et al. (2012) have predicted a mean concentration of 1.53 ± 0.1 ng m⁻³ compared to 1.56 ± 0.3 ng m⁻³ from the observations. In our simulations the Hg⁰ concentration in the measurement sites considered by Lin et al. (2012) shows also a low variability (the mean Hg⁰ concentration is 1.39 ± 0.1 ng m⁻³); however a
direct comparison against the observed data is not possible due to the different simulation periods. Hg^{2+} levels are often overpredicted by the models; e.g., Zhang et al. (2012b) predicted an average value of 15 ± 9.2 pg m^{-3} compared to the measured value of 6.2 ± 4.1 pg m^{-3}. However, there are major uncertainties associated with at least some of the corresponding reactive gaseous mercury (RGM) measurements (Aspmo et al., 2005; Lyman et al., 2010). The PMCAMx results for Hg^{2+}, in spite of the different simulation periods, have the same spatial distribution as those of Zhang et al. (2012) with a mean concentration of 16.5 ± 7.7 pg m^{-3}. Our model seems to overpredict Hg(p) concentrations in the measurement sites considered by Zhang et al. (2012) (obs.: 7.8 ± 4.2 pg m^{-3}, PMCAMx: 13 ± 5.9 pg m^{-3}, Zhang’s model: 8.8 ± 6.7 pg m^{-3}).

5.4 Results and discussion

In our simulations, we used a set of three hundred winter and three hundred summer days, which are distributed in 10 one-month periods, and the present-day model predictions (2000s) were compared to model predictions for future winter and summer. In order to examine only the climate change effects on mercury concentration and deposition, all emissions were kept constant at present-day levels. Same chemical boundary conditions (representing long-distance transport) were used during the future (2050s) simulations as in the present-day simulations, thus separating the effects from global scale transport. The model domain was divided in five sub-regions (Plains, Midwest, Northeast, TX/OK, and Southeast) to help us identify how the mercury concentration and deposition respond to climate change in different areas. The locations of the five regions are shown in Figure 5.1.
5.4.1 Meteorology

The present-day meteorology generated by downscaling the GCM predictions, showed a significant spatial variability for temperature among the areas of the model domain. During summer, temperature was found to be high in the Southern areas, with an average predicted value of 21.1 °C in TX/OK and 23.2 °C in the Southeast, while in the rest of the domain the predicted average present-day temperature was lower ranging from 16.4 °C (Plains) to 17.3 °C (Northeast). The same spatial variability was also found during wintertime. In comparison with observational data from the National Climate Data Center, the temperature predictions showed a cold bias that was stronger in the summer than in the winter. These findings are consistent with those of Dawson et al. (2008), who compared the average GRE-CAPS predicted temperature for five present-day summer and winter months against observed data for a 5-year period (2001-2005) in four US cities (Kansas City, Atlanta, Boston and Pittsburgh), resulting in a mean bias of -1.0 °C in winter temperatures and -2.7 °C in during the summer.

The model-predicted amounts of precipitation were also spatially variable in both periods. In agreement with Dawson et al. (2008), the mean predicted total precipitation was underestimated in all four cities considered in that study during winter, while in the summer, total precipitation was underestimated in Atlanta and Kansas City and overestimated in Pittsburgh and Boston. From our results the mean bias across the four locations was -51% in winter and +5.5% in summer while in Dawson’s study the corresponding values were -41% and +13% respectively.

The future climate period was based on the Intergovernmental Panel on Climate Change (IPCC, 2007) A2 scenario for the 2050s (Racherla and Adams, 2006). On a domain average basis, temperature is predicted to increase by 1.6 K and 2.1 K during
summer and winter respectively. These temperature changes lie within the range of predicted temperature changes from other modeling studies (Hogrefe et al., 2004; Murazaki and Hess, 2006; Racherla and Adams, 2006). In addition, the model predicts an increase of absolute humidity, while wind speed decreases in most of the model domain, during both periods. These changes are largely consistent with those predicted by Mickley et al. (2004) and Murazaki and Hess (2006) who suggest that the frequency of future air pollution episodes in the northeastern United States will increase due to reduced cyclone frequency in a future warmer climate. Significant changes are also predicted for rainfall which increases by 7% on average during summer, and 15% during winter. The predicted changes of precipitation show a strong spatial variability, with several areas having an opposite trend than the domain-wide averages.

5.4.2 Present-day Simulations

The predicted average concentrations for Hg\(^0\), Hg\(^{2+}\) and Hg(p) for the present climate summer and winter are shown in Figure 5.2. Hg\(^0\) concentration is predicted to be lower during summer compared to winter due to the enhanced temperature and oxidant levels which favor the oxidation of Hg\(^0\) to Hg\(^{2+}\). On a domain average basis, Hg\(^0\) concentration is 1.34 ng m\(^{-3}\) during summer and 1.41 ng m\(^{-3}\) during winter (Fig 5.2a, b), while in both periods, elevated Hg\(^0\) concentrations are predicted in areas close to emissions sources. The GRE-CAPS predictions for Hg\(^0\) concentration are relatively close to those of PMCAMx when used for standard retrospective episode modeling (see Section 5.3.3), (predicted Hg\(^0\) from the GRE-CAPS simulation was 1.34 ± 0.06 ng m\(^{-3}\) during summer and 1.41 ± 0.05 ng m\(^{-3}\) during winter, compared to the PMCAMx predicted values of 1.35 ± 0.1 ng m\(^{-3}\) during summer and 1.43 ± 0.05
ng m\textsuperscript{-3} in the winter). The same seasonal trend and the low variability of predicted Hg\textsuperscript{0} levels, has been also reported by other modeling studies (Holloway et al., 2012; Zhang et al., 2012b).

For Hg\textsuperscript{2+}, the increased oxidant levels during summer result in higher concentrations than winter (Fig. 5.2c, d). Hg\textsuperscript{2+} concentrations are predicted to be higher in urban areas (up to 60 pg m\textsuperscript{-3}) mainly due to the presence of local emissions sources, while in rural areas the predicted enhanced Hg\textsuperscript{2+} is attributed to transport and local chemical production. Significant levels of Hg\textsuperscript{2+}, during summer, are also predicted in Texas (32 pg m\textsuperscript{-3} on average) mainly due to the low wet deposition rate in this area and the accompanying high concentration of oxidant levels. During winter, the average predicted concentration of Hg\textsuperscript{2+} does not exceed 30 pg m\textsuperscript{-3} in the entire domain, with quite similar spatial trends as summer. On a domain average basis, the mean monthly predicted Hg\textsuperscript{2+} concentration is 21.7 ± 10.8 pg m\textsuperscript{-3} during summer and 9.8 ± 5.7 pg m\textsuperscript{-3} during winter respectively, close to PMCAMx predictions for July 2001 and January 2002, and consistent with other modeling studies (e.g., Baker and Bash, 2012; Holloway et al., 2012, Zhang et al., 2012b).

Hg(p) concentrations predicted by GRE-CAPS have a similar seasonal and spatial pattern as those predicted by PMCAMx when used for standard retrospective episode simulation. During summer, the mean monthly predicted Hg(p) concentration is 10.1 ± 4.5 pg m\textsuperscript{-3}, and in the winter 10.9 ± 4.9 pg m\textsuperscript{-3}, quite close to those from the PMCAMx simulations (summer and winter).
Figure 5.2: Average predicted ground-level concentrations of (a-b) Hg$^0$ (ng m$^{-3}$), (c-d) Hg$^{2+}$ (pg m$^{-3}$) and (e-f) Hg(p) (pg m$^{-3}$) from three hundred present summer and winter days respectively. Different concentration scales are used for each graph.
The model predictions for mercury wet deposition show a strong spatial variability (Fig. 5.3). During summer, mercury wet deposition is predicted to be higher compared to wintertime, due largely to the higher predicted concentrations for Hg\(^{2+}\) and Hg(p), while its spatial trend is strongly affected by the predicted rainfall rate. In comparison with observed data from 50 MDN sites across US (same as those used for the comparison of PMCAMx standard retrospective episode simulation), during a 5-year period (2001-2005), the monthly total mercury wet deposition predicted by GRE-CAPS agrees reasonably well with the observations, during both seasons. During summer, the GRE-CAPS predicted average total wet deposition of mercury is 1030 ± 532 ng m\(^{-2}\) compared to a measured average of 1383 ± 765 ng m\(^{-2}\). The corresponding normalized mean bias (NMB) and fractional bias (FBIAS) are higher compared to the PMCAMx simulation (-25\% and -0.24 respectively), while the GRE-CAPS predictions are also subject to significant scatter (normalized mean error, NME = 42\%, mean error = 584 ng m\(^{-2}\), fractional error, FERROR = 0.49).

![Figure 5.3](image.png)

**Figure 5.3:** Predicted Hg wet deposition (ng m\(^{-2}\) yr\(^{-1}\)) under present climate conditions during (a) summer and (b) winter.
In the winter, the monthly total mercury wet deposition predicted by the model is $245 \pm 195 \text{ ng m}^{-2}$ compared to a measured value of $311 \pm 205 \text{ ng m}^{-2}$. In contrast to PMCAMx simulations for January 2002, GRE-CAPS tends to undepredict mercury wet deposition by 21% having a fractional bias of -0.43. In addition, the model shows a mean error of 148 ng m$^{-2}$, and larger NME and FERROR compared to summertime (48% and 0.7 respectively).

5.4.3 Effect of Future Climate Change on Elemental Mercury ($\text{Hg}^0$)

The predicted changes in average ground-level concentrations of $\text{Hg}^0$ for the future climate are shown in Figure 5.4. During summer, climate change does not seem to have a significant effect on $\text{Hg}^0$ concentrations. A slight decrease of $\text{Hg}^0$ levels (up to 0.07 ng m$^{-3}$ or 4%) is predicted in most areas of the model domain. On a domain average basis the reduction of $\text{Hg}^0$ is approximately 0.03 ng m$^{-3}$ (0.7%). This small change of $\text{Hg}^0$ concentrations is mainly attributed to the increase of oxidant levels in most of the model domain, due to the increased temperature.

**Figure 5.4:** Predicted differences (future - present climate) in ground-level $\text{Hg}^0$ concentrations (ng m$^{-3}$) during (a) summer and (b) winter. A positive value corresponds to an increase.
During winter, Hg⁰ has a similar but even smaller response to climate change. Concentrations are slightly changed in the entire model domain, with a small decrease predicted in most areas (up to 0.01 ng m⁻³) (Fig. 5.4b). The Hg⁰ reduction is lower compared to the reduction in the summer due to lower concentrations of oxidant levels along with the lower temperatures.

5.4.4 Effect on Gaseous Oxidized Mercury (Hg²⁺)

The changes in average predicted Hg²⁺ concentration due to climate change are shown in Figure 5.5. During the summer period, Hg²⁺ is predicted to increase in most of the model domain (3% on average), although there are areas where Hg²⁺ decreases. The highest increase of Hg²⁺ is predicted in the Southeast (2.1 pg m⁻³ or 8% on average), whereas the peak increase occurs in the west coast of Florida and is approximately 45 pg m⁻³ (29%) (Fig. 5.5a). The higher future temperature along with the corresponding effects on oxidant levels, explain this trend of Hg²⁺ concentration. In addition, decreases of wet deposition, due to precipitation, and wind speed also contribute to the changes. Hg²⁺ also increases in the Midwest (1.2 pg m⁻³ or 6.8% on average), while in the Plains and Northeast the predicted increase is smaller, 1% and 1.6% respectively. On the contrary, in several parts of the domain, mainly in TX/OK, the response of Hg²⁺ to climate change differs. Decreases of Hg²⁺ concentrations are predicted in these areas, reaching up to 8.5 pg m⁻³ (29%) in western Texas (Fig. 5.5a). On average, Hg²⁺ is predicted to decrease in Texas by 1.2 pg m⁻³ (4%). The predicted reduction of Hg²⁺ is mainly attributed to changes in wet deposition due to changes in precipitation, indicating that rainfall could have a significant effect on Hg²⁺ concentrations in the future.
Figure 5.5: Predicted differences (future - present climate) in ground-level Hg$^{2+}$ concentrations (pg m$^{-3}$) during (a) summer and (b) winter. A positive value corresponds to an increase.

In the winter, the predicted response of Hg$^{2+}$ to climate change is quite variable in space indicating that many meteorological variables affect the Hg$^{2+}$ concentration. Hg$^{2+}$ is predicted to increase over most of the southern parts of the domain, with the maximum increase predicted in Florida (16.3 pg m$^{-3}$ or 10%) (Fig. 5.5b). On average, Hg$^{2+}$ increases by 6.6% in the Southeast and 5.1% in TX/OK. Increases of Hg$^{2+}$ are also predicted in the Northeast (7.5% on average) and in the Midwest, where the predicted increase of Hg$^{2+}$ reaches up to 11 pg m$^{-3}$ (12%) in Michigan (Fig. 5.5b). However, there are also areas where Hg$^{2+}$ decreases due to climate change. In the Plains the Hg$^{2+}$ concentration decreases by 3.2% on average, while in several Midwest areas (e.g., Indiana), the predicted decrease of Hg$^{2+}$ exceeds 1 pg m$^{-3}$ (or 8%) (Fig. 5.5b). Changes in precipitation and oxidant levels are the major factors governing these changes but changes in mixing are also important locally.
5.4.5 Effect on Particulate Mercury

During the summer, Hg(p) shows a similar spatial response to climate change as Hg$^{2+}$. The highest increase of Hg(p) concentration is predicted in the Southeast (6.5% on average), where Hg(p) increases up to 20.5 pg m$^{-3}$ (22%) in the west coast of Florida (Fig. 5.6a) and also in the western part of Midwest (up to 4 pg m$^{-3}$ or 5.2%). On the contrary, Hg(p) is predicted to decrease in TX/OK (2.1% on average) and also in several areas in the Midwest and Northeast areas of the domain. The predicted concentration change of Hg$^{2+}$ affects the amount of Hg$^{2+}$ adsorbed on atmospheric PM and along with the changes in precipitation determines the response of Hg(p) to climate change.

Figure 5.6: Predicted differences (future - present climate) in ground-level Hg(p) concentrations (pg m$^{-3}$) during (a) summer and (b) winter. A positive value corresponds to an increase.

During winter, the concentration change of Hg(p) is even lower compared to summertime. Over most of the southern parts of the domain (TX/OK, Southeast), Hg(p) decreases by less than 2 pg m$^{-3}$, while increases of Hg(p) are predicted in areas over the Midwest and Northeast (Fig. 5.6b). These concentration changes are
consistent with changes in precipitation, indicating that rainfall is the dominant process rather than the changes of the of Hg$^{2+}$ concentration. The predicted changes in average ground-level concentrations of the Hg species, for each sub-region of the domain are summarized in Table 5.1.

**Table 5.1:** Regional changes (future - present) in average ground-level Hg species concentrations.

<table>
<thead>
<tr>
<th>Season</th>
<th>Regions</th>
<th>Species</th>
<th>$Hg^0$ (ng m$^{-3}$)</th>
<th>$Hg^{2+}$ (pg m$^{-3}$)</th>
<th>$Hg(p)$ (pg m$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td><strong>Summer</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Plains</td>
<td>$Hg^0$</td>
<td>-0.009 (-0.7%)</td>
<td>+0.13 (+1%)</td>
<td>+0.07 (+1%)</td>
</tr>
<tr>
<td></td>
<td>Midwest</td>
<td>$Hg^0$</td>
<td>-0.01 (-0.08%)</td>
<td>+1.2 (+6.8%)</td>
<td>+0.3 (+2.2%)</td>
</tr>
<tr>
<td></td>
<td>Northeast</td>
<td>$Hg^0$</td>
<td>+0.005 (+0.4%)</td>
<td>+0.3 (+1.6%)</td>
<td>+0.002 (+0.02%)</td>
</tr>
<tr>
<td></td>
<td>TX/OK</td>
<td>$Hg^0$</td>
<td>+0.0001 (+0.1%)</td>
<td>-1.2 (-4%)</td>
<td>-0.22 (-2.1%)</td>
</tr>
<tr>
<td></td>
<td>Southeast</td>
<td>$Hg^0$</td>
<td>-0.02 (-1.1%)</td>
<td>+2.1 (+8.2%)</td>
<td>+0.7 (+6.5%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td><strong>Winter</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Plains</td>
<td>$Hg^0$</td>
<td>0</td>
<td>-0.09 (-3.2%)</td>
<td>+0.06 (+1%)</td>
</tr>
<tr>
<td></td>
<td>Midwest</td>
<td>$Hg^0$</td>
<td>-0.001 (-0.1%)</td>
<td>+0.11 (+2.4%)</td>
<td>+0.03 (+0.3%)</td>
</tr>
<tr>
<td></td>
<td>Northeast</td>
<td>$Hg^0$</td>
<td>0</td>
<td>+0.4 (+7.5%)</td>
<td>+0.1 (+1.2%)</td>
</tr>
<tr>
<td></td>
<td>TX/OK</td>
<td>$Hg^0$</td>
<td>-0.001 (-0.1%)</td>
<td>+0.4 (+5.1%)</td>
<td>-0.1 (-1%)</td>
</tr>
<tr>
<td></td>
<td>Southeast</td>
<td>$Hg^0$</td>
<td>-0.002 (-0.2%)</td>
<td>+0.7 (+6.6%)</td>
<td>-0.05 (-0.4%)</td>
</tr>
</tbody>
</table>
5.4.6 Effects on Mercury Deposition

The change of climate is predicted to affect mercury total deposition in both periods (Fig. 5.7, 5.8). On a domain average basis total deposition increases in the future by 6% during the summer and 4% in the winter. However, among the areas of the model domain the predicted mercury total deposition change is quite spatially variable ranging from -50% to 50% during summer and -30% to 50% during winter. The variable changes of rainfall rates in the future, over the modeling areas, affect mercury wet deposition and could partly explain this spatially variable response of mercury total deposition. Generally, in areas where the rainfall will increase in the future, wet deposition of mercury is going to increase too with a similar spatial trend for the mercury total deposition.

During summer, total deposition is predicted to increase in most areas in the western parts of the domain (Plain, TX/OK) (Fig. 5.7a). On average, mercury total deposition increases by 1.95 ng m\(^{-2}\) yr\(^{-1}\) (8%) in TX/OK and 1.7 ng m\(^{-2}\) yr\(^{-1}\) in the Plains (9%) while the respective increase in wet deposition was 2.8 ng m\(^{-2}\) yr\(^{-1}\) (37%) and 1.45 ng m\(^{-2}\) yr\(^{-1}\) (20%) respectively (Fig. 5.7b). In these areas, the increase of rainfall was 18% on average in Texas and 23% on average in the Plains. Additionally, increases of total deposition were predicted in several other parts of the domain (e.g., Florida). On the contrary, the predicted decrease of rainfall in the Northeast (11% on average) and also in many areas in the Midwest and Southeastern parts of the domain, resulted in decreases of mercury wet deposition (10% on average in Northeast) and to a similar response for the mercury total deposition.
Figure 5.7: Predicted differences (future - present climate) in (a) Hg total deposition (ng m$^{-2}$ yr$^{-1}$), (b) Hg wet deposition (ng m$^{-2}$ yr$^{-1}$) and (c) predicted rainfall change (mm yr$^{-1}$) during summer. A positive value corresponds to an increase.

The strong spatial relationship between rainfall and wet deposition was found to determine the predicted response of mercury total deposition to future climate change also during the winter (Fig. 5.8). Total deposition of mercury is predicted to increase in TX/OK (1 ng m$^{-2}$ yr$^{-1}$ or 13% on average) and in a large fraction of the Southeast (0.7 ng m$^{-2}$ yr$^{-1}$ or 5% on average) (Fig. 5.8a). The enhanced mercury wet deposition in these areas (68% and 12% respectively) due to the increased rainfall in the future explains this trend. Increases of mercury total deposition are also predicted in the
Midwest (e.g., Lakes Michigan, and Erie, up to 2.2 ng m\(^{-2}\) yr\(^{-1}\) or 17%), while several areas located mainly in Northeast and also in Florida show an opposite trend due to the decreased rainfall and the accompanying wet deposition decrease. The predicted deposition changes of mercury, for each sub-region of the domain are summarized in Table 5.2.

**Figure 5.8:** Predicted differences (future - present climate) in (a) Hg total deposition (ng m\(^{-2}\) yr\(^{-1}\)), (b) Hg wet deposition (ng m\(^{-2}\) yr\(^{-1}\)) and (c) predicted rainfall change (mm yr\(^{-1}\)) during winter. A positive value corresponds to an increase.
Table 5.2: Regional changes (future - present) in average Hg deposition (ng m\(^{-2}\) yr\(^{-1}\)).

<table>
<thead>
<tr>
<th>Season</th>
<th>Regions</th>
<th>Species</th>
<th>Dry Deposition</th>
<th>Wet Deposition</th>
<th>Total Deposition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Summer</td>
<td>Winter</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Plains</td>
<td>+0.24</td>
<td>+1.45</td>
<td>-0.024</td>
<td>+0.024 (+0.8%)</td>
</tr>
<tr>
<td></td>
<td>Midwest</td>
<td>+1.56</td>
<td>-1.32</td>
<td>-0.24</td>
<td>+0.24 (+0.6%)</td>
</tr>
<tr>
<td></td>
<td>Northeast</td>
<td>+0.48</td>
<td>-1.56</td>
<td>-0.3</td>
<td>+0.3 (+3.2%)</td>
</tr>
<tr>
<td></td>
<td>TX/OK</td>
<td>-0.85</td>
<td>+2.8</td>
<td>+0.1</td>
<td>+1 (+13%)</td>
</tr>
<tr>
<td></td>
<td>Southeast</td>
<td>+0.36</td>
<td>+0.72</td>
<td>-0.18</td>
<td>+0.7 (+5%)</td>
</tr>
</tbody>
</table>

5.5 Sensitivity analysis

There are several sources of uncertainty in the model predictions for mercury concentrations and deposition that need further investigation. These include limitations of the corresponding emission inventories (Lin et al., 2006; Pacyna et al., 2010, 2006; Seigneur et al., 2004a; Walcek et al., 2003), the simulation of mercury removal processes (Bergan and Rodhe, 2001; Bullock and Brehme, 2002; Lee et al., 2001; Lin and Tao, 2003), as well as the effect of boundary conditions (Lin et al., 2007, 2006; Pongprueksa et al., 2008). We explore here, through a sensitivity analysis, the model response (mercury concentrations and removal) to the above
parameters. The results from the different sensitivity tests are compared to the base case results from the two PMCAMx retrospective episode simulations (July 2001 and January 2002).

During summertime, the inclusion of Hg\(^0\) vegetative emissions (approximately 4.8 tons month\(^{-1}\) in July 2001) results in an increase of Hg\(^0\) concentration ranging from 0.01 to 0.26 ng m\(^{-3}\) with an average increase of 0.04 ng m\(^{-3}\) or 3.5% on a domain average basis. The highest increases of Hg\(^0\) are predicted in the Southeast (0.08 ng m\(^{-3}\) or 6% on average) and Midwest (0.07 ng m\(^{-3}\) or 5% on average). These changes are consistent with those of Lin et al. (2007), who reported an increase of 0.05-0.2 ng m\(^{-3}\). For the January simulation, the predicted increase of Hg\(^0\) concentration is negligible (0.001 ng m\(^{-3}\) or 0.1% on average) due to the much lower emissions during winter months (Gbor et al., 2007; Lin et al., 2005). This relatively small increase in Hg\(^0\) concentrations during both periods does not significantly change Hg\(^{2+}\) levels. On average, Hg\(^{2+}\) is predicted to increase by 1 pg m\(^{-3}\) (1.9%) during summer and 0.1 pg m\(^{-3}\) (0.9%) in the winter, while the predicted change of Hg(p) is even smaller. This small change on mercury species concentrations indicates that the inclusion of Hg\(^0\) vegetative emissions has also a small impact on the simulated total mercury dry and wet deposition in this region.

In order to study the sensitivity of predicted concentrations to the boundary conditions, we performed an additional simulation, using altitude-dependent concentrations at the four boundaries of the domain, following the work of Yarwood et al. (2003). In the base-case simulation, we used a fixed value for the Hg\(^0\) concentration in the boundaries while in the sensitivity simulation, Hg\(^0\) concentration in the boundaries was changed by 5% considering also its reduction with height. For Hg\(^{2+}\), in the summer base case simulation we set a value of 29 pg m\(^{-3}\) as boundary
conditions in the west, 26 pg m\(^{-3}\) in the east, 30 pg m\(^{-3}\) in the south and 22 pg m\(^{-3}\) in the north boundary, while in the sensitivity simulation, Hg\(^{2+}\) boundary concentrations were changed by approximately 20%, taking also account the fact that Hg\(^{2+}\) increases with height (Holmes et al., 2010; Lyman and Jaffe, 2011). For the winter simulation the change in the Hg\(^{2+}\) boundary conditions was also approximately 20%. Hg(p) boundary concentrations, during summer, were changed by approximately 25% in the sensitivity simulation (compared to the base case values of 4.4 pg m\(^{-3}\) in the west boundary, 3 pg m\(^{-3}\) in the east, 5.9 pg m\(^{-3}\) in the south and 3.8 pg m\(^{-3}\) in the north boundary) with a similar average change also for the winter sensitivity simulation. The Hg\(^0\), Hg\(^{2+}\) and Hg(p) concentrations in the boundaries affect their concentrations and deposition, mainly in areas close to the domain boundaries. During summer, Hg\(^0\) levels are predicted to change up to 0.08 ng m\(^{-3}\) (6%) near the domain boundary (200-400 km into the domain), while further away the predicted change is smaller, ranging from 0.005 ng m\(^{-3}\) (0.6%) (Plains) to 0.03 ng m\(^{-3}\) (2%) (Northeast). In areas close to the boundaries, the predicted change of Hg\(^{2+}\) levels reaches up to 6 pg m\(^{-3}\) (25%). In the rest of the domain, the boundary conditions have a small effect on Hg\(^{2+}\). Its concentration is predicted to change from 0.7 pg m\(^{-3}\) (4%) in the Midwest to 2 pg m\(^{-3}\) (5.5%) in TX/OK. Hg(p) has also a similar response being, as expected, more sensitive to these conditions close to the boundaries (up to 3.5 pg m\(^{-3}\) or 30%), compared to the rest of the domain. The influence of boundary conditions for the predicted mercury total deposition is significant mainly near to the domain boundaries. In these areas, mercury total deposition is predicted to change up to 1.6 ng m\(^{-2}\) month\(^{-1}\) (30%) due to changes in both dry and wet deposition (up to 0.4 ng m\(^{-2}\) month\(^{-1}\) or 55% and 1.3 ng m\(^{-2}\) month\(^{-1}\) or 35% respectively). In the rest of the domain mercury total deposition is less sensitive to these conditions, with the highest change.
predicted in TX/OK, around 0.17 ng m$^{-2}$ month$^{-1}$ (5%). The influence of the boundary conditions during winter is quite similar as during summer.

The sensitivity of the model predictions to the parameterization of the Hg$^0$ deposition was studied in another sensitivity simulation by neglecting Hg$^0$ dry deposition. In the base case simulation, in both periods, approximately 35% of the predicted total dry deposition was attributed to Hg$^0$, while dry deposition accounts for approximately one third of the predicted total mercury deposition. The assumption of zero Hg$^0$ dry deposition, using a very small Henry’s law constant (similar to CO) (Environ, 2003) resulted in only small decreases of mercury total deposition compared to the base case simulations. During summer, total deposition is predicted to decrease by 0.3 ng m$^{-2}$ month$^{-1}$ (7%) on average, while in the winter the predicted decrease of total deposition is 0.5 ng m$^{-2}$ month$^{-1}$ (8%). The exclusion of Hg$^0$ dry deposition processes leads also to a slight increase of Hg$^0$ concentration, in both periods (0.03 ng m$^{-3}$ or 2.5% in the summer and 0.05 ng m$^{-3}$ or 4% in the winter), while it does not significantly affect the Hg$^{2+}$ and Hg(p) concentrations as well as the simulated wet deposition.

5.6 Conclusions

The effects of climate change on the concentration and deposition of atmospheric mercury over the eastern United States were investigated using the global-regional climate-air pollution modeling system (GRE-CAPS). Overall, these results suggest a shift of Hg$^0$ to Hg$^{2+}$ (which indirectly affects Hg(p)) due to a climate change with a corresponding increase in regional deposition. That spatial pattern of changes is highly variable, depending on predicted changes in precipitation and wet deposition.
The effects of climate change on regional-scale precipitation, however, are not robustly predicted by climate models, so the spatial patterns presented here should be interpreted with care.

Our results suggest that regional climate change will not have a significant effect on $\text{Hg}^0$ concentrations. In both periods there was a small decrease of $\text{Hg}^0$ concentration in most of the model domain (approximately 1% on average), due mainly to the increase of oxidant levels ($\text{OH}$, $\text{O}_3$) which favours the oxidation of $\text{Hg}^0$.

$\text{Hg}^{2+}$ levels during the summer are predicted to change in the future from -30% to 30% depending on the area. On a domain average basis $\text{Hg}^{2+}$ levels are predicted to increase in the future by 3% during the summer. Increases of $\text{Hg}^{2+}$ are predicted mostly in the Southeast (8% on average, up to 45 pg m$^{-3}$ or 29% in Florida) and Midwest (7% on average) while a small increase of $\text{Hg}^{2+}$ levels is also predicted in the Plains and the Northeast. However in several parts of the domain, mainly in TX/OK the changes in $\text{Hg}^{2+}$ concentrations are of the opposite sign of the domain-wide averages. Similar to the summer, the predicted response of $\text{Hg}^{2+}$ to climate change during winter is also quite variable in space ranging from -20% to 40%. $\text{Hg}^{2+}$ is predicted to increase over most of the southern parts of the domain (7% in Southeast and 5% in TX/OK), and also in the Midwest (up to 12% in Michigan) and Northeast (8% on average). On the contrary, there are several areas (e.g., Plains, Indiana), where $\text{Hg}^{2+}$ is predicted to decrease in the future due to climate change.

The different response of $\text{Hg}^{2+}$ over the model domain areas, during both simulation periods indicates that several factors affect the $\text{Hg}^{2+}$ concentration. The higher future temperature in association with the higher oxidant levels could lead to even more $\text{Hg}^0$ getting oxidized and to an increase of $\text{Hg}^{2+}$ concentration in some
areas. In addition changes in mercury wet deposition caused by changes in precipitation and also ventilation changes will have a significant effect on Hg$^{2+}$ levels.

Hg(p) concentrations show a similar spatial response to climate change as Hg$^{2+}$ during summertime. Significant increases of Hg(p) concentration are predicted in Southeast (6% on average), and also in the western part of Midwest (up to 4 pg m$^{-3}$ or 5%), while in TX/OK and in several Midwest and Northeast areas Hg(p) is predicted to decrease in the future. Changes in rainfall seem to be the dominant factor for the Hg(p) concentration response to climate change, during January. Increases of Hg(p) are predicted in areas located in the Midwest and Northeast, while over most of the southern parts of the domain (TX/OK, Southeast), Hg(p) is predicted to decrease.

Climate change in the future is predicted to affect also mercury total deposition, during both periods. On average, mercury total deposition is predicted to increase by 6% during summer and 4% during winter. Although, among the different Eastern US areas the predicted response to climate change is quite spatially variable ranging from -50% to 50% in the summer and from -30% to 50% during winter. This different response of mercury total deposition to climate change among the different areas is mainly attributed to the predicted spatially variable changes of rainfall in the future and the accompanying changes in mercury wet deposition. During summertime increases of mercury total deposition are predicted mainly in the western parts of the domain (9% on average in the Plains and 8% in TX/OK) while mercury deposition is predicted to decrease in the Northeast and also in several areas in the Midwest and Southeast. In the winter increases of mercury total deposition are predicted in the South (13% on average in TX/OK and 5% in the Southeast), while several areas located mainly in Northeast had an opposite trend.
The main focus of this study has been the quantification of the climate effects on mercury concentrations and deposition. Thus, for the future-day simulations, emissions were kept constant at present-day levels. However, projections of future anthropogenic mercury emissions by Streets et al. (2009) have shown that global mercury emissions may at worst double in the future or at best stay constant. The implications of these future emissions scenarios on Hg deposition has been studied by Corbitt et al. (2011) and their results show that the impact of future emissions on mercury levels and deposition rates should be at least as important as meteorology in a future climate.
5.7 References


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Chapter 6

Summary and Recommendations
6.1 Summary

The scope of this dissertation was to enhance our knowledge regarding the potential effects that emissions and climate change could have on the concentration levels of different air pollutants (e.g., particulate matter, ozone, Hg), in order to design effective mitigation strategies for improving air quality.

In Chapter 2, a detailed three dimensional chemical transport model, PMCAMx-2008, was applied over Europe to evaluate the response of fine aerosol (PM$_{2.5}$) mass concentrations to changes in emissions of precursor gases (SO$_2$, NH$_3$, NO$_x$, VOCs) and anthropogenic primary OA (POA) as well as to changes in temperature. A summer and a winter simulation period were used, to investigate also the seasonal dependence of the PM$_{2.5}$ response to emissions and temperature changes. The reduction of NH$_3$ emissions seems to be the most effective control strategy in reducing PM$_{2.5}$, in both periods, resulting in a decrease of PM$_{2.5}$ over Europe by 5.5% during summer and 4% during winter, due mainly to significant decreases of ammonium nitrate (up to 40%). In areas with high ammonium nitrate levels the predicted decrease is even higher (15% on average in Western Europe). The SO$_2$ control strategy is more effective during summer, especially over Balkans, where total PM$_{2.5}$ is reduced by 10% due mainly to a significant reduction of sulfate (34%). The anthropogenic POA control strategy reduces total OA by 15% during the modeled winter period and 8% in the summer, being more effective in areas close to emissions sources. A slight decrease of OA is also predicted after a 50% reduction of VOCs emissions due to the linear decrease of anthropogenic SOA. On the contrary, the NO$_x$ emissions control strategy seems to be problematic in both periods. During summer, the 50% reduction of NO$_x$ emissions reduces PM$_{2.5}$ due to a decrease of ammonium nitrate (25% on average), causing although an increase of ozone concentration in
major urban areas and over Western Europe (up to 10%). Additionally, the NOx control strategy increases PM$_{2.5}$ levels during the winter period, due to more oxidants becoming available to react with SO$_2$ and VOCs. The increase of temperature by 2.5 K leads to a reduction of PM$_{2.5}$ in both periods over Central Europe, mainly due to a decrease of NH$_4$NO$_3$ in the summer (18%) and fresh POA in the winter (35%). Increases of OA are predicted in most areas during the summer, due to the increase of biogenic VOC emissions. On the contrary, OA is predicted to decrease in the winter period 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 leads also to an increase of sulfate levels in both periods, mainly over North Europe and the Atlantic Ocean. The doubling of temperature increase (from 2.5 K to 5 K) approximately doubles the corresponding concentration change of OA components during summer and leads to even larger concentration changes of inorganic PM$_{2.5}$, in both periods.

Our findings from Chapter 2 regarding the sensitivity of PM$_{2.5}$ concentrations to temperature changes, supported us with evidences that climate affects air quality through a complex web of interactions starting with changes in the major meteorological variables like temperature, wind speed, absolute humidity, precipitation intensity, precipitation area, mixing height, etc. and progressing through changes in pollutant concentrations, formation and removal rates. In Chapter 3, we used PMCAMx-2008, in order to quantify the individual effects of the major meteorological parameters on the concentration and composition of PM$_{2.5}$ over Europe. Our simulations covered three periods, representative of different seasons (summer, winter, and fall). Precipitation is expected to have the largest impact on PM$_{2.5}$ concentrations under a changed future climate. PM$_{2.5}$ concentrations could
potentially change by several $\mu g \ m^{-3}$ (up to 2 $\mu g \ m^{-3}$ in the fall) due to the expected future changes in precipitation, driven mainly from changes in wet removal of PM$_{2.5}$ species and their gas precursors. Wind speed could also have appreciable effects on future PM$_{2.5}$ levels which are arising mainly from its effects on dispersion and transport, dry deposition and marine aerosol production. In a future climate, the projected changes in wind speed over Europe are expected to change PM$_{2.5}$ levels up to 1.4 $\mu g \ m^{-3}$. Changes in absolute humidity influence mainly the inorganic PM$_{2.5}$ species, resulting in competing responses. As absolute humidity is expected to rise in the future, will favor the partitioning of nitrate to the aerosol phase leading to higher concentration levels. During periods when the increased particulate nitrate levels dominate the overall PM$_{2.5}$ response, absolute humidity can potentially lead to large increases of PM$_{2.5}$ (up to 2 $\mu g \ m^{-3}$ during fall in our study). Otherwise, the decreases in sulfate, and sea salt levels due to the increase in the size of the particles and the accelerated dry deposition may, in some extent, offset the predicted increases in nitrate. Temperature is expected to have a lower impact on future PM$_{2.5}$ levels compared to the rest meteorological parameters due to the competing effects among the individual processes and the different responses of the PM$_{2.5}$ species. The evaporation of semi-volatile PM$_{2.5}$ species was found to be the dominant process causing significant effects mainly on particulate ammonium nitrate, as the increase in temperature reduces its concentration levels up to 15% $K^{-1}$. During, periods when the predicted reduction of nitrate dominates, the expected temperature rise in the future climate could potentially lead to decreases in PM$_{2.5}$ levels (up to 1.1 $\mu g \ m^{-3}$ during fall in our study). However as temperature increases, leads to higher biogenic VOC emissions as well as accelerates the gas-phase chemical reactions, which may cancel.
in some extent the expected reductions of PM$_{2.5}$. The expected effects on future PM$_{2.5}$ levels from changes in mixing height are not as significant as the other parameters.

In Chapter 4, PMCAMx-2008 was used as part of the global-regional climate-air pollution modeling system, GRE-CAPS, to investigate the effects of climate change on the concentrations of PM$_{2.5}$ and ozone in Greece (as well as over Europe). Summertime periods were simulated both for the present (2000s) and the future (2050s) assuming constant anthropogenic pollutant emissions. The future time period investigated was the 2050s, using the IPCC A1B scenario. Our results suggest that regional climate change will generally decrease PM$_{2.5}$ levels in Greece by 1.1 μg m$^{-3}$ (5%) on average. However the predicted changes are quite variable in space and range from -20% to 20% depending on the area. The highest PM$_{2.5}$ decrease is predicted in Central Greece, 1.2 μg m$^{-3}$ (5.5%) on average and up to 5 μg m$^{-3}$ (Athens), due to the increase in wind speed and the lower absolute humidity which dominate the overall PM$_{2.5}$ change, offsetting the predicted increases of OA (due to higher temperature). Decreases of PM$_{2.5}$ levels are also predicted in North Greece (5% on average) as well as over the northern parts of the Aegean. On the contrary, future PM$_{2.5}$ levels are higher in Peloponnese and Crete. Average PM$_{2.5}$ is predicted to increase by 3% in Peloponnese and 1% in Crete respectively due mainly to increases in OA and nitrate levels. The higher future temperatures (and the accompanying effects on biogenic VOC emissions and oxidant levels) as well as the increases in absolute humidity are the dominant factors, while decreases of wet deposition, due to precipitation, and wind speed also contribute to the changes. Ozone concentrations are also predicted to change in a future climate. Higher levels of O$_3$ are predicted in the future over Greece. On average, O$_3$ will increase by 2.5 ppb (4.5%), with Central Greece experiencing the highest changes (8% on average). Significant increases are also predicted in the major
urban areas (e.g., Athens), approximately 7-8%. The predicted changes on the daily peak O₃ concentrations (1-hr maximum and maximum 8-hr average) are even larger (up to 8 ppb or 10%) showing a similar spatial trend. The higher temperature in the future appears to be the governing factor that determines the O₃ response, while the wind speed in several areas also contributes. Over Europe, the model predicts variable responses of PM₂.₅ concentrations to climate change. The predicted changes range from -25% to 25%, with decreases in North and Central Europe and increases in the Balkans, indicating that changes in several meteorological parameters, especially precipitation, temperature, wind speed, and absolute humidity may have appreciable (and sometimes competing) effects on PM₂.₅ concentrations in several areas. Regarding O₃, the results show a general trend to increase in the future in the South Europe (up to 17%) and also in the Balkans, and to decrease in North Europe, with changes in temperature being the dominant factors.

In Chapter 5, the GRE-CAPS system was applied over the eastern United States to study the impact of future climate change on the concentration and deposition of atmospheric mercury. Summer and winter periods (300 days for each) were simulated, and the present-day model predictions (2000s) were compared to the future ones (2050s) assuming constant emissions. The future time period investigated was the 2050s, using the IPCC A2 scenario Regional climate change will not have a significant effect on Hg⁰ concentrations. In both periods, a small decrease of Hg⁰ is predicted (approximately 1% on average), due mainly to the increase of oxidant levels (OH, O₃) which favours the oxidation of Hg⁰. Hg²⁺ levels are predicted to increase in the future summer by 3% on average, although the predicted concentration changes vary significantly in space, ranging from -20% to 20%. Increases are predicted mostly in the Southeast and Midwest (on average 8% and 7% respectively), while in TX/OK
Hg\textsuperscript{2+} is predicted to decrease. During winter the predicted concentration changes of Hg\textsuperscript{2+} to climate change range from -20\% to 40\%. Hg\textsuperscript{2+} is predicted to increase over most of the southern areas (7\% in Southeast and 5\% in TX/OK), and also in the Northeast (8\% on average). On the contrary, there are several areas in the Midwest (e.g., Plains, Indiana), where Hg\textsuperscript{2+} is predicted to decrease in the future. The different response of Hg\textsuperscript{2+} indicates that several factors affect its concentration. The higher future temperature in association with the higher oxidant levels could lead to even more Hg\textsuperscript{0} getting oxidized and to an increase of Hg\textsuperscript{2+} concentration in some areas. In addition changes in mercury wet deposition caused by changes in precipitation and also ventilation changes will have a significant effect on Hg\textsuperscript{2+} levels. Hg(p) concentrations show a similar spatial response to climate change as Hg\textsuperscript{2+} during summertime, while changes in rainfall seem to be the dominant factor for the Hg(p) concentration response to climate change, during winter. Climate change affects also mercury total deposition. On average, mercury total deposition is predicted to increase by 6\% during summer and 4\% during winter. Although, the predicted response to climate change is quite spatially variable ranging from -50\% to 50\% in the summer and from -30\% to 50\% during winter. This different response of mercury total deposition to climate change is mainly attributed to the predicted spatially variable changes of rainfall in the future and the accompanying changes in mercury wet deposition. During summer increases of mercury total deposition are predicted mainly in the western parts of the domain (9\% on average in the Plains and 8\% in TX/OK) while mercury deposition is predicted to decrease in the Northeast and also in several areas in the Midwest and Southeast. In the winter increases of mercury total deposition are predicted in the South (13\% on average in TX/OK and 5\% in the Southeast), while several areas located mainly in Northeast had an opposite trend.
6.2 Recommendations for future work

The work presented here can serve as the basis of future research on the potential links among emissions, climate change, and the concentration levels of air pollutants. Our results have shown that the emissions reductions of the major gaseous and particulate precursors may have a significant impact on PM$_{2.5}$ levels. Nevertheless, a more comprehensive study is essential in order to enhance our knowledge regarding the impact of emissions to PM$_{2.5}$ levels and subsequently on air quality. A step forward could potentially be the investigation of multi-pollutant reduction scenarios rather than individual control strategies of the major precursors, which generally are expected to be more effective for reducing PM$_{2.5}$. In addition, one can examine the implication of a range of alternative emissions reduction measures in key emissions sectors (e.g., transport, energy, residential heating, agricultural) for a given region. These reductions scenarios could be either oversimplified cases in order to give an estimate regarding the importance of each emission source on air quality but could be also based on current air quality legislation for the area examined.

Climate change and its accompanying effects on air quality could be also a topic of future research. This study highlights the importance of changes in meteorology, under future climate period, on the concentrations of various air pollutants. However, projections for anthropogenic emissions have also shown a substantial change in the future. Therefore, in order to assess the overall effect of climate change on air quality and to provide the scientific committee with more robust results, future studies should incorporate the projected changes of meteorology under future climate period along with the implication of future anthropogenic emissions scenarios.

Finally, a challenging research topic can be the integration of air pollution and climate change in a common policy framework. Climate change and air pollution are
closely inter-related in their mitigation, their functioning, and their impacts. Therefore, a potential risk of keeping research and policy on climate change and air quality separate is that abatement strategies may not recognize the synergies or trade-offs that may exist. For example the reduction of atmospheric sulfate aerosols will generate a warming of the surface in addition to the warming expected from the increasing concentration of GHGs. On the contrary, where emission sources of both climate change and air pollution related pollutants are the same, emission reductions can yield mutual benefits for climate and air quality and subsequently for public health. For example, a reduction in the atmospheric abundance of CO, an atmospheric pollutant resulting from combustion, would enhance the concentration of the OH radical, and hence would reduce the lifetime of CH₄, an important GHG. Therefore, it is essential to develop “win-win” strategies that inform decision-makers about cost-effective ways to reduce concentrations of air pollutants as well as the harmful health impacts while at the same time minimizing undesired climate change. A critical need for indentifying these cost-effective and cost-benefit risk reduction strategies is to improve the quantification of regional and global links between air quality and climate change, as well as to provide better estimates of current and future air pollution and its impact on climate change. For this purpose, PMCAMx-2008 is a well suited tool, as it can provide with accuracy and robustness the necessary scientific knowledge, regarding the source-receptor relationships of air pollutants. The main results from these source-receptor studies, using PMCAx-2008, can be the basis in integrated assessment frameworks that will be developed to identify portfolios of measures that improve air quality and reduce greenhouse gas emissions at least cost.
Appendix A

The PMCAMx model
An Overview

The PMCAMx model is the research version of the publicly available, Comprehensive Air Quality Model with extensions (CAMx) (Environ, 2013). CAMx is an Eulerian photochemical dispersion model that allows for integrated “one-atmosphere” assessments of gaseous and particulate air pollution (ozone, PM$_{2.5}$, PM$_{10}$, air toxics, and mercury) over different spatial scales ranging from sub-urban to continental. It is designed to unify all of the technical features required of “state-of-the-science” air quality models into a single open-source system that is computationally efficient, flexible, easy to use, and publicly available. The model code has a highly modular and well-documented structure which eases the insertion of new, update or alternate algorithms and features. The input/output file formats are based on the Urban Airshed Model (UAM) and are compatible with many existing pre- and post-processing tools. Meteorological fields are supplied to CAMx from separate weather prediction models.

CAMx simulates the emission, dispersion, chemical reaction, and removal of pollutants in the troposphere by solving the pollutant continuity equation for each chemical species ($l$) on a system of nested three-dimensional grids. The Eulerian continuity equation describes the time dependency of the average species concentration ($c_l$) within each grid cell volume as a sum of all of the physical and chemical processes operating on that volume. This equation is expressed mathematically in terrain-following height ($z$) coordinates as follows:

$$\frac{\partial c_l}{\partial t} = -\nabla_H \cdot V_H c_l + \left[ \frac{\partial (c_l \eta)}{\partial z} - c_l \frac{\partial h}{\partial z} \frac{\partial h}{\partial t} \right] + \nabla \cdot \rho K \nabla (c_l / \rho)$$

$$+ \frac{\partial c_l}{\partial t} \bigg|_{\text{chemistry}} + \frac{\partial c_l}{\partial t} \bigg|_{\text{emissions}} + \frac{\partial c_l}{\partial t} \bigg|_{\text{removal}}$$

\hspace{1cm} (1)
where \( V_H \) is the horizontal wind vector, \( \eta \) is the net vertical transport rate, \( h \) is the layer interface height, \( \rho \) is atmospheric density, and \( K \) is the turbulent exchange (or diffusion) coefficient. The first term on the right-hand side represents horizontal advection, the second term represents net resolved vertical transport across an arbitrary space- and time-varying height grid, and the third term represents sub-grid scale turbulent diffusion. Chemistry is treated by simultaneously solving a set of reaction equations defined from specific chemical mechanisms. Pollutant removal includes both dry surface uptake (deposition) and wet scavenging by precipitation.

CAMx can perform simulations on three types of Cartesian map projections: Universal Transverse Mercator, Rotated Polar Stereographic, and Lambert Conic Conformal. CAMx also offers the option of operating on a curvi-linear geodetic latitude/longitude grid system. The vertical grid structure is defined externally, so layer interface heights may be specified as any arbitrary function of space and/or time. This flexibility in defining the horizontal and vertical grid structures allows CAMx to be configured to match the grid of any meteorological model that is used to provide environmental input fields.

CAMx inputs are developed using independent third-party models and processing tools that characterize meteorology, emissions, and various other environmental conditions (land cover, radiative/photolysis properties, and initial/boundary conditions). Interface programs are needed to translate the products of each of these models/processors into the specific input fields and formats required by CAMx. Table A1 summarizes the input data requirements of CAMx. After the air quality simulation is completed, additional programs are used to post-process the concentration fields, develop model performance statistics and measures, manipulate
output into various reportable formats, and further translate raw results into forms necessary for regulatory purposes.

Table A1: Data requirements of CAMx

<table>
<thead>
<tr>
<th>Data Types</th>
<th>Data Fields</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Meteorology</strong></td>
<td>• Temperature</td>
</tr>
<tr>
<td><em>Supplied by Prognostic Meteorological Models</em></td>
<td>• Pressure</td>
</tr>
<tr>
<td></td>
<td>• Water Vapor</td>
</tr>
<tr>
<td></td>
<td>• Horizontal Wind Components</td>
</tr>
<tr>
<td></td>
<td>• Vertical Diffusivity</td>
</tr>
<tr>
<td></td>
<td>• Clouds/Precipitation</td>
</tr>
<tr>
<td><strong>Air Quality</strong></td>
<td>• Gridded Initial Concentrations</td>
</tr>
<tr>
<td><em>Developed from other Models or Measurement Data</em></td>
<td>• Gridded Boundary Concentrations</td>
</tr>
<tr>
<td><strong>Emissions</strong></td>
<td>• Elevated Point Sources</td>
</tr>
<tr>
<td><em>Supplied by Emissions Models and Processors</em></td>
<td>• Area Sources</td>
</tr>
<tr>
<td></td>
<td>• Biogenic</td>
</tr>
<tr>
<td></td>
<td>• Wild Fires</td>
</tr>
<tr>
<td></td>
<td>• Sea salt</td>
</tr>
<tr>
<td><strong>Geographic</strong></td>
<td>• Landuse/Landcover</td>
</tr>
<tr>
<td><em>Developed from Terrain, Landuse/Landcover and Vegetation Datasets</em></td>
<td>• Terrain Elevation</td>
</tr>
<tr>
<td></td>
<td>• Land/Ocean</td>
</tr>
<tr>
<td><strong>Photolysis</strong></td>
<td>• Photolysis Rates</td>
</tr>
<tr>
<td><em>Derived from Satellite Measurements</em></td>
<td>• Ozone Column</td>
</tr>
</tbody>
</table>

A2 Core model formulation

This section outlines the basic numerical approach employed in CAMx, and describes the technical formulation of the transport and removal processes.

A2.1 Numerical approach

The physical representations and the numerical methods used for each term of the pollutant continuity equation (described in Section A1) are summarized in Table A2.
CAMx includes peer-accepted algorithms and component formulations, and its modular framework permits easy substitution of additional and/or updated algorithms in the future.

**Table A2:** Summary of the CAMx modules for key physical processes.

<table>
<thead>
<tr>
<th>Process</th>
<th>Physical Model</th>
<th>Numerical Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Horizontal advection/diffusion</td>
<td>Eulerian continuity equation closed by K-theory</td>
<td>Bott or PPM for advection, Explicit Diffusion</td>
</tr>
<tr>
<td>Vertical transport/diffusion</td>
<td>Eulerian continuity equation closed by K-theory</td>
<td>Implicit advection and diffusion</td>
</tr>
<tr>
<td>Gas-Phase Chemistry</td>
<td>SAPRC/Carbon Bond IV mechanisms Inorganic/organic aerosol precursors</td>
<td>ENVIRON CMC solver, IEH solver, or LSODE</td>
</tr>
<tr>
<td>Aerosol Chemistry</td>
<td>Dry and aqueous inorganic and organic chemistry/thermodynamics; static 2-mode or evolving multi-section size models</td>
<td>RADM-AQ, ISORROPIA, 1D-VBS, CMU sectional model</td>
</tr>
<tr>
<td>Dry Deposition</td>
<td>Separate resistance models for gases and aerosols</td>
<td>Deposition velocity as surface boundary condition for vertical diffusion</td>
</tr>
<tr>
<td>Wet Deposition</td>
<td>Separate scavenging models for gases and aerosols</td>
<td>Uptake as a function of rainfall rate, cloud water content, gas solubility and diffusivity, PM size</td>
</tr>
</tbody>
</table>

The continuity equation is numerically marched forward in time over a series of time steps. At each step, the continuity equation is integrated by way of an operator-splitting approach that calculates the separate contribution of each major process (advection, diffusion, chemistry, etc.) to concentration change within each grid cell. The specific equations that are solved individually in the operator-splitting process are shown in order below:
\[
\frac{\partial c_l}{\partial t}_{\text{Emissions}} = m^2 \frac{E_l}{\partial x \partial y \partial z}
\]

(2)

\[
\frac{\partial c_l}{\partial t}_{\text{X advection}} = -m^2 \frac{\partial}{A_{yz}} \left( \frac{u A_{yz} c_l}{m} \right)
\]

(3)

\[
\frac{\partial c_l}{\partial t}_{\text{Y advection}} = -m^2 \frac{\partial}{A_{xz}} \left( \frac{v A_{xz} c_l}{m} \right)
\]

(4)

\[
\frac{\partial c_l}{\partial t}_{\text{Z transport}} = \frac{\partial (c \rho)}{\partial z} - c_l \frac{\partial (h \rho)}{\partial t}
\]

(5)

\[
\frac{\partial c_l}{\partial t}_{\text{Z diffusion}} = \frac{\partial}{\partial z} \left[ \rho K_v \frac{\partial (c_l / \rho)}{\partial z} \right]
\]

(6)

\[
\frac{\partial c_l}{\partial t}_{\text{XY diffusion}} = m \left\{ \frac{\partial}{\partial x} \left[ m \rho K_x \frac{\partial (c_l / \rho)}{\partial x} \right] + \frac{\partial}{\partial y} \left[ m \rho K_y \frac{\partial (c_l / \rho)}{\partial y} \right] \right\}
\]

(7)

\[
\frac{\partial c_l}{\partial t}_{\text{Wet Scavenging}} = - \Lambda_l c_l
\]

(8)

\[
\frac{\partial c_l}{\partial t}_{\text{Chemistry}} = \text{Mechanism – specific reaction equations}
\]

(9)

where \( c_l \) is species concentration (μmol/m\(^3\) for gasses, μg/m\(^3\) for aerosols), \( E_l \) is the local species emission rate (μmol/s for gasses, μg/s for aerosols), \( \partial t \) is time step length (s), \( u \) and \( v \) are the respective east-west (x) and north-south (y) horizontal wind components (m/s), \( A_{yz} \) and \( A_{xz} \) are cell cross-sectional areas (m\(^2\)) in the y-z and x-z planes, respectively, \( m \) is the ratio of the transformed distance on the various map projections to true distance (\( m=1 \) for curvi-linear latitude/longitude coordinates), and \( \Lambda_l \) is the wet scavenging coefficient (s\(^{-1}\)). A master time step for the model is internally determined during the simulation to ensure numerical stability for horizontal advection in the largest and coarsest (master) grid. Time steps typically range from 5-15 minutes for grid cell sizes of 10-50 km, to a minute or less for small
cell sizes of 1-2 km. As a result, transport calculations on nested grids require multiple time steps per master step depending on their grid sizes relative to the master grid spacing. Furthermore, multiple chemistry time steps per driving step are used as necessary to ensure accurate solutions for the chemical reaction equations. The first process in each time step for a given grid is the injection of emissions from all sources. CAMx then performs horizontal advection, but alternates the order of advection in the $x$ and $y$ directions each master time step. This alleviates any potential numerical biases that can develop when the $x/y$ advection order is constant. Vertical advection is simulated after horizontal advection, followed by vertical diffusion, horizontal diffusion, wet scavenging and finally chemistry. Although advection is simulated separately in the $x$ (east-west), $y$ (north-south), and $z$ (vertical) directions, the numerical linkage between these components has been developed in a mass consistent fashion to preserve the density field at each time step. This maintains the flexibility to allow many types of meteorological models, and modeling grid resolutions, projections, and layer structures, to characterize transport in CAMx.

Trace gases and particles are removed from the atmosphere via deposition to the ground. Dry deposition refers to the direct sedimentation and/or diffusion of material to various terrestrial surfaces and uptake into biota. Wet deposition refers to the uptake of material into cloud water and precipitation, and its subsequent transfer to the surface. The efficiency with which wet and dry deposition processes can remove pollutants from the air depends upon the physical and chemical properties of the pollutants, local meteorological conditions, the type of surface on which they are being deposited, and on the frequency, duration, and intensity of precipitation events. Dry deposition is an important removal mechanism, but it is not explicitly treated as a separate process in the time-splitting approach. Instead, deposition velocities for each
species are calculated, and used as the lower boundary condition for vertical diffusion. This appropriately couples the surface removal of pollutants through each column of cells via the vertical mixing process.

A2.2 Horizontal advection

The advection equations are solved using the Piecewise Parabolic Method of Colella and Woodward (1984) as implemented by Odman and Ingram (1996). The order of directions of horizontal advection is alternated to avoid any numerical biases that can develop when this order is constant.

A2.3 Vertical advection

The equation for vertical transport is:

\[
\left. \frac{\partial c_i}{\partial t} \right|_{z_{\text{advection}}} = \frac{\partial (c_i w)}{\partial z} \quad (10)
\]

where \( w \) is the net vertical velocity. To calculate the vertical velocity profile, the atmospheric continuity equation is locally integrated through the depth of the vertical column.

A2.4 Vertical dispersion

Vertical dispersion is represented by the equation:

\[
\left. \frac{\partial c_i}{\partial t} \right|_{z_{\text{diffusion}}} = \frac{\partial}{\partial z} \left[ \rho K_v \frac{\partial (c_i / \rho)}{\partial z} \right] \quad (11)
\]

where \( K_v \) is the vertical dispersion coefficient and is provided as a meteorological input, and \( \rho \) is the atmospheric density.
A2.5 Horizontal dispersion

Horizontal dispersion is simulated using the equation:

$$\frac{\partial c_i}{\partial t}\bigg|_{XY \text{ diffusion}} = \frac{\partial}{\partial x} \left( \rho K_x \frac{\partial (c_i/\rho)}{\partial x} \right) + \frac{\partial}{\partial y} \left( \rho K_y \frac{\partial (c_i/\rho)}{\partial y} \right)$$  \hspace{1cm} (12)

where $K_x$ and $K_y$ are the horizontal dispersion coefficients determined using a deformation approach based on the methods of Smagorinsky (1963):

$$K_{x/y} = K_o + \frac{\Delta x \Delta y}{4 \sqrt{2}} \left( \frac{\partial u}{\partial y} + \frac{\partial v}{\partial x} \right)^2 + \left( \frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} \right)^2 \right)^{1/2}$$  \hspace{1cm} (13)

The value of $K_o$ is specified according to the approach of Anthes and Warner (1978):

$$K_o = 3 \times 10^{-3} \frac{\Delta x \Delta y}{\Delta t}$$  \hspace{1cm} (14)

$K_x$ and $K_y$ are calculated for each face of the grid cell and a maximum value is set to maintain numerical stability.

A2.6 Gas-phase chemistry

In most of our studies, PMCAMx uses the SAPRC99 mechanism (Carter, 2013; Environ, 2013) to describe the gas-phase chemistry which includes 211 chemical reactions of 56 gases and 18 free radicals. SAPRC99 uses the most recent updates for volatile organic compounds (VOCs) lumping while it has been tested extensively against environmental chamber data. Another mechanism, supported by PMCAMx to describe gas-phase chemistry is the Carbon Bond (CB) mechanism and its different versions (CB-4, Gery et al., 1989; CB-5, Yarwood et al., 2005).
The gas-phase chemistry reactions are numerically integrated using the Chemical Mechanism Compiler (CMC) solver (Environ, 2013). The CMC solver is a fast and robust solver. It uses the steady-state approximation for fast reacting species (radicals) while the slower reacting (state) species are separated into two groups. Fast state species (with chemical lifetimes of seconds to a few minutes) are solved using a second order implicit Runge-Kutta method, while slow state species (with longer chemical lifetimes) are solved explicitly.

### A2.7 Wet deposition

The change in concentration within or below a cloud due to precipitation is parameterized using a scavenging coefficient, $\Lambda$:

$$\frac{\partial c_l}{\partial t} = -\Lambda c_l$$  \hspace{1cm} (15)

The scavenging coefficient is determined differently for gases and particles, based upon relationships described by Seinfeld and Pandis (2006). Below the clouds, the mass transfer coefficient depends on the raindrop diameter and falling speed, which are calculated based on the empirical estimates of Scott (1978) which has been modified to better agree with the data provided by Seinfeld and Pandis (2006).

Wet scavenging of gases by precipitation occurs within and below precipitating clouds. Below the cloud, the total gas concentration in a given grid cell is available for scavenging. Within a cloudy cell the total gas concentration must first be partitioned into an aqueous fraction $c_{aq}$ within cloud water and the remaining gaseous fraction $c_g$ within the interstitial air. Both aqueous and interstitial gasses within a cloudy cell are available for scavenging, but are removed at different rates. The aqueous concentration in liquid cloud water is determined by Henry’s Law.
For the case of aerosols, all aerosol species are assumed to be within the cloud water. Below the cloud layer, the collection efficiency depends on the particle diameter (Seinfeld and Pandis, 2006).

**A2.8 Dry deposition**

Due to the difficulty of making direct measurements of dry deposition and the need for a suitable model parameterization, dry deposition is often treated as a first-order removal mechanism, where the flux of a pollutant to the surface is the product of a characteristic deposition velocity and its concentration in the “surface layer” (i.e., the lowest model layer). Dry deposition is simulated using the resistance model of Wesely (1989).

For gas species, deposition velocity $V_d$ is calculated from three primary resistances $r$ (s/m) in series:

\[
V_d = \frac{1}{r_a + r_b + r_s}
\]  

(16)

where $r_a$ is the aerodynamic resistance, $r_b$ the quasi-laminar sublayer resistance and $r_s$ the surface resistance. The aerodynamic resistance $r_a$, represents bulk transport through the lowest model layer by turbulent diffusion and depends on the intensity of turbulent motion. The quasi-laminar sublayer resistance $r_b$, represents molecular diffusion through the thin layer of air directly in contact with the surface to which material is being deposited. The surface resistance $r_s$, is expressed as several more serial and parallel resistances that depend upon the physical and chemical properties of the surface in question. The surface resistances for strong acids (e.g., nitric acid, hydrochloric acid) are set to zero given their high rates of uptake onto most surfaces.
For aerosol species, the resistance approach of Slinn and Slinn (1980), as implemented by Kumar et al. (1996) is used. Particle deposition velocity for a given aerosol size is calculated using the following resistance equation:

\[ v_d = v_{sed} + \frac{1}{r_a + r_b + r_a r_b v_{sed}} \]  

(17)

where \( v_{sed} \) is the gravitational settling velocity. This velocity is dependent on aerosol size and density.

### A2.9 Nucleation and Coagulation

The nucleation rate is calculated using the ternary NH\(_3\)-H\(_2\)SO\(_4\)-H\(_2\)O parameterization of Napari et al. (2002). The parameterization uses the NH\(_3\) gas-phase concentration, H\(_2\)SO\(_4\) gas-phase concentration, temperature, and relative humidity as inputs, and provides a nucleation rate as output. Because of the relatively large concentrations of water vapor, water is assumed to be in equilibrium with the aerosol phase. The amount of water in the aerosol phase is calculated using the thermodynamic module ISORROPIA (Nenes et al., 1998).

The coagulation rate of aerosol particles was modeled using the approach of Tambour and Seinfeld (1980). The generalized coagulation coefficient for the collision of two particles is defined as:

\[ K_{12} = 2\pi(D_{p1} + D_{p2})(D_1 + D_2)\beta \]  

(18)

where \( \beta \) is the Fuchs correction factor (Fuchs, 1964). A high-resolution distribution is used for the coagulation calculations by subdividing each section of the original distribution into three sections.
A2.10 Inorganic and organic aerosol formation

Three main approaches are available in PMCAMx for the simulation of inorganic aerosol growth, depending on the computational efficiency and level of accuracy desired. The simplest and most efficient approach is the “bulk equilibrium” approach, in which the bulk inorganic aerosol and gas phase are assumed to be always in equilibrium. The equilibrium model employed in this work has been described by Capaldo et al. (2000). 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 factor for each size section \( k \), \( f_k \), based on their surface area (Pandis et al., 1993; Lurmann et al., 1997):

\[
f_k = \frac{N_k d_k / (\beta_k + 1)}{\sum_k N_k d_k / (\beta_k + 1)}
\]

where \( N_k \) and \( d_k \) are the number and diameter, respectively of particles in section \( k \), \( \beta_k = 2\lambda / ad_k \), \( a \) is the accommodation coefficient, and \( \lambda \) is the mean free path of the species transferred (Pandis et al., 1993).

The second approach is the “hybrid” approach, which assumes equilibrium for the particles less than 1 \( \mu \)m in size (PM\(_1\)) and solves the mass transfer differential equations for the coarse particles (Capaldo et al., 2000). Finally, the most accurate but computationally demanding method is the “dynamic” approach where mass transfer is simulated explicitly for all particles (Pilinis et al., 2000).

Primary Organic Aerosol (POA). Primary organic aerosol in PMCAMx is assumed to be semivolatile, based on the approach of Shrivastava et al. (2008). Nine surrogate POA species are used, with effective saturation concentrations at 298 K.
ranging from $10^{-2}$ to $10^6 \, \mu g \, m^{-3}$. POA is simulated in the model in two types, “fresh” (unoxidized) POA and oxidized POA (OPOA).

*Secondary Organic Aerosol (SOA).* The modeling framework used by PMCAMx for the simulation of secondary organic aerosol is based on the SOA volatility basis-set approach (Lane et al., 2008a) and includes four SOA species for each VOC with 4 volatility bins (1, 10, 100, 1000 $\mu g \, m^{-3}$). Laboratory results from recent smog-chamber experiments (Ng et al., 2006; Hildebrandt et al., 2009) have been used to update the SOA module in PMCAMx in order to include anthropogenic aerosol yields. The SOA module incorporates NO$_x$-dependent SOA yields (Lane et al., 2008b) which are based on an assumed density of 1.5 g cm$^{-3}$.

PMCAMx assumes equilibrium between the gas and aerosol phase of the organic components using the Secondary Organic Aerosol Model (SOAM II) of Strader et al. (1999) as implemented by Koo et al. (2003). The condensable gas products are partitioned between the gas and aerosol phases similar to the inorganics with an additional factor to account for the aerosol composition using the pseudo-ideal solution assumption (Koo et al., 2003). The temperature dependence of saturation concentrations is considered by the Clausius-Clapeyron equation.

*Chemical Aging Reactions.* PMCAMx treats all organic species (primary and secondary) as chemically reactive. Primary organic gases (POG), formed due to evaporation of semivolatile POA in the atmosphere, are assumed to react with OH radicals reducing their volatility. The products of this oxidation (secondary vapours) are allowed to partition between gas and particle phase according to their volatilities. This resulted in the formation of oxidized organic aerosol (referred also as OPOA or S-SOA) (Shrivastava et al., 2008; Donahue et al., 2009; Tsimpidi et al., 2010). Chemical aging of organic condensable gases (OCG), generated from VOCs that are
traditional SOA precursors, is an important source of OA as well. For both cases, aging is modelled with a gas-phase OH reaction with a rate constant of \( k = 1 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1} \) for anthropogenic SOA and \( k = 4 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1} \) for the primary OA (Atkinson and Arey, 2003). Each reaction is assumed to reduce the volatility of the vapor material by a factor of 10.

**A2.11 Aqueous-phase chemistry**

For the simulation of aqueous phase chemistry, PMCAMx uses the variable sizes resolution model (VSRM) of Fahey and Pandis (2001). The model is based on the chemical mechanism of Pandis and Seinfeld (1989), with the addition of Ca\(^{2+}\) to the list of aqueous-phase species and \( \text{H}_2\text{SO}_4 \) to the gas phase (Fahey and Pandis, 2001). When the liquid water content is larger than 0.05 g m\(^{-3}\), aerosol particles larger than the activation diameter of 0.7 µm (Strader et al., 1998) are assumed to instantly form cloud droplets. The model selects whether to use a bulk or two-section (split at 2.5 µm dry diameter) approach for each operator time step for each cell using the decision algorithm of Fahey and Pandis (2001).

**A2.12 Mercury chemistry module**

Three mercury species are simulated by PMCAMx: elemental gaseous mercury (Hg\(^0\)), gaseous oxidized mercury (Hg\(^{2+}\)) and primary particulate mercury (Hg(p)). The model requires that all three or none of these species be included in a simulation. Therefore, mercury chemistry is not required for PM modeling, but if mercury chemistry is selected then all three mercury species must be modeled. The mercury transformation processes include the gas-phase oxidation of Hg\(^0\) to Hg\(^{2+}\), the aqueous
phase oxidation of Hg$^0$ to Hg$^{2+}$, the aqueous-phase reduction of Hg$^{2+}$ to Hg$^0$, various aqueous phase equilibria of Hg$^{2+}$ and the aqueous-phase adsorption of Hg$^{2+}$ on PM.

The gas-phase transformations include the oxidation of Hg$^0$ to Hg$^{2+}$ by bromine (Br) (Goodsite et al., 2004), hypobromite (BrO) (Raofie and Ariya, 2004), hydroxyl radical (OH) (Sommar et al., 2001), ozone (O$_3$) (Hall, 1995), HCl (Hall and Bloom, 1993), hydrogen peroxide (H$_2$O$_2$), (Tokos et al., 1998) and molecular chlorine (Cl$_2$) (Ariya et al., 2002). The reaction rate constants in all the gas-phase reactions are for temperatures in the range of 20 to 25°C; no temperature dependence information is available.

The aqueous-phase chemistry includes the oxidation of Hg$^0$ to Hg$^{2+}$ by dissolved OH (Lin and Pehkonen, 1997), O$_3$ (Munthe, 1992) and Cl$_2$ (Lin and Pehkonen, 1998) as well as the reduction of Hg$^{2+}$ to Hg$^0$ via reaction with hydroperoxyl radicals (HO$_2$) (Pehkonen and Lin, 1998) and by the formation of the sulfite complexes, HgSO$_3$ and Hg(SO$_3$)$_2^{2-}$ (van Loon et al., 2000). The rate constants for the aqueous-phase kinetics are for temperatures in the range of 20 to 25°C. Temperature dependence information is available only for the HgSO$_3$ reduction reaction. Adsorption of Hg$^{2+}$ species on atmospheric particulate matter (PM) is simulated, using an adsorption coefficient ($K = 34 \text{ L g}^{-1}$) recommended by Seigneur et al. (1998).

The concentrations of most of the species reacting with mercury are available from PMCAMx. However Br, BrO and Cl$_2$ are not explicitly simulated and vertical profiles for their concentrations are specified. For Br and BrO, vertical profiles over land and ocean are prescribed, with higher values over ocean than over land. During nighttime Br and BrO concentrations are assumed to be zero (Holmes et al., 2010). The Cl$_2$ concentrations are prescribed to be non-zero over the ocean and zero elsewhere. Its vertical concentrations during daytime are lower than nighttime values.
to account for the photolysis of Cl₂ during the day. The aqueous concentrations of OH and HO₂ are calculated from the gas-phase concentrations using their temperature-dependent Henry’s law constants (Jacobson, 1999). However, since there is not an explicit treatment for the cloud chemistry of OH and HO₂ radicals and due to the fact that the concentrations of these radicals can be reduced by their heterogeneous chemistry within clouds (Jacob, 2000; Jaegle et al., 2001), in the PMCAMx implementation the gas-phase concentrations of OH and HO₂ within clouds are reduced by factors of 2 and 10 respectively.

PMCAMx simulates both dry and wet deposition for mercury. Dry deposition is simulated using the resistance model of Wesely (1989) while the change in concentration within or below a cloud due to precipitation is parameterized using a scavenging coefficient. For Hg₀, its dry deposition is simulated by assuming a Henry’s law constant equal to 0.1 M atm⁻¹ at 298 K. The Henry’s Law constant of Hg²⁺ is assumed to be similar to that of HNO₃ based on the assumption that the two gases have similar solubility. No temperature dependence is assumed for the Hg²⁺ Henry constant because there is no information available to determine this. As it mentioned before, the surface resistance for strong acids, such as HNO₃ is neglected by setting the surface reactivity to zero. Although, the surface reactivity for Hg²⁺ is set to unity so that surface resistance will be calculated based on the Henry’s Law constant using Wesely’s module.
A3 References


Σύνοψη Διδακτορικής Διατριβής
ΠΕΡΙΛΗΨΗ

Η πλήρης κατανόηση των φυσικών και χημικών διεργασιών της ατμόσφαιρας καθώς και η μελέτη των αλληλεπιδράσεων του κλίματος και των εκπομπών, με τις συγκεντρώσεις των ρύπων αποτελεί απαραίτητη προϋπόθεση για την εφαρμογή αποτελεσματικών στρατηγικών μείωσης της ατμοσφαιρικής ρύπανσης. Κατάλληλα για αυτόν τον σκοπό είναι τα τρισδιάστατα μοντέλα χημικής μεταφοράς.

Ένα τρισδιάστατο μοντέλο χημικής μεταφοράς, το PMCAMx-2008, χρησιμοποιήθηκε για να μελετήσουμε την επίδραση που έχει η μείωση κατά 50% των εκπομπών των κυριότερων πρόδρομων αέριων ενώσεων (SO₂, NH₃, NOₓ, ανθρωπογενών πτητικών οργανικών ενώσεων) και των πρωτογενών οργανικών σωματιδίων που προέρχονται από ανθρωπογενείς πηγές (POA), καθώς και η αύξηση της θερμοκρασίας κατά 2.5 και 5 K, στην συγκέντρωση των ατμοσφαιρικών σωματιδίων διαμέτρου έως 2.5 μμ (PM₁.₅) στην Ευρώπη. Προσομοιώθηκαν δύο περιόδοι (καλοκαίρι και χειμώνας), προκειμένου να ελεγχθεί και η εποχιακή εξάρτηση της απόκρισης των PM₂.₅. Η μείωση των εκπομπών NH₃ φαίνεται να είναι η πιο αποτελεσματική στρατηγική μείωσης των PM₂.₅, κατά την διάρκεια και των δύο περιόδων, μειώνοντας τη συγκέντρωσή τους έως 5.1 μg m⁻³ το καλοκαίρι και 1.8 μg m⁻³ τον χειμώνα, κυρίως λόγω μείωσης του νιτρικού αμμωνίου (NH₄NO₃) (20% κατά μέσο όρο σε όλη την Ευρώπη). Η μείωση των εκπομπών SO₂ είναι ιδιαίτερα αποτελεσματική το καλοκαίρι κυρίως στα Βαλκάνια όπου η συγκέντρωση των PM₂.₅ μειώνεται έως 1.6 μg m⁻³ (34% μείωση των θειίκων). Η μείωση των εκπομπών πρωτογενών οργανικών σωματιδίων μειώνει την συγκέντρωση των οργανικών και τες 2 περιόδους. Η μείωση είναι μεγαλύτερη τον χειμώνα (15%) κυρίως σε αστικές περιοχές. Μικρή μείωση των οργανικών περιμένουμε και από την μείωση των ανθρωπογενών εκπομπών πτητικών οργανικών ενώσεων. Η στρατηγική μείωσης των
NO_\text{x} \ \text{μειώνει} \ \text{τα} \ \text{PM}_{2.5} \ \text{το} \ \text{καλοκαίρι}, \ \text{προκαλώντας} \ \text{ωστόσο} \ \text{αύξηση} \ \text{του} \ \text{O}_3 \ \text{στην} \ \text{Δυτική} \ \text{Ευρώπη} \ \text{και} \ \text{τα} \ \text{μεγάλα} \ \text{αστικά} \ \text{κέντρα}. \ \text{Επιπρόσθετα,} \ \text{τον} \ \text{χειμώνα} \ \text{αυξάνει} \ \text{και} \ \text{τα} \ \text{PM}_{2.5} \ \text{στις} \ \text{περισσότερες} \ \text{περιοχές} \ \text{της} \ \text{Ευρώπης}. \ \text{Η} \ \text{αύξηση} \ \text{της} \ \text{θερμοκρασίας} \ \text{οδηγεί} \ \text{σε} \ \text{μείωση} \ \text{των} \ \text{PM}_{2.5} \ \text{στην} \ \text{κεντρική} \ \text{Ευρώπη,} \ \text{κατά} \ \text{την} \ \text{διάρκεια} \ \text{και} \ \text{των} \ 2 \ \text{περιόδον,} \ \text{κυρίως} \ \text{λόγω} \ \text{μείωσης} \ \text{του} \ \text{NH}_4\text{NO}_3 \ \text{το} \ \text{καλοκαίρι} \ (18\% \ \text{κατά} \ \text{μέσο} \ \text{όρο}) \ \text{και} \ \text{των} \ \text{POA} \ \text{τον} \ \text{χειμώνα} \ (35\% \ \text{κατά} \ \text{μέσο} \ \text{όρο}). \ \text{Η} \ \text{αύξηση} \ \text{της} \ \text{θερμοκρασίας} \ \text{αυξάνει} \ \text{επίσης} \ \text{τα} \ \text{οξειδωτικά} \ \text{μέσα} \ \text{(OH, O}_3, \ \text{κτλ.}) \ \text{και} \ \text{κατά} \ \text{συνέπεια} \ \text{ευνοεί} \ \text{το} \ \text{σχηματισμό} \ \text{των} \ \text{θειικών} \ \text{σωματιδίων}, \ \text{κυρίως} \ \text{στην} \ \text{Βόρεια} \ \text{Ευρώπη} \ \text{και} \ \text{τον} \ \text{Ατλαντικό} \ \text{Ωκεανό.}

\text{Τα} \ \text{προηγούμενα} \ \text{αποτελέσματα} \ \text{δείχνουν} \ \text{πως} \ \text{οι} \ \text{συγκεντρώσεις} \ \text{των} \ \text{PM}_{2.5} \ \text{είναι} \ \text{ιδιαίτερα} \ \text{ευαίσθητες} \ \text{στις} \ \text{αλλαγές} \ \text{της} \ \text{θερμοκρασίας}. \ \text{Παρόμοια} \ \text{αποτελέσματα} \ \text{σχετικά} \ \text{με} \ \text{τον} \ \text{ρόλο} \ \text{της} \ \text{μετεωρολογίας} \ \text{στις} \ \text{συγκεντρώσεις} \ \text{των} \ \text{PM}_{2.5} \ \text{έχουν} \ \text{βρεθεί} \ \text{και} \ \text{σε} \ \text{παλαιότερες} \ \text{μελέτες,} \ \text{ωστόσο} \ \text{οι} \ \text{περισσότερες} \ \text{από} \ \text{αυτές} \ \text{δίνουν} \ \text{έμφαση} \ \text{στην} \ \text{συνολική} \ \text{επίδραση} \ \text{των} \ \text{αλλαγών} \ \text{του} \ \text{κλίματος}, \ \text{χωρίς} \ \text{να} \ \text{εξετάζουν} \ \text{την} \ \text{σημασία} \ \text{που} \ \text{έχει} \ \text{η} \ \text{κάθε} \ \text{παράμετρος} \ \text{ξεχωριστά.} \ \text{Για} \ \text{τον} \ \text{λόγο} \ \text{αυτό,} \ \text{εφαρμόσαμε} \ \text{το} \ \text{PMCAMx-2008} \ \text{στην} \ \text{Ευρώπη,} \ \text{μελετώντας} \ \text{την} \ \text{επίδραση} \ \text{που} \ \text{έχουν} \ \text{διάφορες} \ \text{παράμετροι} \ \text{της} \ \text{μετεωρολογίας} \ \text{θερμοκρασία,} \ \text{άνεμος,} \ \text{απόλυτη} \ \text{υγρασία,} \ \text{βροχόπτωση,} \ \text{όψεις} \ \text{ανάμειξης} \ \text{στις} \ \text{συγκεντρώσεις} \ \text{των} \ \text{PM}_{2.5}, \ \text{καλύπτοντας} \ \text{τρεις} \ \text{περιόδους} \ \text{προσομοίωσης} \ \text{καλοκαίρι,} \ \text{χειμώνας} \ \text{και} \ \text{φθινόπωρο}. \ \text{Τα} \ \text{αποτελέσματα} \ \text{μας} \ \text{δείχνουν} \ \text{πως} \ \text{τα} \ \text{PM}_{2.5} \ \text{είναι} \ \text{ιδιαίτερα} \ \text{ευαίσθητα} \ \text{στις} \ \text{αλλαγές} \ \text{στην} \ \text{θερμοκρασία} \ \text{σε} \ \text{σχέση} \ \text{με} \ \text{τις} \ \text{υπόλοιπες} \ \text{παραμέτρους.} \ \text{Η} \ \text{αύξηση} \ \text{της} \ \text{θερμοκρασίας} \ \text{κατά} \ 2 \ \text{K} \ \text{οδηγεί} \ \text{σε} \ \text{μείωση} \ \text{της} \ \text{συγκέντρωσης} \ \text{των} \ \text{PM}_{2.5} \ \text{και} \ \text{τες} \ \text{τρεις} \ \text{περιόδους.} \ \text{Ωστόσο,} \ \text{οι} \ \text{προβλεπόμενες} \ \text{αλλαγές} \ \text{δεν} \ \text{είναι} \ \text{χωρικά} \ \text{ομοιόμορφες,} \ \text{λόγω} \ \text{της} \ \text{διαφορετικής} \ \text{απόκρισης} \ \text{των} \ \text{συστατικών} \ \text{των} \ \text{PM}_{2.5} \ \text{στην} \ \text{αύξηση} \ \text{της} \ \text{θερμοκρασίας,} \ \text{και} \ \text{κυμαίνονται} \ \text{από} \ -700 \ \text{ng} \ \text{m}^{-3} \ \text{K}^{-1} \ (-8\% \ \text{K}^{-1}) \ \text{έως} \ 300 \ \text{ng} \ \text{m}^{-3} \ \text{K}^{-1} \ (7\% \ \text{K}^{-1}). \ \text{Η} \ \text{μείωση} \ \text{των} \ \text{PM}_{2.5} \ \text{οφείλεται} \ \text{κυρίως} \ \text{στην} \ \text{εξάτμιση} \ \text{του} \ \text{νιτρικού} \ \text{αμμωνίου} \ (15\% \ \text{κατά} \ \text{μέσο}
όρο), ενώ αντίθετα η αύξηση των βιογενών VOC εκπομπών καθώς και των ρυθμών αντίδρασης στην αέρια φάση, αυξάνει τα οργανικά και θειικά σωματίδια. Η αύξηση της απόλυτης υγρασίας κατά 5% οδηγεί σε αλλαγές της συγκέντρωσης των PM$_{2.5}$ που κυμαίνονται από -130 ng m$^{-3}$ %$^{-1}$ (-1.6% %$^{-1}$) έως 160 ng m$^{-3}$ %$^{-1}$ (1.6% %$^{-1}$). Το καλοκαίρι και το φθινόπωρο, η αύξηση της απόλυτης υγρασίας ευνοεί την κατανομή του ελεύθερου νιτρικού οξέος στην σωματιδιακή φάση (αύξηση έως 15%), αυξάνοντας την μέση συγκέντρωση των PM$_{2.5}$, ενώ αντίθετα τον χειμώνα κυριαρχεί η μείωση των θειικών και των σωματιδίων από θαλασσινό αλάτι. Η μείωση της ταχύτητας του ανέμου (χωρίς αλλαγή στις εκπομπές από θαλασσινό αλάτι) αυξάνει τα PM$_{2.5}$ (0.6% %$^{-1}$ κατά μέσο όρο για όλες τις περιόδους), κυρίως λόγω μείωσης της ξηρής εναπόθεσης (περίπου 10%) και των διεργασιών μεταφοράς. Αντίστοιχα οι αλλαγές στις εκπομπές από θαλασσινό αλάτι (λόγω μείωσης του ανέμου κατά 10%) επηρεάζουν σημαντικά τα PM$_{2.5}$ κυρίως στις θαλάσσιες περιοχές και τον ωκεανό. Η αύξηση της βροχόπτωσης αυξάνει τον ρυθμό υγρής εναπόθεσης, τόσο των PM$_{2.5}$ όσο και των αέριων πρόδρομων ενώσεων τους, οδηγώντας σε μείωση των συγκεντρώσεων τους. Οι αλλαγές στο ύψος ανάμειξης δεν προβλέπεται να έχουν πολύ μεγάλη επίδραση στην συγκέντρωση των PM$_{2.5}$. Με βάση τις εκτιμώμενες αλλαγές της κάθε μετεωρολογικής παραμέτρου για το μέλλον, οι αλλαγές στην βροχόπτωση αναμένεται να έχουν πολύ μεγάλη επίδραση στην συγκέντρωση των PM$_{2.5}$. Με βάση τις εκτιμώμενες αλλαγές της κάθε μετεωρολογικής παραμέτρου για το μέλλον, οι αλλαγές στην βροχόπτωση αναμένεται να έχουν πολύ μεγάλη επίδραση στη συγκέντρωση των PM$_{2.5}$, κατά την διάρκεια όλων των περιόδων, οδηγώντας σε αλλαγές των συγκεντρώσεων τους έως 2 μg m$^{-3}$. Οι εκτιμώμενες αλλαγές στην ταχύτητα του ανέμου είναι επίσης σημαντικές για τα PM$_{2.5}$, επηρεάζοντας τις συγκεντρώσεις τους παρόμοια με τις 3 περιόδους, οδηγώντας ωστόσο σε μικρότερες αλλαγές σε σχέση με την βροχόπτωση (έως 1.4 μg m$^{-3}$). Οι αλλαγές στην απόλυτη υγρασία αναμένεται να είναι σημαντικές κυρίως σε περιόδους και περιοχές με υψηλές συγκεντρώσεις νιτρικού αμμωνίου, ενώ οι αλλαγές
της θερμοκρασίας αναμένεται να έχουν μικρότερη επίδραση λόγω της διαφορετικής απόκρισης των συστατικών των PM$_{2.5}$.

Για να μελετήσουμε την επίδραση που έχει η κλιματική αλλαγή στις συγκεντρώσεις των PM$_{2.5}$ και του όζοντος (O$_3$), το PMCAMx-2008 χρησιμοποιήθηκε σαν μέρος ενός συστήματος μοντέλων, του GRE-CAPS, το οποίο εφαρμόστηκε πάνω από την Ευρώπη, εστιάζοντας στην Ελλάδα. Η προσομοίωση του κλίματος έγινε για την εποχή του καλοκαιριού, ενώ για την προσομοίωση του κλίματος στο μέλλον, υιοθετήθηκε το σενάριο A1B της Διακυβερνητικής Επιτροπής για την Αλλαγή το Κλίματος (IPCC) για το 2050. Τα αποτελέσματα δείχνουν πως οι συγκεντρώσεις των PM$_{2.5}$ στην Ελλάδα προβλέπεται να μειωθούν στο μέλλον. Βάσει του σεναρίου A1B τα PM$_{2.5}$ μειώνονται 1.1 µg m$^{-3}$ (5%) κατά μέσο όρο σε όλο το πεδίο εφαρμογής, ωστόσο οι προβλεπόμενες αλλαγές της συγκέντρωσης είναι αρκετά μεταβλητές και κυμαίνονται από -20% έως 20%. Η μεγαλύτερη μείωση προβλέπεται στην Κεντρική Ελλάδα (5.5% κατά μέσο όρο), λόγω αύξησης της ταχύτητας του ανέμου και μείωσης της απόλυτης υγρασίας. Μείωση προβλέπεται επίσης στην Βόρεια Ελλάδα και το Βόρειο Αιγαίο. Στην Κρήτη και την Πελοπόννησο, η αύξηση της θερμοκρασίας και της απόλυτης υγρασίας ευνοεί τους σχηματισμούς οργανικών και νιτρικών σωματιδίων οδηγώντας σε αύξηση των PM$_{2.5}$. Η συγκέντρωση του O$_3$ αυξάνει στην Ελλάδα 4.5% κατά μέσο όρο, με την αύξηση της θερμοκρασίας να καθορίζει σε μεγάλο βαθμό την απόκριση του στην αλλαγή του κλίματος. Στην υπόλοιπη Ευρώπη, οι αλλαγές στην συγκέντρωση των PM$_{2.5}$, λόγω κλιματικής αλλαγής, κυμαίνονται από -25% έως 25%, ενώ η συγκέντρωση του O$_3$ προβλέπεται να αυξηθεί στην Νότια Ευρώπη (έως 17%) καθώς επίσης και στα Βαλκάνια, και να μειωθεί στις βόρειες περιοχές (έως 10%).

Το σύστημα μοντέλων GRE-CAPS εφαρμόσθηκε στις ανατολικές ΗΠΑ για την μελέτη της επίδρασης της αλλαγής του κλίματος στην συγκέντρωση και εναπόθεση
του υδραργύρου. Η προσομοίωση του κλίματος στο παρόν και το μέλλον έγινε για δύο περιόδους, καλοκαίρι και χειμώνας (300 ημέρες προσομοίωσης σε κάθε περίοδο).

Κατά μέσο όρο σε όλο το πεδίο εφαρμογής, η συγκέντρωση του Hg\(^{2+}\) στο μέλλον αυξάνεται κατά 3% το καλοκαίρι και 5% τον χειμώνα. Ωστόσο οι προβλεπόμενες αλλαγές είναι αρκετά μεταβλητές, και κυμαίνονται από -30% έως 30% το καλοκαίρι και από -20% έως 40% τον χειμώνα. Η αύξηση της συγκέντρωσης της ρίζας του ΟΗ λόγω αύξησης της θερμοκρασίας στο μέλλον, η οποία ευνοεί την αντίδραση οξείδωσης του Hg\(^{0}\) για τον σχηματισμό Hg\(^{2+}\), καθώς και οι προβλεπόμενες, ιδιαίτερα μεταβλητές τοπικά, αλλαγές στην βροχόπτωση επηρεάζουν την απόκριση του Hg\(^{2+}\) στην αλλαγή του κλίματος. Η επίδραση της αλλαγής του κλίματος στην συγκέντρωση των πρωτογενών σωματιδίων υδραργύρου, Hg(p) είναι παρόμοια με εκείνη του Hg\(^{2+}\). Ωστόσο, οι αλλαγές δεν είναι ομοιόμορφες και κυμαίνονται από -50% έως 50% το καλοκαίρι και από -30% έως 50% τον χειμώνα. Η αλλαγή της υγρής εναπόθεσης του Hg\(^{0}\), λόγω αλλαγής της βροχόπτωσης, φαίνεται να εξηγεί την απόκριση της εναπόθεσης του Hg, στις περισσότερες περιοχές.

**Β2 ΕΙΣΑΓΩΓΗ**

Η ατμοσφαιρική ρύπανση αποτελεί ένα σημαντικό πρόβλημα στις μέρες μας τόσο σε τοπική όσο και σε παγκόσμια κλίμακα. Η διαρκής ανάπτυξη των ανθρωπογενών δραστηριοτήτων από την προ-βιομηχανική εποχή έως σήμερα έχει ως αποτέλεσμα την αύξηση των εκπομπών των αέριων και σωματιδιακών ρύπων, καθώς και των βαρών μετάλλων, με σοβαρές επιπτώσεις στην ανθρώπινη υγεία, τα
οικοσυστήματα και το κλίμα. Παράλληλα η αύξηση των αερίων του θερμοκηπίου
tους τελευταίους 3 αιώνες έχει οδηγήσει σε θέρμανση του πλανήτη. Σύμφωνα με
έκθεση της Διακυβερνητικής Επιτροπής για την Αλλαγή του Κλίματος, (IPCC) [1], η
θερμοκρασία της Γης αυξήθηκε κατά την διάρκεια του προηγούμενου αιώνα, περίπου
0.7 °C. Αντίστοιχες εκτιμήσεις της IPCC για τον 21ο αιώνα αναφέρουν αύξηση της
μέσης θερμοκρασίας της Γης που θα κυμαίνεται μεταξύ 1.1-6.4 °C.

Τα αεροζόλα είναι σωματίδια τα οποία αιωρούνται στην ατμόσφαιρα και
προέρχονται είτε από απευθείας εκπομπή τους από διάφορες πηγές είτε από την
χημική μετατροπή αέριων ρύπων σε σωματίδια. Σε υψηλές συγκέντρώσεις μπορούν
να προκαλέσουν σημαντικά προβλήματα υγείας στους ανθρώπους, ενώ ιδιαίτερα τα
ατμοσφαιρικά σωματίδια με διάμετρο έως και 2.5 μ (PM2.5), σύμφωνα με
επιδημιολογικές μελέτες, προκαλούν σημαντική αύξηση της θνησιμότητας. Σύμφωνα
με έκθεση του Παγκόσμιου Οργανισμού Υγείας [2], υπολογίζεται πως στην Ευρώπη
περίπου 100.000 άτομα τον χρόνο πεθαίνουν εξαιτίας της έκθεσης τους σε υψηλές
συγκέντρώσεις αεροζόλ. Τα ατμοσφαιρικά σωματίδια εμπλέκονται επίσης στον
σχηματισμό της οξινής βροχής και ομίχλης [3], την μείωση της ορατότητας [4],
kαθώς σε άλλες περιπτώσεις επηρεάζουν την ορατότητα [4]. Τα
ατμοσφαιρικά σωματίδια είναι επίσης οι πυρήνες συμπύκνωσης πάνω στους οποίους
συμπυκνώνονται το νερό και δημιουργούνται οι σταγόνες των σύννεφων. Αν δεν
υπήρχαν αυτά τα σωματίδια στην ατμόσφαιρα μας η σχετική υγρασία θα έφτανε
μέχρι και 500%.

Τα βαρέα μέταλλα (υδράργυρος, μόλυβδος, κάδμιο, κ.α.) αποτελούν, και αυτά
μέρος του προβλήματος της ατμοσφαιρικής ρύπανσης. Παρόλο που η συγκέντρωση
tους στην ατμόσφαιρα είναι μικρή σε σχέση με άλλους αέριους ρύπους, η τοξικότητα

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τους, ωστόσο, τους κάνει ιδιαίτερα επικίνδυνους τόσο για την ανθρώπινη υγεία όσο και για το περιβάλλον. Ο υδράργυρος για παράδειγμα, αν και βρίσκεται σε χαμηλά επίπεδα στην ατμόσφαιρα [5,6], όταν εναποτεθεί και καταλήξει σε υδάτινους φορείς μετατρέπεται σε μία ιδιαίτερα τοξική μορφή, τον μεθυλυδράργυρο ο οποίος συσσωρεύεται στους οργανισμούς των ψαριών, και σε υψηλές συγκεντρώσεις μπορεί να επηρεάσει την τροφική αλυσίδα και κατ’ επέκταση την ανθρώπινη υγεία [7,8].

Για να μπορέσουμε να αναπτύξουμε αποτελεσματικές στρατηγικές ελέγχου, ώστε να επιτευχθούν ικανοποιητικά επίπεδα ποιότητας της ατμόσφαιρας, θα πρέπει να μπορούμε να προσδιορίσουμε τις συγκεντρώσεις των ρύπων της ατμόσφαιρας (ατμοσφαιρικά σωματίδια, βαρέα μέταλλα, O₃), τις πηγές τους, τις ιδιότητές τους καθώς και την σημασία τους τόσο στο τοπικό όσο και το παγκόσμιο κλίμα. Κατάλληλα για τον σκοπό αυτό είναι τα τρισδιάστατα μοντέλα προσομοίωσης της ατμόσφαιρας καθώς παρέχουν το απαραίτητο πλαίσιο εργασίας για την ακριβή και αποτελεσματική περιγραφή των φυσικών και χημικών διεργασιών της ατμόσφαιρας, καθώς και για την πλήρη κατανόηση των αλληλεπιδράσεων του κλίματος, και των εκπομπών με τις συγκεντρώσεις των ρύπων.

**Β3 ΠΕΡΙΓΡΑΦΗ ΤΟΥ ΜΟΝΤΕΛΟΥ**

Στην παρούσα εργασία, το τρισδιάστατο μοντέλο χημικής μεταφοράς που χρησιμοποιείται είναι PMCAMx-2008 [9]. Η γενική εξίσωση που επιλύει για την περιγραφή της αλλαγής της συγκέντρωσης σαν συνάρτηση του χρόνου ενός συγκεκριμένου ρύπου, cₓ, είναι:
Η αλλαγή της συγκέντρωσης $c_i$ ενός ρύπου όπως περιγράφεται από την προηγούμενη εξίσωση εξαρτάται από την κίνηση της αέριας μάζας, τη διασπορά, την αέρια χημεία, τις εκπομπές, την υγρή και ξηρή εναπόθεση, τις διεργασίες των αεροζόλων (πυρηνογένεση, συσσωμάτωση και συμπύκνωση/εξάτμιση) και την χημεία στα σύννεφα. Ο χημικός μηχανισμός που χρησιμοποιείται σε αυτό το μοντέλο για την περιγραφή της αέριας χημείας είναι βασισμένος στον μηχανισμό SAPRC99 [10] ο οποίος περιλαμβάνει 211 αντιδράσεις με 56 αέριες ενώσεις και 18 ελεύθερες ρίζες. Αντίστοιχα, τα συστατικά των σωματιδίων που προσομοιώνει το μοντέλο είναι 16 και ανάλογα με την διάμετρό τους, η οποία κυμαίνεται από 40 nm έως 40 μμ, χωρίζονται σε 10 τμήματα.

Η προσομοίωση της κάθε διεργασίας στο μοντέλο γίνεται ξεχωριστά σε κάθε χρονικό βήμα ενώ για την αριθμητική επίλυση των αντίστοιχων μερικών διαφορικών εξισώσεων χρησιμοποιείται μία προσέγγιση χωρίζομενων διαφορικών εξισώσεων (operator splitting). Το χρονικό βήμα της προσομοίωσης μεταβάλλεται προκειμένου να διαφυλάχτει η αριθμητική σταθερότητα κατά την οριζόντια μεταφορά ρύπων και τυπικά κυμαίνεται από 5 έως 15 λεπτά, ενώ μικρότερα χρονικά βήματα χρησιμοποιούνται για την προσομοίωση της κάθε διεργασίας προκειμένου να διατηρηθεί η ακρίβεια της λύσης. Η σειρά με την οποία το μοντέλο προσομοιώνει την κάθε διεργασία είναι: εκπομπές αέριων και σωματιδιακών ρύπων, οριζόντια μεταφορά ρύπων, κατακόρυφη μεταφορά ρύπων, κατακόρυφη διασπορά, οριζόντια διασπορά, υγρή εναπόθεση, αέρια χημεία, διεργασίες των αεροζόλων (πυρηνογένεση,
συσσωμάτωση, συμπύκνωση και εξάτμιση των ανόργανων ενώσεων), σχηματισμός
dευτερογενών οργανικών σωματιδίων και υγρή χημεία.

Μία σημαντική βελτίωση του PMCAMx-2008 σε σχέση με τις προηγούμενες
eκδόσεις του μοντέλου, έγινε στον τρόπο περιγραφής των οργανικών σωματιδίων. Οι προηγούμενες εκδόσεις του PMCAMx (καθώς και όλα τα υπάρχοντα μοντέλα) υπέθεταν ότι τα πρωτογενή οργανικά σωματίδια είναι μη πτητικά και μη ενεργά, κάτι που στην πραγματικότητα δεν συμβαίνει. Το PMCAMx-2008 προσομοιώνει τον καταμερισμό των πρωτογενών οργανικών εκπομπών θεωρώντας τα πρωτογενή οργανικά σωματίδια ως ημιπτητικά. Για το σκοπό αυτό, βάσει της προσέγγισης που ανέπτυξαν οι Shrivastava et al. [11] χρησιμοποιούνται εννέα ομάδες ενώσεων με συγκεντρώσεις κορεσμού από $10^{-2}$ μg m$^{-3}$ έως $10^{6}$ μg m$^{-3}$ στους 298 Κ.

Το μοντέλο θεωρεί επίσης, ότι όλα τα οργανικά συστατικά των σωματιδίων (πρωτογενή και δευτερογενή) είναι χημικώς ενεργά. Στην προσέγγιση αυτή, οι πρωτογενείς ατμοί που σχηματίστηκαν λόγω της εξάτμισης ενός μέρους των πρωτογενών εκπομπών, αντιδρούν με την ρίζα του υδροξυλίου μειώνοντας την πτητικότητά τους. Η σταθερά ρυθμού της αντίδρασης είναι $4 \times 10^{11}$ cm$^3$ mol$^{-1}$ s$^{-1}$ ενώ κάθε τέτοια αντίδραση θεωρείται ότι μειώνει την πτητικότητα του οργανικού ατμού κατά μία τάξη μεγέθους.

**Β4 ΕΠΙΔΡΑΣΗ ΤΗΣ ΑΛΛΑΓΗΣ ΤΗΣ ΘΕΡΜΟΚΡΑΣΙΑΣ ΚΑΙ ΤΩΝ ΕΚΠΟΜΠΩΝ ΣΤΗΝ ΣΥΓΚΕΝΤΡΩΣΗ ΤΩΝ ΑΤΜΟΣΦΑΙΡΙΚΩΝ ΣΩΜΑΤΙΔΙΩΝ ΣΤΗΝ ΕΥΡΩΠΗ**

Τα ατμοσφαιρικά σωματίδια, το O$_3$ καθώς και άλλοι αέριοι ρύποι συνδέονται μεταξύ τους μέσω ενός πολύπλοκου δικτύου κοινών εκπομπών, μετεωρολογικών διαδικασιών και φωτοχημικών αντιδράσεων. Η αλλαγή στις εκπομπές ενός ρύπου

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μπορεί να οδηγήσει σε αλλαγές (θετικές ή αρνητικές) της συγκέντρωσης άλλων ρύπων. Επιπρόσθετα, μια ενδεχόμενη αλλαγή στην μετεωρολογία, όπως η αύξηση της θερμοκρασίας, μπορεί να επηρεάσει διάφορες διεργασίες (π.χ. αύξηση των βιογενών εκπομπών, αλλαγή στους ρυθμούς αντίδρασης της αέριας χημείας) που επηρεάζουν τις συγκεντρώσεις των ρύπων της ατμόσφαιρας. Στόχος αυτής της εργασίας είναι να μελετήσουμε την επίδραση που έχουν διαφορετικές στρατηγικές μείωσης εκπομπών καθώς και διαφορετικά σενάρια αύξησης της θερμοκρασίας, στην συγκέντρωση των ατμοσφαιρικών σωματιδίων διαμέτρου έως 2.5 μ m (PM2.5) στην Ευρώπη. Η χρήση του τρισδιάστατου μοντέλου PMCAMx-2008 εξυπηρετεί στην υλοποίηση αυτού του στόχου καθώς συνδέει την μετεωρολογία, τις εκπομπές των πρόδρομων ρύπων και τις συγκεντρώσεις των σωματιδίων μέσω μιας αναλυτικής περιγραφής των φυσικών και χημικών διεργασιών της ατμόσφαιρας.

B4.1 Εφαρμογή του μοντέλου

Το PMCAMx-2008 [9] εφαρμόστηκε πάνω από την Ευρώπη, καλύπτοντας μία περιοχή 5400×5832 km με ανάλυση πλέγματος 36×36 km και 14 κατακόρυφα επίπεδα περίπου 6 km. Τα μετεωρολογικά δεδομένα του μοντέλου περιλαμβάνουν οριζόντιους ανέμους, θερμοκρασία, πίεση, υδρατμός, κατακόρυφη διάχυση, σύννεφα και βροχοπτώσεις. Όλα αυτά προέρχονται από το μετεωρολογικό μοντέλο WRF (Weather Research and Forecasting) [12]. Αντίστοιχα, χρησιμοποιήθηκαν οριαίες εκπομπές αέριων και σωματιδιακών ρύπων τόσο από ανθρωπογενείς [13, 14, 15] όσο και από βιογενείς πηγές [16,17,18].
B4.2 Ανάλυση Ευαισθησίας

Για να μελετήσουμε την απόκριση των PM_{2.5} στις αλλαγές των εκπομπών ρύπων πραγματοποιήσαμε μία ανάλυση ευαισθησίας μειώνοντας κατά 50% τις εκπομπές των κυριότερων πρόδρομων αέριων ενώσεων (SO_{2}, NH_{3}, NO_{x}, ανθρωποπογενών πτητικών οργανικών ενώσεων VOCs) καθώς και των πρωτογενών οργανικών σωματιδίων(POA) που προέρχονται από ανθρωποπογενείς πηγές. Για την επίδραση της θερμοκρασίας, πραγματοποιήσαμε δύο σενάρια αύξησης της κατά 2.5 και 5 K. Δύο περιόδοι προσομοιώθηκαν (καλοκαίρι και χειμώνας), ώστε να ελεγχθεί και η εποχιακή εξάρτηση της απόκρισης των PM_{2.5} στις αλλαγές των εκπομπών και της θερμοκρασίας.

B4.3 Αποτελέσματα – Ανάλυση

Η μέση προβλεπόμενη συγκέντρωση σε επίπεδο εδάφους των PM_{2.5}, για τις δύο περιόδους παρουσιάζεται στην Εικόνα 1. Το καλοκαίρι, υψηλές συγκέντρωσεις PM_{2.5} προβλέπονται στην δυτική Ευρώπη κυρίως λόγω των υψηλών συγκέντρωσεων NH_{4}NO_{3}. Αντίστοιχα, υψηλές συγκέντρωσεις των PM_{2.5} προβλέπονται και στην Μεσόγειο, κυρίως λόγω αυξημένης συγκέντρωσης των θειικών, ενώ υψηλές συγκέντρωσεις για τα οργανικά σωματίδια προβλέπονται στην κεντρική και βόρεια Ευρώπη.

Για την περίοδο του χειμώνα τα οργανικά σωματίδια κυριαρχούν στην κεντρική και βόρεια Ευρώπη, ιδιαίτερα σε περιοχές με σημαντικές πηγές εκπομπών πρωτογενών οργανικών σωματιδίων. Οι συγκέντρώσεις των ανόργανων σωματιδίων προβλέπονται να είναι χαμηλότερες από το καλοκαίρι.
Η μείωση των εκπομπών NH₃ κατά 50% μειώνει τα PM₂.₅ και τις 2 περιόδους. Η NH₃ στην αέρια φάση έχει την τάση να αντιδρά με το H₂SO₄ για τον σχηματισμό (NH₄)₂SO₄, όταν η αναλογία των μορίων NH₃:H₂SO₄ είναι ίση με 2:1. Ωστόσο, σε περιοχές με περίσσες ελεύθερης NH₃, και υψηλή συγκέντρωση HNO₃, η ελεύθερη NH₃ θα αντιδράσει με το HNO₃ για τον σχηματισμό NH₄NO₃. Επομένως η μείωση των εκπομπών NH₃, θα οδηγήσει σε μείωση της συγκέντρωσης τόσο του NH₄NO₃ όσο και του (NH₄)₂SO₄. Αντίθετα, η μείωση των εκπομπών της NH₃ δεν φαίνεται να επηρεάζει την συγκέντρωση των οργανικών σωματιδίων.

Κατά την περίοδο του καλοκαιριού, η μεγαλύτερη μείωση των PM₂.₅ προβλέπεται στην Δυτική Ευρώπη, η οποία φθάνει τα 5.1 μg m⁻³ (22.5%) (Εικόνα 2). Σε έκεινη την περιοχή η συγκέντρωση του NH₄NO₃ μειώθηκε κατά 38%, ενώ μικρή μείωση προβλέπεται για τα θειικά (περίπου 5%). Τον χειμώνα, η μεγαλύτερη μείωση της συγκέντρωσης των PM₂.₅ προβλέπεται στην κεντρική Ευρώπη (έως 1.8 μg m⁻³ ή 10%). Κατά μέσο όρο για όλο το πεδίο εφαρμογής η μείωση των ολικών PM₂.₅ είναι περίπου 5.5% για το καλοκαίρι και 4% για τον χειμώνα αντίστοιχα.
Εικόνα 2: Μέση προβλεπόμενη αλλαγή συγκέντρωσης σε επίπεδο εδάφους (μg m⁻³) των PM₂.₅ σωματιδίων μετά την μείωση κατά 50% των εκπομπών NH₃ για (α) το καλοκαίρι και (β) τον χειμώνα. Η θετική τιμή υποδηλώνει μείωση.

Η μείωση των εκπομπών NOₓ κατά 50% το καλοκαίρι, μειώνει τα PM₂.₅ 5% κατά μέσο όρο για όλο το πεδίο εφαρμογής (Εικόνα 3). Ωστόσο, η επίδραση που έχει στα επιμέρους συστατικά των PM₂.₅ διαφέρει. Παρόλο που η μείωση των NOₓ μειώνει σημαντικά το NH₄NO₃ σε όλη την Ευρώπη, η απόκριση των θειικών και οργανικών σωματιδίων εξαρτάται από το πώς η μείωση των NOₓ επηρεάζει τα οξειδωτικά μέσα (π.χ. OH, O₃, κτλ.). Συγκεκριμένα, υπάρχει ένας ανταγωνισμός μεταξύ των NOₓ και των VOCs για την ρίζα του OH. Το υδροξύλιο αντιδρά με το NO₂ και τα VOCs με τον ίδιο ρυθμό όταν το κλάσμα συγκέντρωσης VOC:NOₓ είναι περίπου ίσο με 5.5:1 [4]. Σε περιοχές όπου η τιμή του λόγου VOC:NOₓ είναι μεγαλύτερη από 5.5:1 (περιοχές ‘περιορισμένου NOₓ’), το OH αντιδρά κυρίως με τα VOCs. Σε τέτοιες περιοχές ο ρυθμός σχηματισμού του οξέντος μειώνεται γραμμικά, καθώς μειώνεται η συγκέντρωση των NOₓ, οδηγώντας σε χαμηλότερα επίπεδα συγκέντρωσης υδροξυλίου. Επομένως, μείωση στις εκπομπές των NOₓ μπορεί να προκαλέσει μείωση στα επίπεδα των οργανικών σωματιδίων, όπως επίσης και στον
σχηματισμό του \( H_2SO_4 \) (μέσω της οξείδωσης του \( SO_2 \) με το \( OH \)) και κατ’ επέκταση των θειικών σωματιδίων. Αντίθετα, σε περιοχές όπου η τιμή του λόγου VOC:NO\(_x\) είναι μικρότερη από 5.5:1 (περιοχές ‘κορεσμένες σε NO\(_x\)’), η αντίδραση OH+NO\(_2\) κυριαρχεί. Σε αυτές τις περιοχές, μία μείωση των NO\(_x\) μπορεί να προκαλέσει αύξηση στις συγκεντρώσεις του \( O_3 \) και του \( OH \). Επομένως οι συγκεντρώσεις των οργανικών και των θειικών σωματιδίων ενδέχεται να αυξηθούν.

Εικόνα 3: Μέση προβλεπόμενη αλλαγή συγκέντρωσης σε επίπεδο εδάφους (μ\(g\) m\(^{-3}\)) των PM\(_{2.5}\) σωματιδίων μετά την μείωση κατά 50% των εκπομπών NO\(_x\) για (α) το καλοκαίρι και (β) τον χειμώνα. Η θετική τιμή υποδηλώνει μείωση.

Το καλοκαίρι, σημαντική μείωση των PM\(_{2.5}\) προβλέπεται στην κεντρική Ευρώπη (1.1 μ\(g\) m\(^{-3}\) ή 12%), κυρίως λόγω μείωσης του NH\(_4\)NO\(_3\) (38%). Στις περισσότερες περιοχές, ο λόγος VOC:NO\(_x\) είναι μεγαλύτερος του 5.5:1, επομένως η μείωση των εκπομπών NO\(_x\), μειώνει την τα οξειδωτικά μέσα και οδηγεί σε μικρή μείωση των οργανικών και θειικών. Ωστόσο, στην Δυτική Ευρώπη, ο λόγος VOC:NO\(_x\) είναι μικρότερος του 5.5:1. Σε αυτήν την περιοχή τα οξειδωτικά μέσα αυξάνονται (αύξηση \( O_3 \), 4% κατά μέσο όρο) (Εικόνα 4), όπως επίσης και οι συγκεντρώσεις των θειικών.
και οργανικών σωματιδίων. Αύξηση του O₃ προβλέπεται επίσης και στα μεγάλα 
αστικά κέντρα (π.χ. Παρίσι).

Τον χειμώνα, σχεδόν όλες οι περιοχές του πεδίου εφαρμογής, είναι κορεσμένες 
σε NOₓ (λόγος VOC:NOₓ μικρότερος του 5.5:1), επομένως η μείωση των εκπομπών 
NOₓ αυξάνει τα οξειδωτικά μέσα (η αύξηση του O₃ ξεπερνά το 10%), καθώς και την 
συγκέντρωση των PM₂.₅ σωματιδίων.

Εικόνα 4: Μέση προβλεπόμενη αλλαγή συγκέντρωσης σε επίπεδο εδάφους (ppb) του O₃ 
μετά την μείωση κατά 50% των εκπομπών NOₓ για (α) το καλοκαίρι και (β) τον 
χειμώνα. Η θετική τιμή υποδηλώνει μείωση.

Η μείωση των εκπομπών SO₂ κατά 50%, μειώνει τα PM₂.₅ και τις δύο περιόδους, 
kυρίως λόγω μείωσης των θειικών σωματιδίων (23% σε όλη την Ευρώπη). Αντίθετα 
αυξάνει τα νιτρικά ιόντα ενώ δεν φαίνεται να επηρεάζει την συγκέντρωση των 
οργανικών. Μειώνοντας τις εκπομπές του SO₂, μειώνεται η συγκέντρωση του H₂SO₄. Επομένως 
λιγότερο H₂SO₄ θα αντιδράσει με την NH₃ για τον σχηματισμό (NH₄)₂SO₄ 
και η ελεύθερη NH₃ θα αυξηθεί. Σε περιοχές όπου η διαθέσιμη ελεύθερη NH₃ είναι 
χαμηλή, η επιπρόσθετη NH₃ αντιδρά με το HNO₃ και περισσότερο HNO₃ είναι
δυνατόν να μεταφερθεί στην σωματιδιακή φάση. Ωστόσο σε περιοχές όπου η διαθέσιμη ελεύθερη NH₃ είναι υψηλή, ο σχηματισμός του NH₄NO₃ γίνεται εναόστης σε αλλαγές στην σταθερά ισορροπία του, η οποία αυξάνεται με μείωση των θειικών, επομένως το NH₄NO₃ μειώνεται.

Κατά την περίοδο του καλοκαιριού η μείωση των εκπομπών SO₂ είναι ιδιαίτερα αποτελεσματική στα Βαλκάνια (Εικόνα 5), όπου τα PM₂,5 μειώνονται περίπου 10% κατά μέσο όρο, κυρίως λόγω σημαντικής μείωσης των θειικών σωματιδίων (34%). Αντίθετα η συγκέντρωση των νιτρικών ιόντων αυξάνεται, σχεδόν σε όλο το πεδίο εφαρμογής (16% κατά μέσο όρο). Την περίοδο του χειμώνα, η μείωση των PM₂,5 δεν ξεπερνά το 3%, λόγω της περιορισμένης διαθεσιμότητας του H₂O₂ για τον σχηματισμό θειικών ιόντων καθώς και στην αύξηση των νιτρικών.

Εικόνα 5: Μέση προβλεπόμενη αλλαγή συγκέντρωσης σε επίπεδο εδάφους (μg m⁻³) των PM₂,5 σωματιδίων μετά την μείωση κατά 50% των εκπομπών SO₂ για (a) το καλοκαίρι και (b) τον χειμώνα. Η θετική τιμή υποδηλώνει μείωση.
Η μείωση των εκπομπών POA κατά 50% επηρεάζει σημαντικά την συγκέντρωση των οργανικών σωματιδίων και τις δύο περιόδους. Το καλοκαίρι τα οργανικά μειώνονται περίπου 8% κατά μέσο όρο σε όλη την Ευρώπη ενώ τον χειμώνα η μείωση είναι ακόμη μεγαλύτερη (15% κατά μέσο όρο) (Εικόνα 6). Σε περιοχές στην κεντρική και βόρεια Ευρώπη η προβλεπόμενη μείωση ξεπερνά το 20%. Η μείωση των οργανικών, εξήγησε την απόκριση των συνολικών PM\textsubscript{2.5}, καθώς οι εκπομπές POA δεν επηρεάζουν σημαντικά την συγκέντρωση των ανόργανων σωματιδίων.

Εικόνα 6: Μέση προβλεπόμενη αλλαγή συγκέντρωσης σε επίπεδο εδάφους \((\mu g m^{-3})\) των PM\textsubscript{2.5} σωματιδίων μετά την μείωση κατά 50% των εκπομπών POA για (α) το καλοκαίρι και (β) τον χειμώνα. Η θετική τιμή υποδηλώνει μείωση.

Μικρή μείωση των οργανικών περιμένουμε και από την μείωση των ανθρωπογενών εκπομπών VOCs (8% κατά μέσο όρο το καλοκαίρι και 4% τον χειμώνα), ωστόσο η επίδραση τους στην συγκέντρωση των συνολικών PM\textsubscript{2.5} σωματιδίων είναι σχετικά μικρή.
Η αύξηση της θερμοκρασίας κατά 2.5 K, μειώνει τα PM$_{2.5}$ στην κεντρική Ευρώπη, και τις 2 περιόδους, κυρίως λόγω μείωσης του NH$_4$NO$_3$ το καλοκαίρι (18% κατά μέσο όρο) και των POA τον χειμώνα (35% κατά μέσο όρο) (Εικόνα 7). Ωστόσο οι αλλαγές στα PM$_{2.5}$ δεν είναι ομοιόμορφες σε όλη την Ευρώπη, καθώς η αύξηση της θερμοκρασίας αυξάνει την συγκέντρωση των οξειδωτικών μέσων (OH, O$_3$, κτλ.), καθώς και τις εκπομπές VOCs που προέρχονται από βιογενείς πηγές, και κατά συνέπεια ευνοεί τον σχηματισμό θειικών και δευτερογενών οργανικών σωματιδίων (SOA). Σε ορισμένες περιοχές (π.χ. Βόρεια Ευρώπη, Ατλαντικός Ωκεανός), η αύξηση των SOA και των θειικών σωματιδίων φαίνεται να κυριαρχεί. Περαιτέρω αύξηση της θερμοκρασίας (5 K), προβλέπεται να οδηγήσει σε μεγαλύτερες αλλαγές στην συγκέντρωση των PM$_{2.5}$.

Εικόνα 7: Μέση προβλεπόμενη αλλαγή συγκέντρωσης σε επίπεδο εδάφους (μg m$^{-3}$) των PM$_{2.5}$ σωματιδίων μετά την αύξηση της θερμοκρασίας κατά 2.5 K για (a) το καλοκαίρι και (b) τον χειμώνα. Η θετική τιμή υποδηλώνει μείωση.
Επί των Παραμέτρων Της Μετεωρολογίας Στις Συγκέντρωσεις Των Ατμοσφαιρικών Σωματιδίων Στην Ευρώπη

Έως σήμερα, πολλές μελέτες έχουν δείξει πως οι συγκέντρωσεις των PM$_{2.5}$ επηρεάζονται σημαντικά από τις αλλαγές στην μετεωρολογία. Ωστόσο, οι περισσότερες από αυτές δίνουν έμφαση στη συνολική επίδραση της αλλαγής του κλίματος [19, 20, 21], χωρίς να εξετάζουν την σημασία που έχει η κάθε μετεωρολογική παράμετρος ξεχωριστά για την συγκέντρωση των PM$_{2.5}$. Σε αυτήν την εργασία, πραγματοποιήσαμε μία ανάλυση ευαισθησίας, ώστε να μελετήσουμε την επίδραση που έχουν οι αλλαγές στις παραμέτρους της μετεωρολογίας (θερμοκρασία, απόλυτη υγρασία, ταχύτητα ανέμου, βροχόπτωση, ύψος ανάμειξης) σε διάφορες διεργασίες της ατμόσφαιρας και κατ’ επέκταση στην συγκέντρωση των PM$_{2.5}$. Για τον σκοπό αυτό χρησιμοποιήσαμε το μοντέλο PMCAMx-2008, παίρνοντας για παράδειγμα το πεδίο εφαρμογής της Ευρώπης. Η κάθε παράμετρος μελετήθηκε ξεχωριστά, ώστε να προσδιορίσουμε την σχετική σημασία της κάθε παραμέτρου και την αντίστοιχη απόκριση των PM$_{2.5}$. Τρεις περιόδοι προσομοίωσης χρησιμοποιήθηκαν, αντιπροσωπευτικές για τις διαφορετικές εποχές του χρόνου.

B5.1 Αποτελέσματα – Ανάλυση

Η αύξηση της θερμοκρασίας κατά 2 K, οδηγεί σε μείωση της μέσης συγκέντρωσης των PM$_{2.5}$ και τις τρεις περιόδους. Κατά μέσο όρο, σε όλο το πεδίο εφαρμογής, η μείωση κυμαίνεται από 7 ng m$^{-3}$ K$^{-1}$ (0.1% K$^{-1}$) τον χειμώνα έως 33 ng m$^{-3}$ K$^{-1}$ (0.4% K$^{-1}$) το φθινόπωρο. Ωστόσο, οι προβλεπόμενες αλλαγές δεν είναι ομοιόμορφες (Εικόνα 8), λόγω της διαφορετικής απόκρισης των συστατικών των PM$_{2.5}$ και μεταβαλλόμενα από -700 ng m$^{-3}$ K$^{-1}$ (-8% K$^{-1}$) έως 300 ng m$^{-3}$ K$^{-1}$ (7% K$^{-1}$).
Μείωση των PM$_{2.5}$ προβλέπεται κυρίως στην κεντρική Ευρώπη, λόγω μείωσης του NH$_4$NO$_3$, καθώς η αύξηση της θερμοκρασίας δεν ευνοεί τον σχηματισμό του στην σωματιδιακή φάση (15% μείωση κατά μέσο όρο). Αντίθετα, η αύξηση των βιογενών πτητικών οργανικών εκπομπών καθώς και των ρυθμών αντίδρασης στην αέρια φάση, ευνοούν τον σχηματισμό θειικών και οργανικών σωματιδίων (αύξηση έως 7% K$^{-1}$ και 4% K$^{-1}$, αντίστοιχα), αυξάνοντας τα PM$_{2.5}$ σε ορισμένες περιοχές.

Εικόνα 8: Μέση προβλεπόμενη αλλαγή συγκέντρωσης σε επίπεδο εδάφους (μg m$^{-3}$) των PM$_{2.5}$ σωματιδίων μετά την αύξηση της θερμοκρασίας κατά 2 K για (α) το καλοκαίρι, (β) τον χειμώνα και (γ) το φθινόπωρο. Η θετική τιμή υποδηλώνει αύξηση.
Η αύξηση της απόλυτης υγρασίας κατά 5% οδηγεί σε αλλαγές των PM$_{2.5}$ και τις τρεις περιόδους, οι οποίες κυμαίνονται από -130 ng m$^{-3}$ %$^{-1}$ (-1.6% %$^{-1}$) έως 160 ng m$^{-3}$ %$^{-1}$ (1.6% %$^{-1}$), και προέρχονται κυρίως από αλλαγές στις συγκεντρώσεις των ανόργανων σωματιδίων. Κατά την διάρκεια του καλοκαίριου, η αύξηση της απόλυτης υγρασίας ευνοεί την κατανομή του ελεύθερου νιτρικού οξέος στην σωματιδιακή φάση (αύξηση όως 15%) και οδηγεί σε αύξηση της μέσης συγκέντρωσης των PM$_{2.5}$ περίπου 0.2% %$^{-1}$ κατά μέσο όρο σε όλο το πεδίο εφαρμογής (Εικόνα 9). Παρόμοια αποτελέσματα παίρνουμε και το φθινόπωρο. Τον χειμώνα αντίθετα, κυριαρχεί η μείωση της συγκέντρωσης των θειικών και των σωματιδίων από θαλασσινό αλάτι, η οποία προέρχεται κυρίως από αύξηση της ξηρής εναπόθεσης (περίπου 10%) και από αλλαγές στην κατανομή μεγέθους των σωματιδίων. Η συγκέντρωση των PM$_{2.5}$ μειώνεται περίπου 0.2% %$^{-1}$ κατά μέσο όρο σε όλο το πεδίο.

Εικόνα 9: Μέση προβλεπόμενη αλλαγή συγκέντρωσης σε επίπεδο εδάφους (μg m$^{-3}$) των PM$_{2.5}$ σωματιδίων μετά την αύξηση της απόλυτης υγρασίας κατά 5% για (α) το καλοκαίρι, και (β) τον χειμώνα. Η θετική τιμή υποδηλώνει αύξηση.
Η μείωση της ταχύτητας του ανέμου κατά 10%, χωρίς καμία αλλαγή στις εκπομπές από θαλασσινό αλάτι, επηρεάζει όλα τα συστατικά των PM\textsubscript{2.5}, μειώνοντας την συγκέντρωση τους (Εικόνα 10α), περίπου 0.6% \(\%^{-1}\) κατά μέσο όρο για όλο το πεδίο εφαρμογής, και τις 3 περιόδους. Οι προβλεπόμενες αλλαγές είναι ιδιαίτερα σημαντικές στις ηπειρωτικές περιοχές με αυξημένες συγκεντρώσεις PM\textsubscript{2.5}, και οφείλονται κυρίως στην μείωση της ξηρής εναπόθεσης (περίπου 10%) καθώς και σε αλλαγές στην μεταφορά. Η μείωση της ταχύτητας του ανέμου κατά 10% μειώνει επίσης και τις εκπομπές από θαλασσινό αλάτι. Τα αποτελέσματα, αλλάζοντας μόνο τις εκπομπές από το θαλασσινό αλάτι, προβλέπουν μείωση των PM\textsubscript{2.5} και τις 3 περιόδους (μεγαλύτερη τον χειμώνα), κυρίως στις θαλάσσιες περιοχές και τον οικειότατο (Εικόνα 10β). Η μείωση των ιόντων χλωρίου και νατρίου εξηγούν την απόκριση των PM\textsubscript{2.5}.

Εικόνα 10: Μέση προβλεπόμενη αλλαγή συγκέντρωσης σε επίπεδο εδάφους (\(\mu g \text{ m}^{-3}\)) των PM\textsubscript{2.5} συμπεριλαμβάνοντας μετά την (α) μείωση της ταχύτητας του ανέμου κατά 10% (χωρίς καμία αλλαγή στις εκπομπές), και (β) μείωση των εκπομπών από θαλασσινό αλάτι (λόγω μείωσης του ανέμου κατά 10%), για την περίοδο του χειμώνα. Η θετική τιμή υποδηλώνει αύξηση.
Η αύξηση του ρυθμού βροχόπτωσης κατά 10%, μειώνει τα PM$_{2.5}$ και τις τρεις περιόδους, περίπου 0.1% - 0.2% % κατά μέσο όρο σε όλο το πεδίο εφαρμογής. Τοπικά ωστόσο η μείωση είναι μεγαλύτερη (έως 2% %). Η αύξηση της υγρής εναπόθεσης, τόσο των PM$_{2.5}$ όσο και των αέριων πρόδρομων ενώσεων τους, εξηγεί την απόκριση των PM$_{2.5}$. Παρόμοια αποτελέσματα παίρνουμε και με την αύξηση κατά 10% της περιοχής του πεδίου που στην οποία προβλέπεται να βρέχει.

Η αύξηση του ύψους ανάμειξης κατά 150 m περίπου, μειώνει τα PM$_{2.5}$ και τις τρεις περιόδους, ωστόσο οι αλλαγές είναι μικρές σε σχέση με τις υπόλοιπες παραμέτρους.

Για να μπορέσουμε να αξιολογήσουμε την σημασία των παραμέτρων της μετεωρολογίας, υπολογίσαμε την επίδραση της κάθε μίας στις συγκεντρώσεις των PM$_{2.5}$, σε ενδεχόμενη αλλαγή του κλίματος στο μέλλον. Οι υπολογισμοί μας βασίστηκαν στην προβλεπόμενη ευαισθησία των PM$_{2.5}$ στις αλλαγές της κάθε παραμέτρου, και στις εκτιμήσεις της IPCC [1] για τις μελλοντικές αλλαγές των παραμέτρων. Οι εκτιμώμενες αλλαγές στην βροχόπτωση, αναμένεται να έχουν την μεγαλύτερη επίδραση στις συγκεντρώσεις των PM$_{2.5}$ στο μέλλον (έως 2 μg m$^{-3}$ το φθινόπωρο) (Εικόνα 11). Σημαντικές, ενδέχεται να είναι επίσης, οι εκτιμώμενες αλλαγές στην ταχύτητα του ανέμου, κατά την διάρκεια και των 3 περιόδων (οι αλλαγές στα PM$_{2.5}$ φθάνουν έως τα 1.4 μg m$^{-3}$) καθώς και στην απόλυτη υγρασία κυρίως σε περιόδους όπου κυριαρχεί η συγκέντρωση των νιτρικών σωματιδίων (βλ. φθινόπωρο, Εικόνα 11). Οι αλλαγές στην θερμοκρασία αναμένεται να έχουν μικρότερη επίδραση στα PM$_{2.5}$ (οι αλλαγές δεν ξεπερνούν τα 1.1 μg m$^{-3}$), λόγω της διαφορετικής απόκρισης των συστατικών τους, ενώ οι αλλαγές στο ύψος ανάμειξης δεν αναμένεται να επηρεάσουν σημαντικά τα PM$_{2.5}$.
Εικόνα 11: Προβλέπομενη αλλαγή μέσης συγκέντρωσης των PM$_{2.5}$ σωματιδίων στην Ευρώπη λόγω αλλαγής των μετεωρολογικών παραμέτρων στο μέλλον, βάσει των εκτιμήσεων της IPCC, και για τις τρεις περιόδους προσομοίωσης.

Β6 ΕΠΙΔΡΑΣΗ ΤΗΣ ΚΛΙΜΑΤΙΚΗΣ ΑΛΛΑΓΗΣ ΣΤΗΝ ΠΟΙΟΤΗΤΑ ΤΟΥ ΑΕΡΑ ΤΗΣ ΕΛΛΑΔΑΣ

Για να μελετήσουμε την επίδραση που έχει η αλλαγή του κλίματος στο μέλλον στην συγκέντρωση των PM$_{2.5}$ και του όζοντος (O$_3$), το PMCAMx-2008 χρησιμοποιήθηκε σαν μέρος ενός συστήματος μοντέλων, του GRE-CAPS, το οποίο εφαρμόστηκε πάνω από την Ευρώπη. Η μελέτη μας εστιάστηκε στην Ελλάδα, καθώς η Ανατολική Μεσόγειος έχει χαρακτηριστεί ως έδαφος με εστίαση περιοχή ιδιαίτερης σημασίας (“hot spot” area) όσον αφορά τις επερχόμενες κλιματικές αλλαγές [22].

Το σύστημα μοντέλων GRE-CAPS συνδέει το παγκόσμιο κλιματικό μοντέλο και μοντέλο χημικής μεταφοράς, GISS ΙΙ΄ GCM [23], το μέσης κλίμακας μετεωρολογικό
μοντέλο WRF [12] και το τρισδιάστατο μοντέλο χημικής μεταφοράς PMCAMx-2008 [9]. Το GISS Ι' GCM χρησιμοποιήθηκε για την προσομοίωση του κλίματος σε παγκόσμια κλίμακα τόσο για το παρόν όσο και για το μέλλον. Η προσομοίωση της μετεωρολογίας στο πεδίο που μας ενδιέφερε έγινε με το μοντέλο WRF, ενώ το PMCAMx-2008 χρησιμοποιήθηκε για να μελετήσουμε την επίδραση της κλιματικής αλλαγής στις συγκεντρώσεις των PM2.5 σωματιδίων και του O3. Το GRE-CAPS εφαρμόστηκε πάνω από την Ευρώπη, χρησιμοποιώντας άναλυση πλέγματος 36×36 km, ενώ για την Ελλάδα, το μοντέλο χρησιμοποίησε υψηλότερη χωρική άναλυση, 9×9 km. Η προσομοίωση του κλίματος στο παρόν και το μέλλον κάλυψε δύο περιόδους αντιπροσωπευτικές για το καλοκαίρι, θεωρώντας επίσης πως οι ανθρωπογενείς εκπομπές παραμένουν σταθερές στο μέλλον. Η προσομοίωση του κλίματος στο μέλλον, βασίστηκε στο σενάριο A1B της IPCC [1] για το 2050. Το σενάριο περιγράφει ένα μελλοντικό κόσμο ταχείας οικονομικής ανάπτυξης, με παγκόσμιο πληθυσμό που κορυφώνεται στην Ευρώπη, και στην συνέχεια μειώνεται, και με ταχεία επέκταση της Ευρώπης και πιο αποτελεσματικών τεχνολογιών. Στην κατεύθυνση των τεχνολογικών εξελίξεων στον τομέα της ενέργειας, στο A1B υπάρχει εξισορρόπηση της χρήσης των διαφόρων πηγών ενέργειας.

B6.1 Αποτελέσματα – Ανάλυση

Η μέση προβλεπόμενη συγκέντρωση σε επίπεδο εδάφους των PM2.5 και του O3, στην Ελλάδα για το παρόν καλοκαίρι παρουσιάζεται στην Εικόνα 12. Κατά μέσο όρο σε όλα τα περιοχές με σημαντικές πηγές εκπομπών (π.χ. Ρόδος, πυρκαγιές) (Εικόνα 12α)
κυρίως λόγω των υψηλών συγκέντρωσεων των οργανικών σωματιδίων. Συνολικά τα οργανικά σωματίδια αποτελούν το 40% της συνολικής μάζας των PM$_{2.5}$, ενώ ακολουθούν τα θειικά με 35%, το αμμώνιο (10%), ο στοιχειακός άνθρακας (4%) και τα νιτρικά (3%).

Η συγκέντρωση του O$_3$ προβλέπεται να είναι υψηλότερη στα νότια τμήματα της Ελλάδας, και φθάνει τα 58 ppb κατά μέσο όρο στην Πελοπόννησο και τα 53 ppb στην Κρήτη (Εικόνα 12β). Υψηλά επίπεδα O$_3$ προβλέπονται επίσης και σε περιοχές της Κεντρικής Ελλάδας (53 ppb κατά μέσο όρο), ενώ στην Βόρεια Ελλάδα οι συγκέντρωσεις είναι χαμηλότερες (48 ppb).

![Εικόνα 12](image-url)

**Εικόνα 12:** Μέση προβλεπόμενη συγκέντρωση σε επίπεδο εδάφους για το καλοκαίρι των (α) PM$_{2.5}$ σωματιδίων (μg m$^{-3}$) και (β) O$_3$ (ppb) για το παρόν κλίμα.

Η μέση προβλεπόμενη αλλαγή της συγκέντρωσης των ολικών PM$_{2.5}$ σωματιδίων και του O$_3$, στην Ελλάδα, λόγω αλλαγής του κλίματος με βάση το σενάριο A1B παρουσιάζεται στην Εικόνα 13. Η συγκέντρωση των PM$_{2.5}$ στην Ελλάδα προβλέπεται να μειωθεί 1.1 μg m$^{-3}$ (5%) κατά μέσο όρο. Ωστόσο, οι προβλεπόμενες αλλαγές δεν είναι χωρικά ομοιόμορφες και κυμαίνονται από -20% έως 20%, υποδηλώνοντας πως
διαφορετικές παράμετροι καθορίζουν την απόκριση των PM$_{2.5}$ σε κάθε περιοχή. Στην Κεντρική Ελλάδα, η αύξηση της ταχύτητας του ανέμου (7% κατά μέσο όρο) και η μείωση της απόλυτης υγρασίας κυριαρχούν, μειώνοντας τα PM$_{2.5}$ 5.5% κατά μέσο όρο (Εικόνα 13α). Μείωση προβλέπεται επίσης στην Βόρεια Ελλάδα και το Βόρειο Αιγαίο. Αντίθετα, στην Πελοπόννησο και την Κρήτη, προβλέπεται αύξηση των PM$_{2.5}$ στο μέλλον, κατά μέσο όρο 3% και 1% αντίστοιχα, λόγω αύξησης των οργανικών και νιτρικών σωματιδίων. Η αύξηση, οφείλεται κυρίως στην αύξηση της θερμοκρασίας η οποία αυξάνει τις συγκέντρώσεις των οξειδωτικών μέσων και τις εκπομπές βιογενών πτητικών οργανικών, καθώς και σε αύξηση της απόλυτης υγρασίας. Αύξηση προβλέπεται και στις συγκέντρώσεις του O$_3$ στην Ελλάδα, η οποία κατά μέσο όρο είναι 4.5%, με τις μεγαλύτερες αλλαγές να προβλέπονται στην Κεντρική Ελλάδα (8% κατά μέσο όρο) (Εικόνα 13β). Η αύξηση της θερμοκρασίας κυριαρχεί και καθορίζει την απόκριση του O$_3$ στην αλλαγή του κλίματος.

Εικόνα 13: Μέση προβλεπόμενη αλλαγή της συγκέντρωσης σε επίπεδο εδάφους των (α) PM$_{2.5}$ σωματιδίων (μg m$^{-3}$) και (β) O$_3$ (ppb) λόγω αλλαγής του κλίματος με βάση το σενάριο A1B. Η θετική τιμή υποδηλώνει αύξηση.
Το σύστημα μοντέλων GRE-CAPS εφαρμόσθηκε στις ανατολικές ΗΠΑ για την μελέτη της επίδρασης της αλλαγής του κλίματος στην συγκέντρωση και εναπόθεση του υδραργύρου. Η προσομοίωση της μετεωρολογίας στο πεδίο που μας ενδιέφερε (ανατολικές ΗΠΑ) έγινε με το μέσης κλίμακας μετεωρολογικό μοντέλο MM5 [24], ενώ το PMCAMx βασίστηκε σε μία παλαιότερη έκδοση του μοντέλου [25], η οποία βελτιώθηκε ώστε να λαμβάνει υπόψη την χημεία του υδραργύρου στην ατμόσφαιρα καθώς και τις διεργασίες εναπόθεσης του [26]. Το PMCAMx προσομοιώνει και τις τρεις μορφές με τις οποίες συναντάται ο υδράργυρος στην ατμόσφαιρα: αέριος στοιχειακός υδράργυρος (Hg$^0$), την αέρια οξειδωμένη μορφή του (Hg$^{2+}$), και πρωτογενή σωματίδια υδραργύρου (Hg(p)).

Το πεδίο εφαρμογής καλύπτει μια περιοχή διαστάσεων 3492×3240 km στις ανατολικές ΗΠΑ, με ανάλυση πλέγματος 36×36 km και 14 οριζόντιες βαθμίδες. Η προσομοίωση του κλίματος στο παρόν και το μέλλον έγινε για δύο περιόδους, καλοκαίρι και χειμώνας, ώστε να μελετηθεί και η εποχιακή εξάρτηση της απόκρισης του υδραργύρου στις αλλαγές του κλίματος. Συνολικά προσομοιώθηκαν 300 ημέρες για κάθε περίοδο, θεωρώντας επίσης πως οι εκπομπές δεν αλλάζουν στο μέλλον. Η προσομοίωση του κλίματος στο μέλλον, βασίστηκε στο A2 σενάριο της IPCC [1] για το 2050, το οποίο περιγράφει έναν ετερογενή κόσμο που ο παγκόσμιος πληθυσμός αυξάνει συνεχώς, ενώ η οικονομική ανάπτυξη γίνεται κυρίως τοπικά και οι τεχνολογικές αλλαγές γίνονται με αργούς ρυθμούς.
Β7.1 Αποτελέσματα – Ανάλυση

Η μέση προβλεπόμενη συγκέντρωση σε επίπεδο εδάφους των τριών μορφών Hg για το παρόν παρουσιάζεται στην Εικόνα 14. Η συγκέντρωση του Hg⁰ είναι υψηλότερη τον χειμώνα σε σχέση με το καλοκαίρι (1.41 ng m⁻³ έναντι 1.34 ng m⁻³ κατά μέσο όρο σε όλο το πεδίο εφαρμογής), καθώς η υψηλή θερμοκρασία και οι υψηλότερες συγκέντρώσεις των οξειδωτικών μέσων το καλοκαίρι, ευνοούν την οξείδωση του Hg⁰ για τον σχηματισμό Hg²⁺. Και τις δύο περιόδους, υψηλές συγκέντρώσεις Hg⁰ προβλέπονται κυρίως σε περιοχές με σημαντικές πηγές εκπομπών. Για το Hg²⁺, τα επίπεδα συγκέντρωσης του είναι υψηλότερα το καλοκαίρι σε σύγκριση με τον χειμώνα. Σε αστικές περιοχές η συγκέντρωση φθάνει έως τα 60 pg m⁻³, κυρίως λόγω της παρουσίας τοπικών πηγών. Υψηλά επίπεδα Hg²⁺ προβλέπονται και σε αγροτικές περιοχές (π.χ. δυτικά, στην πολιτεία του Τέξας). Οι υψηλές συγκέντρώσεις των οξειδωτικών μέσων, η μεταφορά καθώς και ο μικρός ρυθμός υγρής εναπόθεσης εξηγούν τις υψηλές συγκέντρώσεις σε αυτές τις περιοχές. Τον χειμώνα η συγκέντρωση του Hg²⁺ δεν ξεπερνά τα 30 pg m⁻³. Η συγκέντρωση του Hg(p) είναι παρόμοια και τις δύο περιόδους. Κατά μέσο όρο σε όλο το πεδίο εφαρμογής, η συγκέντρωση του Hg(p) προβλέπεται 10.1 pg m⁻³ το καλοκαίρι και 10.9 pg m⁻³ τον χειμώνα.
Εικόνα 14: Μέση προβλεπόμενη συγκέντρωση σε επίπεδο εδάφους του (α,β) Hg\(^0\) (ng m\(^{-3}\)), (γ,δ) Hg\(^{2+}\) (pg m\(^{-3}\)) και (ε,στ) Hg(p) (pg m\(^{-3}\)) για 300 μέρες προσομοίωσης στο παρόν κλίμα, την περίοδο του καλοκαιριού και του χειμώνα.
Η αλλαγή του κλίματος επηρεάζει σημαντικά την συγκέντρωση του Hg\(^{2+}\) και τις δύο περιόδους. Το καλοκαίρι, αύξηση του Hg\(^{2+}\) προβλέπεται κυρίως στις νοτιοανατολικές και κεντρικές πολιτείες (8% και 7% κατά μέσο όρο) (Εικόνα 15), λόγω αύξησης της θερμοκρασίας η οποία αυξάνει τις συγκέντρωσεις των οξειδωτικών μέσων και ευνοεί την αντίδραση οξείδωσης του Hg\(^0\) για τον σχηματισμό Hg\(^{2+}\). Στις νοτιοδυτικές πολιτείες (Τέξας) η συγκέντρωση του Hg\(^{2+}\) μειώνεται κυρίως λόγω αύξησης της υγρής εναπόθεσης. Τον χειμώνα, αυξήσεις προβλέπονται κυρίως στη νότια τμήματα (περίπου 5-7% κατά μέσο όρο), ενώ στα δυτικά η συγκέντρωση του Hg\(^{2+}\) μειώνεται (3%). Κατά μέσο όρο σε όλο το πεδίο εφαρμογής, η συγκέντρωση του Hg\(^{2+}\) αυξάνει κατά 3% το καλοκαίρι και 5% τον χειμώνα, αντίστοιχα.

*Εικόνα 15:* Μέση προβλεπόμενη αλλαγή της συγκέντρωσης σε επίπεδο εδάφους του Hg\(^{2+}\) (pg m\(^{-3}\)) λόγω αλλαγής του κλίματος για (a) το καλοκαίρι, και (b) τον χειμώνα. Η θετική τιμή υποδηλώνει αύξηση.

Η απόκριση της συγκέντρωσης του Hg(p) στην αλλαγή του κλίματος είναι παρόμοια με εκείνη του Hg\(^{2+}\) κατά την διάρκεια του καλοκαιριού. Στις
νοτιοανατολικές πολιτείες η αύξηση του Hg(p) είναι περίπου 7%, ενώ αντίθετα στην πολιτεία του Τέξας, το Hg(p) μειώνεται 2% κατά μέσο όρο. Τον χειμώνα η προβλεπόμενη αλλαγή της συγκέντρωσης του Hg(p) είναι σχετικά μικρή. Αντίθετα, για τον Hg^0 η αλλαγή του κλίματος δεν επηρεάζει σημαντικά τις συγκεντρώσεις του. Μικρή μείωση, περίπου 0.7% κατά μέσο όρο σε όλο το πεδίο εφαρμογής προβλέπεται για το καλοκαίρι, ενώ τον χειμώνα οι αλλαγές είναι ακόμη μικρότερες.

Η αλλαγή του κλίματος επηρεάζει σημαντικά και την εναπόθεση του υδραργύρου. Κατά μέσο όρο σε όλο το πεδίο εφαρμογής, η ολική εναπόθεση του υδραργύρου αυξάνει περίπου 6% το καλοκαίρι και 4% τον χειμώνα, αντίστοιχα. Ωστόσο, οι αλλαγές δεν είναι ομοιόμορφες και κυμαίνονται από -50% έως 50% το καλοκαίρι και από -30% έως 50% τον χειμώνα. Οι μεταβλητές αλλαγές της βροχόπτωσης στο μέλλον, επηρεάζουν την υγρή εναπόθεση του υδραργύρου και μπορούν να δικαιολογήσουν την μεταβλητή απόκριση της ολικής εναπόθεσης του λόγω αλλαγής του κλίματος (Εικόνα 16). Το καλοκαίρι, αύξηση της ολικής εναπόθεσης προβλέπεται κυρίως στις δυτικές περιοχές (περίπου 8-9% κατά μέσο όρο), ενώ αντίθετα στις βορειοανατολικές πολιτείες η ολική εναπόθεση του υδραργύρου μειώνεται (10% κατά μέσο όρο). Αντίστοιχα, τον χειμώνα αύξηση της ολικής εναπόθεσης του υδραργύρου προβλέπεται κυρίως στις νότιες περιοχές (13% κατά μέσο όρο στο Τέξας).
Εικόνα 16: Μέση προβλεπόμενη αλλαγή της (α) ολικής εναπόθεσης του Hg (ng m\(^{-2}\) yr\(^{-1}\)), (β) υγρής εναπόθεσης του Hg (ng m\(^{-2}\) yr\(^{-1}\)), και (γ) προβλεπόμενη αλλαγή της βροχόπτωσης (mm yr\(^{-1}\)) λόγω αλλαγής του κλίματος για την περίοδο του καλοκαιριού. H θετική τιμή υποδηλώνει αύξηση.


Curriculum Vitae

Athanasios G. Megaritis

Current position: Department of Chemical Engineering, University of Patras, Caratheodory 1, University Campus, GR 26500 Patras, Greece, tel: +30 2610 962510

Institute of Chemical Engineering Sciences (ICE-HT), Foundation for Research & Technology-Hellas (FORTH) Stadiou St., Platani, P.O. Box 1414, 26504 Patras, Greece

Email: athmegaritis@chemeng.upatras.gr

Education

2008-present: PhD. Candidate in Chemical Engineering Laboratory of Air Quality Studies, Department of Chemical Engineering, University of Patras, Greece

- Ph.D. Thesis title: “Simulating the effects of climate change and emissions of pollutants on air quality”
- Research Interests: Air pollution, climate change, emission control strategies, atmospheric particulate matter, air toxics (mercury), regional 3-D air quality modeling, atmospheric chemistry
- Minor: Energy and Environment

2002-2008: B. Sc. (Diploma) in Chemical Engineering University of Patras, Greece

- Grade: 7.58 of 10.
- Diploma thesis: “Study the environmental behavior of the ferroalummina Portland cement”
- Academic Advisor: Prof. George Angelopoulos
- Minor: Materials Science and Technology

Research and Work Experience

2008-present: Graduate Research Assistant Laboratory of Air Quality Studies Dept. of Chemical Engineering, University of Patras, Greece
- Air quality modeling using a 3-D chemical transport model, PMCAMx – Application in regional scale (Europe, Eastern United States, Greece), and urban scale (Paris, London, Athens, Po Valley).
- Study of emission control strategies.
- Quantify the contribution of local sources and long range transport to air quality in large urban areas.
- Air Pollutants – Climate interactions.
- Impact of climate change on regional and urban air quality – Focus on atmospheric particulate matter, ozone, and mercury.

2007-2008: **Undergraduate Research Assistant**
Dept. of Chemical Engineering, University of Patras, Greece
Laboratory of Materials and Metallurgy – in cooperation with TITAN Cement Company
- Experimental studies and chemical analysis in order to assess the long term environmental behavior of Portland cement exposed to the open environment.

06-08/2006 **Research Assistant**
Public Power Corporation, Rio Patras, Greece
- Chemical analysis of insulating oils from transformers

06-08/2004: **Research Assistant**
Bayer CropScience Greece
Ypato Voiotias, Thiva, Greece
- Chemical analysis of agricultural products

**Teaching Experience**

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<td><strong>Graduate Teaching Assistant</strong></td>
<td>Dept. of Chemical Engineering, University of Patras, Greece “Mathematics IV”</td>
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<td>2011 spring</td>
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</table>
Dept. of Chemical Engineering, University of Patras, Greece
“Mathematics IV”

2009 fall: **Graduate Teaching Assistant**
Dept. of Chemical Engineering, University of Patras, Greece
“Mechanics of Materials”

2009 spring: **Graduate Teaching Assistant**
Dept. of Chemical Engineering, University of Patras, Greece
“Unit Operations II”

2008 fall: **Graduate Teaching Assistant**
Dept. of Chemical Engineering, University of Patras, Greece
“Mechanics of Materials”

2008 spring: **Graduate Teaching Assistant**
Dept. of Chemical Engineering, University of Patras, Greece
“Unit Operations II”

Awards and Honors

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<td>2010-2012</td>
<td>Fellowship during the EUCAARI project (European Integrated Project on Aerosol Cloud Climate and Air Quality Interactions).</td>
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<td>2008-2010</td>
<td>Fellowship during the MEGAPOLI project (Megacities: Emissions, urban, regional, and Global Atmospheric POLution and climate effects, and Integrated tools for assessment and mitigation).</td>
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<td>2002</td>
<td>Greek Ministry of Education Scholarship for my admission to the Department of Chemical Engineering within the top 20 students.</td>
</tr>
<tr>
<td>2002</td>
<td>Hellenic Football Federation Scholarship for my admission to the Department of Chemical Engineering.</td>
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<td>2002</td>
<td>Excellence award of graduation from the Greek Ministry of Education.</td>
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Professional Affiliations

- European Geosciences Union (EGU)
- European Aerosol Assembly (EAA)
- Hellenic Association for Aerosol Research (HAAR)
Journal Publications


Conference Presentations


