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SENSITIVITY OF OZONE AND PARTICULATE MATTER CONCENTRATIONS IN GREATER ATHENS AREA, GREECE

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Abstract: Sensitivity of ozone and particulate matter concentrations to their precursor emissions (i.e., NO_X, VOCs, SO_2 and NH_3) on regional air quality over Athens (Greece) using the Community Multiscale Air Quality (CMAQ) Modeling System is investigated. Particulate matter concentration is more sensitive to SO_2 and NO_X emissions. Gas emitted SO_2, is oxidized to sulfuric acid, which reacts with ammonia to form ammonium sulfate while gas emitted NO_X, is oxidized to nitric acid, which reacts with ammonia to form ammonium nitrate. When NO_X and VOCs mix in the presence of sunlight ground level ozone is formed. The response of ambient ozone formation to reductions in NOx and VOC emissions depend on NO_X sensitive and VOC sensitive regimes.

Key words: *Ozone, particulate matter, sensitivity, CMAQ, Athens, Greece*

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1. INTRODUCTION

The Athens Larger Urban Zone (ALUZ) is one of the most populous Larger Urban Zones in the EU with a population of more than 4 million inhabitants. ALUZ is surrounded by mountains (i.e., Pendeli, Parnitha and Hymettus) with elevation up to 1400 m and the coast (south west). Between those mountains there are three big physical gaps. As most metropolitan areas in the world, ALUZ faces air pollution problems. These problems are the result of high population density, the accumulation of major economic activities, the topography and the intense sunshine, which contributes particularly during the summer months. Although the concentrations of most pollutants (i.e., SO_2, NO_2, CO, Pb, and benzene) were below the EU air quality limits in 2008 according to the most recent report of the Hellenic Ministry for the Environment on air quality in Athens, ozone (O_3) and particulate matter (PM) remain an issue of concern (http://www.minenv.gr/4/41/g4100.html). Industry, transportation and heating are the main sources of air pollution in the area (e.g., Sotiropoulou *et al.*, 2004). The objective of this study is to assess the sensitivity of O_3 and $PM_{2.5}$ (particulate matter with aerodynamic diameter less than 2.5μm) concentrations to their precursor emissions on regional air quality over ALUZ. The information provided here will enhance the ability of air quality managers to consider appropriate emissions reductions in their mitigation planning.

2. METHODS

The Community Multiscale Air Quality model (CMAQ) (Byun and Schere, 2006) ver. 4.7 with the CBIV chemical mechanism is used to simulate pollutant concentrations (i.e, O_3 and $PM_{2.5}$) over the modeling domain (Figure 1). The domain is divided in 103 × 103 cells of 1 km × 1 km resolution while 14 vertical layers are employed in the simulations. The episode of June 24, 2003 has been selected in order to examine the responses of O_3 and $PM_{2.5}$ concentrations to emissions reductions of NO_X, VOCs, SO_2 and NH_3. The Fifth-Generation NCAR/Penn State Mesoscale meteorological Model (MM5) (Grell *et al.*, 1994) is used to simulate the meteorology while an updated emission inventory based on our previous work (Sotiropoulou *et al.*, 2004) is employed. A spin up time of one day was used to wash out errors in the initial conditions and to emphasize the physics and chemistry simulated by the model.

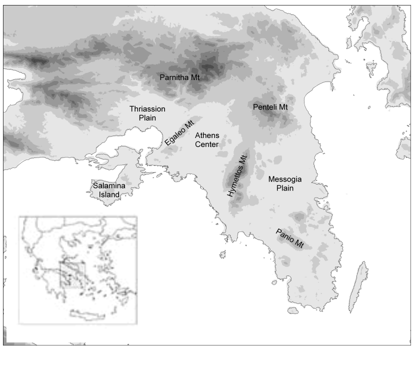
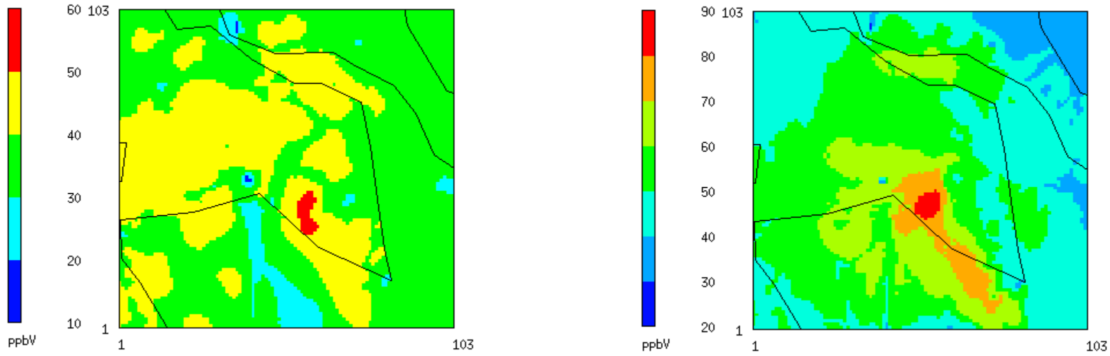


Figure 1: Modeling domain

3. RESULTS AND DISCUSSION

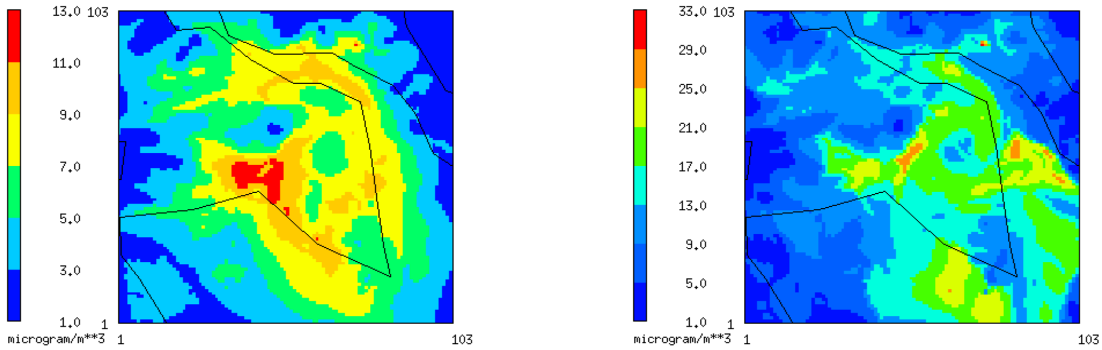
O_3 concentrations above 70ppbV have been simulated around the city center between 10:00 and 16:00 hours, since O_3 is a photochemical pollutant. The daily average O_3 concentration is estimated at 55ppbV with hourly maximum of 84ppbV at 13:00 and 14:00 hours (Figure 2). The daily average $PM_{2.5}$ concentration is simulated at 13 μg/m^3 with hourly maximum concentration at 31.6 μg/m^3 (Figure 3).

$PM_{2.5}$ concentrations above 18 μg/m^3 are simulated around the city center between 16:00 and 23:00 hours. The sulfate and nitrate $PM_{2.5}$ components are dominant.



(a) (b)

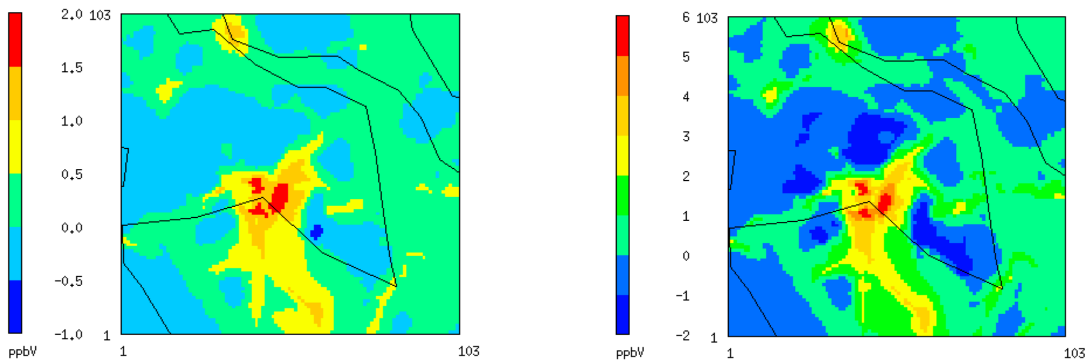
Figure 2: O_3 daily average (a) and hourly maximum (b) concentrations on June 24, 2003



(a) (b)

Figure 3: $PM_{2.5}$ daily average (a) and hourly maximum (b) concentrations on June 24, 2003

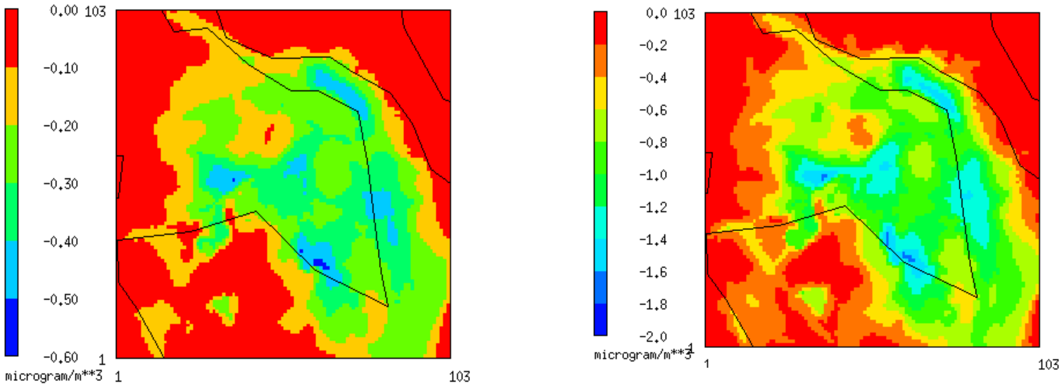
The response of ambient ozone formation to reductions in NOx emissions depend on NO_X sensitive and VOC sensitive regimes. NOx emissions reduction leads to higher O_3 concentrations around the city center (VOCs limited area) (Figure 4).



(a) (b)

Figure 4: Δ_O_3 daily average concentrations for 10% (a) and 30% (b) NOx emissions reduction

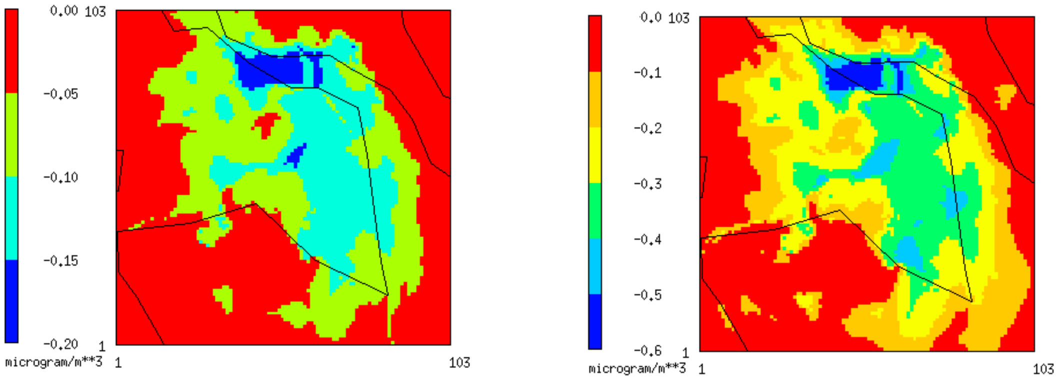
On the other hand, significant reduction in $PM_{2.5}$ concentrations are simulated for NOx emissions reductions, coming from the nitrate $PM_{2.5}$ components (Figure 5). Gas emitted NO_X, is oxidized to nitric acid which reacts with ammonia to form ammonium nitrate.



(a) (b)

Figure 5: Δ_$PM_{2.5}$ in daily average concentrations for 10% (a) and 30% (b) NOx emissions reduction

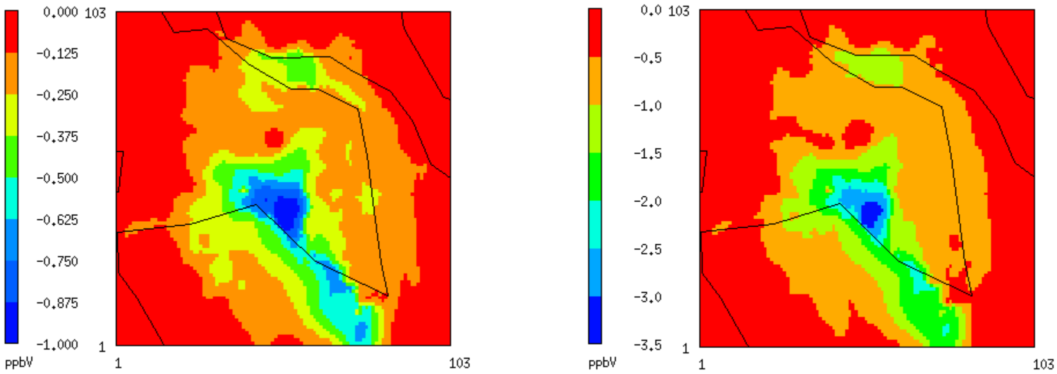
SO_2 emissions reduction does not affect O_3 levels but leads to lower $PM_{2.5}$ concentrations (Figure 6). Gas emitted SO_2, is oxidized to sulfuric acid, which reacts with ammonia to form ammonium sulfate. SO_2 emissions reduction reduces the sulphate $PM_{2.5}$ fraction (e.g. up to 0.9 $\mu g/m^3$ of the daily average concentration, for 30% SO_2 emissions reduction) but increases the nitrate $PM_{2.5}$ fraction (e.g. up to 0.6 $\mu g/m^3$ for 30% SO_2 emissions reduction), as more ammonia is available to react with the nitric acid to form ammonium nitrate.



(a) (b)

Figure 6: Δ_$PM_{2.5}$ in daily average concentrations for 10% (a) and 30% (b) SO_2 emissions reduction

Lower O_3 concentrations up to 1ppbV and 3.5ppbV are simulated for 10% and 30% VOC emissions reduction, respectively (Figure 7). The reduction of VOC emissions causes a small increase of the oxidant levels and a small increase in $PM_{2.5}$ concentrations. This small net change is due to increases in the inorganic components and decreases of the organic ones. The reduction of NH_3 emissions is simulated to not effect O_3 concentrations while a marginal local change in $PM_{2.5}$ levels has been found.



(a) (b)

Figure 7: Δ_O_3 in daily average concentrations for 10% (a) and 30% (b) VOC emissions reduction

4. CONCLUSION

Control of VOC emissions is simulated to be the most effective way to reduce O_3 concentration mainly in the city center of Athens. Control of NOx emissions is simulated to be the most effective way to reduce $PM_{2.5}$ concentrations but since the reductions in NOx emissions results in an increase of O_3 levels in the city center (VOCs limited area), the reduction in SO_2 emissions is suggested as a better way to be adopted in air pollution mitigation strategy.

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