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SENSITIVITY OF OZONE AND AEROSOLS TO PRECURSOR EMISSIONS IN EUROPE

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Abstract: We modeled the air quality in Europe during June and January 2006 using the MM5/CAMx model system. In this paper, we discuss the sensitivity of ozone and aerosol formation to precursor emissions such as isoprene, NO_x, VOC and NH_3. Model results suggested that increased isoprene emissions by a factor of four in June 2006 would lead to an increase in afternoon ozone by up to 10% mainly in southern Europe. On the other hand, the effect of increased isoprene emissions on secondary organic aerosols was predicted to be very small due to low yields for the SOA production pathway from isoprene in the model. Our predictions indicate that NO_x emission reductions are more effective to reduce ozone concentrations in a large part of Europe. On the other hand, anthropogenic VOC emission reductions are effective only around the urban areas. Sensitivity tests with reduced NO_x and NH_3 emissions suggest that aerosol formation is more sensitive to ammonia emissions in winter except a small area in central Europe. In summer, effects of NO_x and NH_3 emission reductions on aerosol concentrations are predicted to be lower mostly because of lower ammonium nitrate concentrations.

Key words: *ozone, aerosols, isoprene, ammonia, precursor emissions, Europe, CAMx.*

INTRODUCTION
Tropospheric ozone and aerosols are known to have adverse impacts on health and climate (IPCC, 2007; Davidson et al., 2005). Ozone and particulate matter (PM) levels frequently exceed the national air quality standards. In order to reduce the pollutant concentrations effectively, their sensitivity to precursor emissions has to be understood. Anthropogenic ozone precursor emissions (NO_x and VOC) have been substantially reduced in Europe since early 1990s. Measurements at polluted sites confirm the decrease of the primary pollutants such as NO_x and total VOC by up to a factor of two between the early 1990s and 2005, as expected from the national anthropogenic emission inventories (Hueglin et al., 2006). However, long-term ozone measurements indicated a rather small or no reduction during this time period (Ordóñez et al., 2005; Jonson et al., 2006). Model studies and data analyses suggested that a simultaneous increase in background ozone might have compensated the decrease in local ozone production (Andreani-Aksoyoglu et al., 2008a; Ordóñez et al., 2007). Isoprene is an important biogenic precursor for ozone. It can also contribute to the formation of as secondary organic aerosols, SOA (Claeys et al., 2004). However, there is still a large uncertainty in isoprene emissions in Europe (Steinbrecher et al., 2009) and likely factors given in literature range from 3-10 (Smiatek and Bogacki, 2005; Guenther et al., 2006). It is therefore important to estimate the effect of emission uncertainty on the pollutant formation.

Inorganic aerosols are formed from various gas-phase and aqueous reactions. Ammonia (NH_3) emissions are important for the formation of ammonium sulfate and ammonium nitrate. Ammonia reacts with nitric acid (HNO_3) to form ammonium nitrate after sulfate is neutralized. Therefore both NO_x (as precursor for HNO_3) and NH_3 emissions are crucial for the formation of inorganic aerosols (Andreani-Aksoyoglu et al., 2008b). There are a few studies in Europe about the aerosol sensitivity to precursor emissions, mainly in UK and northern Italy (Redington et al., 2009; Derwent et al., 2009; de Meij et al., 2009). In this paper, we discuss the sensitivity of ozone and aerosols to their precursor emissions in Europe for summer and winter periods in 2006 using the MM5/CAMx model system.

MODELLING METHOD
We used the CAMx (Comprehensive Air Quality Model with extensions) model, version 4.51 (Environ, 2008) to simulate air quality in January and June 2006. The meteorological fields for CAMx were generated by the meso-scale model MM5, version 3.7.4 (PSU/NCAR, 2004). Three nested model domains used in a Lambert Conic Conformal projection cover Europe, central Europe and Switzerland with a horizontal resolution of 27 km x 27 km, 9 km x 9 km, and 3 km x 3 km, respectively. The MM5 simulations with 31 terrain-following σ–levels up to 100 hPa, were initialized by data from COSMO7 analysis (COSMO, 2002). Four-dimensional data analysis (FDDA) using COSMO7 data was applied only for domains 1 and 2. The planetary boundary layer (PBL) height was calculated using the Eta PBL option, with the Mellor-Yamada scheme (Janjić, 1994). The CAMx simulations used a subset of 14 of the MM5 σ-layers, of which the lowest had a thickness of about 40 m at a surface pressure of 950 hPa. The model top was set at σ=0.55 which corresponds to a geometric layer top of about 7000 m above sea level. The initial and boundary concentrations for the first domain were obtained from the global model MOZART (Horowitz et al., 2003). The photolysis rates were calculated using the TUV photolysis pre-processor (Madronich, 2002). The required ozone column densities were extracted from TOMS data (NASA/GSFC, 2005). Dry deposition of gases was based on the resistance model of Wesely (1989). Surface deposition of particles occurs via diffusion, impaction and/or gravitational settling. Separate scavenging models for gases and aerosols were implemented in CAMx to calculate the wet deposition (Environ, 2008). The CB05 gas-phase mechanism was used (Yarwood et al., 2005). Description of anthropogenic emissions is given elsewhere (Aksoyoglu et el., 2011). Biogenic emissions for the CAMx domains were calculated using European and Swiss land use inventories and MM5 meteorological data. The method for the estimation of biogenic emissions is given in (Andreani-Aksoyoglu and Keller, 1995), which was updated using recent literature data. Simulations were carried out for January and June 2006 using the fine/coarse option for particles. We validated the model performance by comparing the model results with detailed measurements (Aksoyoglu et al., 2011). Sensitivity tests were performed with modified precursor emissions. In case of ozone, simulations were performed with NO_x and VOC emissions reduced by 30% as well as with increased isoprene emissions by a factor of four. Effect of isoprene emissions on secondary organic aerosols was also investigated. On the other hand, sensitivity of aerosol formation was studied using reduced NO_x and NH_3 emissions by 15%.

RESULTS AND DISCUSSION

Ozone

The model results were compared with measurements and model performance was discussed elsewhere (Aksoyoglu et al., 2011). Isoprene is an important biogenic precursor for ozone formation. However, its emissions have a large uncertainty. We investigated the sensitivity of ozone to isoprene emissions by increasing them by a factor of four (based on the uncertainties in the literature) in our model domain in order to estimate the variability due to emission uncertainties. These tests were carried out only for the summer period because isoprene is emitted mostly from deciduous trees and emission rates are correlated with temperature and irradiation. In addition to the base case, simulations were repeated with increased isoprene emissions in whole domain. Figure 1 shows the increase in mean afternoon ozone concentration due to increased isoprene emissions. The influence of increased emissions can be seen mostly in the southern part of the model domain. These results suggest that variability of isoprene emissions due to uncertainties might lead to about 10% difference in the afternoon ozone concentrations.

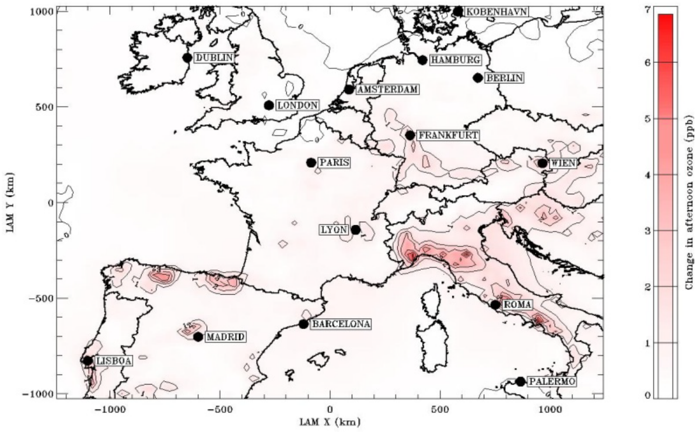

Figure 1. Increase in monthly average concentrations of ozone in the afternoon (12:00-18:00 UTC) due to increased isoprene emissions by a factor of four in June 2006.

In order to control ozone levels in a certain area, sensitivity of ozone formation to its anthropogenic precursor emissions such as NO_x and VOC must be known (Andreani-Aksoyoglu et al., 2008a). We investigated the sensitivity of ozone formation in Europe to 30% reductions in anthropogenic NO_x and VOC emissions in June 2006. The results of these simulations suggest that NO_x reductions are effective to reduce afternoon ozone in a large part of Europe while causing an increase in ozone in urban areas. On the other hand, reducing VOC emissions leads to a decrease in ozone mainly around big cities. The difference in afternoon average ozone concentrations between two simulations with 70% NO_x and 70% VOC emissions in June 2006 is shown in Figure 2. The blue color shows the regions with NO_x-sensitive and red color VOC sensitive regimes.

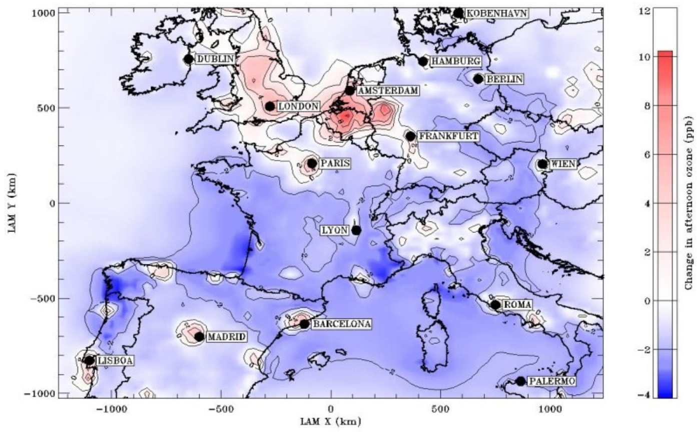

Figure 2. Difference in afternoon average (12:00-18:00 UTC) ozone concentrations between two simulations with a 30% emission reduction of either NO_x or VOC in June 2006 (blue color indicates NO_x-sensitive, red color VOC-sensitive regimes).

Aerosols

Inorganic aerosols such as ammonium sulfate and ammonium nitrate are formed through various gas-phase and aqueous-phase reactions. Ammonia (NH_3) reacts with nitric acid (HNO_3) to form ammonium nitrate after sulfate is neutralized. Ammonia and NO_x (as precursor for HNO_3) emissions are therefore crucial for inorganic aerosol formation. The sensitivity of aerosol formation to these emissions was investigated with two simulations where either NH_3 or NO_x emissions were reduced by 15%. The difference between the results of two simulations shows the regions where NO_x or NH_3 emissions are more effective to reduce aerosol concentrations (Figures 3 and 4, for January and June 2006, respectively). These predictions indicate that inorganic aerosol formation is more sensitive to NH_3 emissions in a large part of Europe in winter (red color in

Figure 3). The effect of ammonia emission reductions on aerosol mass is predicted to be lower in summer due to higher ammonia emissions (Figure 4).

Secondary organic aerosol formation due to isoprene oxidation with OH is included in the aerosol module of CAMx. Model predictions indicated that increased isoprene emissions would lead to a small increase (1%) in aerosol concentrations in June 2006 (not shown). This is due to very low yield of this pathway compared to other biogenic species such as monoterpenes and sesquiterpenes (Aksoyoglu et al., 2011).

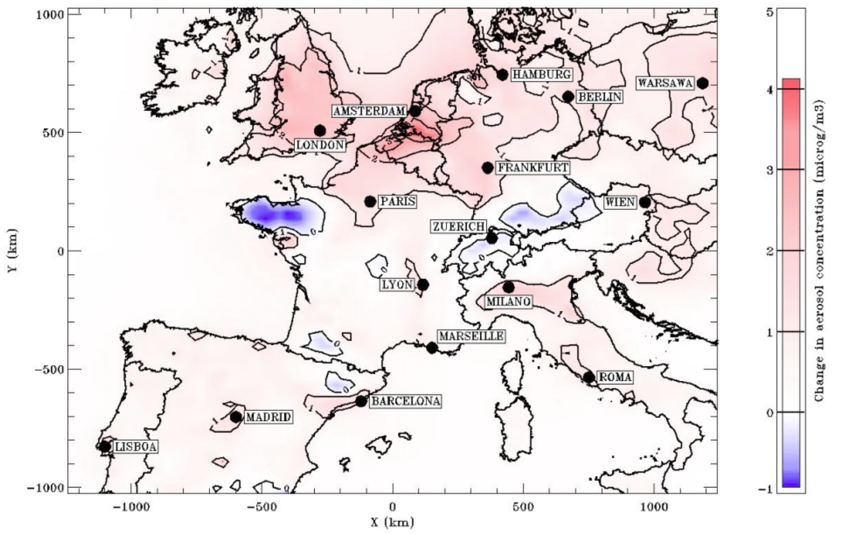

Figure 3: Difference in monthly average aerosol concentration (µg m^{-3}) between two simulations with a 15% emission reduction of either NO_x or NH_3 in January 2006. Blue and red colors show the regions where aerosol formation is more sensitive to NO_x and NH_3 emissions, respectively.

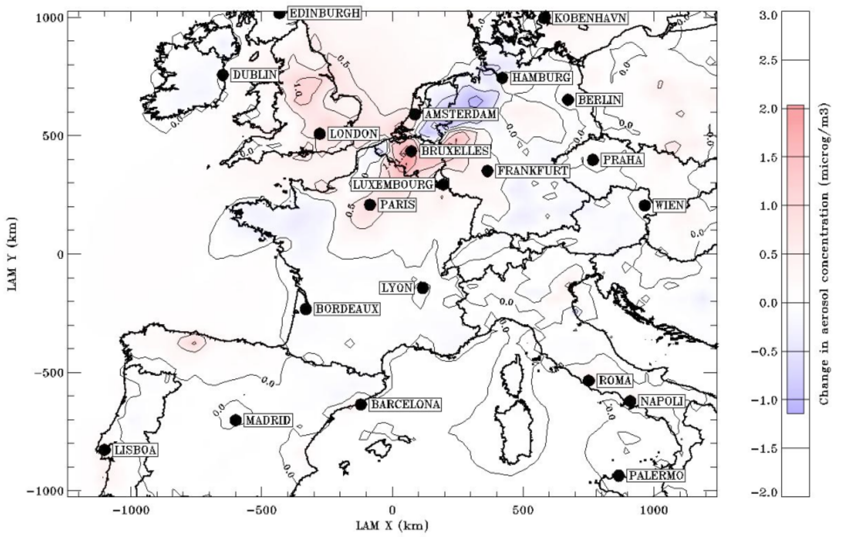

Figure 4: Difference in monthly average aerosol concentration (µg m^{-3}) between two simulations with a 15% emission reduction of either NO_x or NH_3 in June 2006. Blue and red colors show the regions where aerosol formation is more sensitive to NO_x and NH_3 emissions, respectively.

CONCLUSIONS

We studied the sensitivity of ozone and aerosols to their precursor emissions in Europe using CAMx air quality model in January and June 2006. In case of ozone, only June 2006 was evaluated whereas both summer and winter months were simulated for aerosol sensitivity studies. Isoprene is an important biogenic precursor for ozone and it can also contribute to the formation of as secondary organic aerosols. We investigated the effect of the uncertainty in isoprene emissions on ozone and SOA. Isoprene emissions were increased by a factor of four based on the literature data. Model results showed an increase in afternoon ozone concentrations by up to 10% especially in southern Europe where isoprene emissions are more abundant. Aerosol concentrations increased only by a small amount (1%) when isoprene emissions were increased because the SOA yield of isoprene is much lower compared to other biogenic species such as monoterpenes and sesquiterpenes.

Simulations with reduced precursor emissions suggested that NO_x reductions are more effective to reduce afternoon ozone concentrations in a large part of the European domain. On the other hand, VOC reductions lead to lower ozone levels around urban areas.

Sensitivity of inorganic aerosol formation to precursor emissions was studied using reduced ammonia and NO_x emissions. The model predicted that inorganic aerosol formation is more sensitive to ammonia emissions in a large part of Europe in winter. On the other hand, the effect of ammonia emission reductions on aerosol mass is predicted to be lower in summer due to higher ammonia emissions.

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