Chemical effects of UV fluctuations inferred from total ozone and tropospheric aerosol variations

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Abstract. A regional-scale photochemistry model with 50 km horizontal resolution and 20 layers in the vertical is described. The model's domain includes Europe and most of the North Atlantic and the Arctic region. Model results for the summer months April-September 1996 are presented and compared to measurements. Emphasis is on the Aegean Sea where extensive measurements were made as part of the European Union project Photochemical Activity and Solar Ultraviolet Radiation (PAUR). The model sensitivity with respect to changes in UV radiation, caused by moderate variations in the total ozone column (25 Dobson units), are explored and shown to be small. Aerosol optical depth was calculated from Mie scattering theory using the modeled total sulphate column and used to calculate perturbations of the photolysis rates due to sulphate aerosols. Only small effects on monthly averaged ozone are found with the inclusion of aerosols. For individual days, occasional large variations in calculated ozone levels are seen when the aerosol optical depth is fixed at a high value. The inclusion of aerosols result in a slight reduction of high ozone events over central parts of Europe.

1. Introduction

Episodes with high concentrations of ozone in the planetary boundary layer (PBL) over Europe are regularly observed during spring and summer. The enhanced ozone levels are known to cause significant damages to agricultural production and human health. The episodes are caused by enhanced regional chemical production of ozone due to anthropogenic emissions of NOx, CO, and hydrocarbons. In addition to the chemical ozone precursors, solar radiation in the UV to visible range plays an important role in the ozone production process. In the UV-B range, solar radiation affects the photooxidant chemistry through production of the hydroxyl radical (OH) which initiates photochemical processes by starting the oxidation of pollutants in the troposphere. The amount of solar UV-B radiation reaching the lower troposphere is a function of the overhead ozone. Solar radiation is also affected by Rayleigh scattering, scattering and absorption by aerosols and clouds, and backscattering of the Earth's surface. In addition to variations in cloudiness, observations have shown that there are significant short-term and long-term variations both in stratospheric ozone amount and aerosol amount, and since both these processes affect the photolysis rates (J values), the photochemical activity in the PBL is likely to be affected.

There are complicated nonlinear relations between the concentrations of ozone precursors, the amount of UV radiation, and the production and destruction of ozone [Fuglestvedt et al., 1994; Isaksen et al., 1978; Lin et al., 1988]. To model the ozone levels over Europe, where there are large gradients in emissions and concentrations of ozone precursors, a model with high spatial resolution is needed.

In this study we use a new regional chemical tracer model, Multilayer Atmospheric Chemistry Model, Oslo (MACHO), developed at the Norwegian Meteorological Institute in cooperation with the University of Oslo, to study the interactions between tropospheric aerosols, UV radiation, and photochemistry in the planetary boundary layer (PBL). The model results are compared with observations of key chemical parameters carried out during June 1996, as part of the project Photochemical Activity and Solar Ultraviolet Radiation (PAUR) [Zerefos, 1998; Zerefos et al., 1998], as well with measurements from the Cooperative Program for Monitoring and Evaluation of Long Range Transmission of Air Pollutants in Europe (EMEP) network.

Using the observations taken during the PAUR campaign, Kylling et al. [1998] found that, compared with an aerosol–free sky, the aerosol loading reduced the surface UV irradiance by 5–35% depending on the aerosol optical depth and single-scattering albedo. Further-
more, the changes in aerosol loading gave larger variations in the surface UV irradiances than the changes seen in the ozone column, but contrary to aerosol effects the effect of changes in the ozone column is very wavelength-dependent. Therefore one might expect different effects on the photolysis of O(1D) compared to NO2. Model studies by Dickerson et al. [1997] have shown that aerosols may accelerate photochemical smog production in the PBL. To investigate these effects, model sensitivity studies are made with changes in UV caused by fluctuations in the total ozone column and by aerosol optical depth inferred from the total vertical column of sulphate calculated by the MACHO model.

2. Model Formulation

The MACHO model is a regional-scale Eulerian photochemistry model with approximate 50 km resolution in the horizontal and 20 layers in the vertical, of which 10 are below 3 km. The model time step is 10 min, but for the vertical advection the time step is reduced to 5 min. The model is operated on the extended EMEP domain, covering most of Europe and the Mediterranean, large parts of the North Atlantic, and the Arctic region. A description of the model for nitrogen and sulphur chemistry is given by Jonson et al. [1998a], and for sulphur only by Berge and Jakobsen [1998]. A detailed model description is included in the latest EMEP report on photochemistry [Jonson et al., 1998b].

2.1. Transport

Meteorological input data to the MACHO model are generated by a dedicated version of a numerical weather prediction (NWP) model developed at the Norwegian Meteorological Institute [Nordeng, 1986, 1992]. The input data are archived every 6 hours. The MACHO model solves the mass continuity equations for trace gases on the same horizontal and vertical grids as the meteorological data, that is, σ coordinates (normalized vertical pressure), together with a polar stereographic projection true at 60°N. Time splitting is used to solve the system of equations. In the horizontal a fourth-order Bott scheme is used for space discretization of the advection, and a second-order scheme is used in the vertical [Bott, 1989a, b]. An implicit central-difference scheme is applied for space discretization of the vertical diffusion [Berge and Jakobsen, 1998]. The vertical subgrid scale turbulent transport is modeled as a diffusive effect. In the MACHO model the diffusivity coefficient $K_Z$ is derived from the basic meteorological parameters following the same procedure as utilized in the NWP model. In the work of Berge and Jakobsen [1998] a detailed description of the model formulation is given.

2.2. Emissions

Estimates for emission fields for SO2, NH3, NOx, CO, and volatile organic compounds (VOC) are based on data submitted officially to EMEP for 1996 from the participating countries. For most countries the emission data are available on the 50 km EMEP grid. A distinction is made between surface sources (below 100 m) and high stack sources (above 100 m). For SO2 and NOx, emissions from international shipping are included from the Atlantic including the North Sea. For countries bordering the North Sea and the northeast Atlantic Ocean (The Netherlands, Belgium, United Kingdom, etc.), 10 to 15% of the total deposition of total nitrogen can be attributed to emissions from international shipping. For Portugal and Ireland, as much as 25 and 19%, respectively, is from international shipping [Tsyro and Berge, 1997]. Unfortunately, no information on international shipping is at present available from other sea areas, for example, the Mediterranean. Seasonally averaged aircraft emissions are included for NOx [Gardner et al., 1997]. Emissions of NOx from lightning is included as monthly averages on a T21 resolution (5.6°x 5.6°) [Köhler et al., 1995]. Biogenic emissions of isoprene are calculated based on the E-94 inventory [Simpson et al., 1995].

2.3. Chemistry

The chemical mechanism is based on the Oslo CTM1 [Bernsen and Isaksen, 1997], and the Oslo CTM2 [Sundet, 1997] models. The mechanism in the MACHO model has been extended to also include sulphur and ammonium parameterized in the same way as in the EMEP Eulerian acid deposition model [Jonson et al., 1998a]. The aqueous phase chemistry applied in the EMEP Eulerian acid deposition model is also implemented as described in more detail below. While acetone and dimethyl sulfide (DMS) are calculated in the Oslo CTM1 and CTM2 models, this is not done in the MACHO model. A detailed description of the chemistry is also included by Jonson et al. [1998b].

2.3.1. Oxidation of SO2 to sulphate. SO2 is oxidized to sulphate both in the gas and aqueous phase. In the calculations we always assume equilibrium between the two phases. It should also be noted that in case only a fraction of the grid volume is occupied by clouds, the total concentration (gas plus aqueous) of soluble components is assumed to be uniformly distributed in the grid volume. If the cloud evaporates, the total concentration is always equal to the gas phase concentration. For both gas and aqueous phase reactions we scale the reaction rates, rather than the concentrations, by the solubility and cloud volume fractions. In the present calculations we have assumed a constant pH value of 4.5.

2.3.1.1. Oxidation of SO2 in the gas phase: In the gas phase, SO2 is oxidized by OH. For this reaction we have found it convenient to define a pseudo reaction rate $k'_{SO2}$ where the reaction rate $k_{SO2} (2.0 \times 10^{-12}$ molecules$^{-1}$cm$^3$) [Atkinson et al., 1996] is scaled by the fractional cloud volume $W$ in the grid volume and the fractional solubility of SO2 in clouds, $f_{SO2}$:

$$ k'_{SO2} = k_{SO2} [(1 - f_{SO2})W + 1 - W]. \tag{1} $$
A definition of the fractional solubility factor is given by Jonson and Isaksen [1993] and by Seinfeld and Pandis [1998, pp. 343–344]. With the above equation, SO₂ is oxidized both in the cloud free parts of the grid box and in interstitial cloud air.

2.3.1.2. Oxidation of SO₂ in the aqueous phase: Although a number of oxidants may contribute in the oxidation, only O₃ and H₂O₂ are considered here. The rate of production for sulphuric acid in cloud droplets is expressed as

\[ P = \frac{k'_{c1}}{k_{c1}} \left( H_{SO_2} \right) \frac{f_{SO_2}}{f_{H}} \left( W \right) \]

where \( k_{c1} = 8.3 \times 10^{5} \text{ mol}^{-1} \text{L} \) [Martin and Darnschen, 1981] is the reaction rate for the oxidation by H₂O₂, and \( k_{c2} = 1.8 \times 10^{4} \text{[H⁺]}^{-0.4} \text{mol}^{-1} \) [Möller, 1980] is the reaction rate for the oxidation by O₃. For the aqueous phase reactions we define pseudo reaction rates, taking into account the solubility of SO₂, H₂O₂, and O₃, the liquid water content, and the fractional cloud cover. The pseudo reaction rates then become

\[ k'_{c1} = k_{c1} \Gamma \left( H_{SO_2} \right) \frac{f_{SO_2}}{f_{H}} \left( W \right) \]

and

\[ k'_{c2} = k_{c2} \Gamma f_{SO_2} f_{O_3} W \]

for the oxidation by H₂O₂ and O₃, respectively. The parameters \( f_{H}, f_{O_3} \) are the fractional solubilities of H₂O₂ and O₃. \( \Gamma \) is a conversion factor converting \( k'_{c2} \) to molecules⁻¹ cm⁻³. HSO₂ is the Henry’s law constant, and H₂SO₄ is the effective Henry’s law constant for SO₂ as defined by Seinfeld and Pandis [1998, pp. 346–347].

2.3.1.3. Oxidation of SO₂ in gas and aqueous phase: With the definitions above, the oxidation of SO₂ to sulphate in gas and aqueous phase is expressed as

\[ P = \left( k'_{c_{OH}} + k'_{c_{f1} H_2O_2} + k'_{c_{f2} O_3} \right) SO_2 T \]

where SO₂ T is the sum of SO₂ dissolved in the droplets and in the gas phase.

2.3.2. Ammonium sulphate and ammonium nitrate. Ammonium sulphate is assumed to be formed instantaneously, only limited by the availability of the least abundant of the two species. In the atmosphere, ammonium sulphate is present in two forms, (NH₄)₂SO₄ or NH₄HSO₄. We assume equal concentrations of the two forms. Any excess NH₄ may then react with HNO₃, forming ammonium nitrate (NH₄NO₃) through an equilibrium reaction [Mozurkewich, 1993]. The ammonia chemistry used in the model, including the equilibrium reaction with HNO₃ forming ammonium nitrate, is described by Jonson et al. [1998a].

2.4. Photodissociation Rates

The photodissociation rates (J values) are calculated off-line as a function of solar zenith angle and latitude for clear-sky conditions and for two predefined clouds using the model of Kylling et al. [1995]. Altogether, 17 photolytic reactions are included. The ozone profiles are from a two-dimensional (2-D) global model which extends from the surface to 50 km [Stordal et al., 1985]. The profiles are scaled by observed total ozone columns from Dutsch [1974]. For the base runs presented in section 3 below, the optical properties of the aerosols, optical depth, single-scattering albedo, asymmetry factor, were taken from the background aerosol model of Shettle [1989]. At 355 nm the optical depth was 0.167, the single-scattering albedo was 0.96, and the asymmetry factor was 0.66. All are functions of the wavelength. Humidity is not taken into account, thus all aerosols are dry, and the optical depth is somewhat smaller than if humidity had been included. In section 4 the Shettle aerosol model is replaced by Mie calculations based on the sulphate columns of the MACCHO model. Cloud base for the two predefined clouds is at 1 km above the surface. The first predefined cloud is 3 km deep, with a water content of 0.7 g cm⁻³ and a mean droplet radius of 10 μm. The second predefined cloud is 1 km deep, with water content of 0.3 g cm⁻³ and a mean droplet radius of 10 μm. The J values are calculated using the new recommendations for absorption cross sections and quantum yields from DeMore et al. [1997]. For most components the changes are small compared to earlier recommendations. However, the photolysis of O₃ to O(¹D) is approximately 30% higher. For the PAUR campaign a model related to the photodissociation model has been compared with surface measurements of the irradiance. The absolute difference between model and measurements ranged between −5% and +5% with little dependence on wavelength [Kylling et al., 1998]. Also for the PAUR campaign, the photodissociation model has been compared with radiometric measurements of J(NO₂) with differences less than ±10% [A. Kylling, unpublished results, 1999].

2.5. Initial and Lateral Boundary Concentrations

For most of the chemical components the initial concentrations and the mass advected into the model domain across the lateral boundaries are calculated with the Oslo CTM2 [Sundet, 1997] with a T21 resolution (5.6° x 5.6°). In the base run, mean concentrations for June 1996 are used. For SO₂ and SO₄, lateral boundary concentrations are based on the results from a hemispheric model [Tarrason and Iversen, 1998], and for ammonia they are zero.

Across the tropopause there are large gradients in the concentrations of O₃. In an attempt to reproduce these gradients, initial and lateral boundary concentrations of O₃ at the four uppermost layers (level four corresponds to the approximate level of the tropopause) are scaled according to the potential vorticity (PV). It has been shown that there is a good correlation between O₃ and PV in the stratosphere and upper troposphere [Bec-
3. Model Results

In the first subsection, model results covering major parts of Europe are presented, and model calculations are compared to selected sets of measurements in the EMEP network for April–September 1996. In the second subsection, model results are compared to measurements made during the PAUR campaign, June 1996.

3.1. Model Results for April–September 1996

In Figure 1 the monthly averaged surface concentrations for June 1996 of O₃, NO₂, peroxyacetyl nitrate (PAN), and the total sulphate column (SO₄²⁻ and ammonium sulphate) are shown. Ozone levels are elevated over central and southern Europe, and in particular in southern parts of Germany, western and southern parts of France, in northern Italy, and in parts of eastern Europe. As NO₂ has a short lifetime, the highest concentrations are found in the source areas. High concentrations are in particular found in and around the English Channel. High PAN levels are found over northwestern parts of the Alps. In the model other organic nitrates than PAN are also represented as PAN. These PAN like components can be formed by biogenic emissions. By excluding biogenic emissions, calculated PAN levels are reduced by about 30% throughout much of Europe. High sulphate columns are found over eastern Europe and in particular around the volcanos in southern Italy.

For NO₂, relatively high concentrations are also seen along the shipping routes. This is clearly seen south of the English Channel, a few kilometers off the coast of the Iberian Peninsula and just west of the entrance to the Mediterranean through the strait of Gibraltar.

In Figure 2, scatterplots of calculated versus measured concentrations of NO₂ and sulphate averaged over the 6-month period April–September are depicted. A perfect fit between calculated and measured concentrations require that the sites lies along the central diagonal line. The two other diagonal lines represent a factor of 2 difference between calculated and measured concentrations. There is a considerable scatter for all the two components shown. However, they both have

\[ \text{O}_3 = 4.5 \times 10^{-8} \times \text{PV}. \]
a characteristic lifetime in the atmosphere of the order of days or less. Combined with large variability of the source strength within the 50 km grid, a large scatter can be expected at the individual sites. For NO$_2$ (Figure 2, left) the overall agreement between model and measurements is good.

Sulphate concentrations are underpredicted by the model, whereas calculated SO$_2$ concentrations are somewhat lower than observed [Jonson et al., 1998b]. We believe that this is caused by an insufficient oxidation in the aqueous phase. In the aqueous phase, dissolved SO$_2$ can be oxidized by other oxidants than O$_3$ and H$_2$O$_2$. Furthermore, H$_2$O$_2$ can be produced in droplets, further increasing the oxidation by this component [Jonson and Isaksen, 1993]. It could also be that the deposition processes for SO$_2$ or sulphate are too fast in the model.

In Figure 3, calculated and measured daily maximum ozone concentrations are shown for a number of measurement sites in Europe. In general, the model is able to reproduce the major ozone events. For Aliartos in Greece the model does not compare well with the measurements. However, this site can be influenced by local industry and a provincial road about 500 m from the site (J. E. Hansen, Chemical Coordinating Centre EMEP, private communication, 1999), and ozone concentrations are likely to be influenced by local NO$_x$ emissions. In northern Europe and in the British Isles, represented by Utø and Mace Head, ozone concentrations are often underpredicted.

3.2. Eastern Mediterranean: June 1996

Measurements of a number of chemical components, including O$_3$, NO, NO$_2$, and PAN, were made on the island Agios Efstratios and at Tatoi, near Athens, Greece, during the first 14 days of June 1996. Ozone was measured with a commercial instrument with a precision/accuracy of 1%/2%. NO, NO$_2$, and PAN were measured with a Luminol instrument, equipped with a NO to NO$_2$ converter (Scintrex/Unisearch) for NO$_2$. For NO$_x$ the precision/accuracy was 5%/10% above 3 ppbv. Below 3 ppbv of NO$_x$ the instrumental accuracy decreased due to interferences from PAN and ozone, and nonlinear responses of the instrument. For PAN the precision/accuracy was 5%/10-20%. A more detailed description of the PAN and NO$_x$ systems used for measurements and the procedures applied for calibration is given by Suppan et al. [1998].

3.2.1. Meteorological situation. The meteorological situation throughout most of the 2-week PAUR campaign (June 1–14) was dominated by a high-pressure system over northern Europe with a ridge extending toward the Balkan, and low pressure over Turkey. The circulation pattern transported air from Scandinavia over eastern Europe to the Black Sea through the Danube valley before entering the Aegean Sea. Above the Aegean Sea there was strong subsidence, and subsequently, apart from the lowest model layer, the lower troposphere was very dry with typical relative humidity often between 30 and 40%. This circulation pattern is typical for this region at this time of the year [Kallos et al., 1998]. Later the high-pressure system moved toward the British Isles, and a more direct flow pattern from eastern Europe toward the Aegean Sea was established. Figure 4 shows the mean sea level pressure (MSLP) and winds in the lower free troposphere at 1200 UTC for June 8 and 14, 1996, as calculated by the
numerical weather prediction model. During the transport over the European continent the air in the planetary boundary layer was subject to significant input of pollutants from surface sources. Calculated ozone concentrations at 1200 UTC for the same 2 days are shown in Figure 5. On the first day (June 8), high calculated ozone levels are seen in the high-pressure region in northwestern Europe. On the second day (June 14), with winds from the northwest for most of Europe, high ozone levels are mostly confined to the Mediterranean region. For western Europe this is also illustrated by the measurements and model calculations at Vredepeel in the Netherlands (Figure 3) with daily maximum ozone levels of up to 100 ppbv in the first part of June, and a local minimum in daily maximum levels in the middle of the month.

Figure 3. Measured (solid line) versus calculated (dotted line) daily maximum concentrations of ozone in ppbv in 1996.
3.2.2. Model results and PAUR measurements: Ozone vertical profiles. For the PAUR campaign, several ozone soundings were made from Thessaloniki, Greece. In Figure 6 the ozone concentration is shown for the troposphere for 6 days in June 1996. The abrupt increase in ozone in the tropopause is well reproduced by the model. In the upper part of the model, ozone is determined by the PV adjustment at the lateral boundaries and the circulation in the model. Even though the model is not capable of reproducing the fine structure seen in the vertical soundings, the overall agreement in the free troposphere is good. At Thessaloniki an "ozone belly" in the PBL with elevated concentrations up to 2 km altitude is seen in the soundings on June 8 and 10. This is probably a regional-scale feature caused by photochemical production during a 3-5 day period when the air was over eastern Europe and vertical mixing was suppressed by the high-pressure system over central Europe (Figure 4). The model is not able to reproduce this, which could be due to a combination of insufficient knowledge of the emissions in eastern Europe and too much vertical mixing between the PBL and the free troposphere in the model. In the period June 6–12, ozone levels are also underpredicted on the island of Agios Efstratios and at Tatoi close to Athens (see below). Ozone soundings from Payern in Switzerland, Legionovo in Poland, and Lindenberg in Germany were also compared with model results, and the agreement is qualitatively similar to that shown in Figure 6.

3.2.2.1. Agios Efstratios: Over the Aegean Sea, the ozone budget is enriched both in ozone and ozone precursors. Over the ocean, surface deposition is slow, and local sources of nitrogen oxides are in general small. The combination of these effects gives much less ozone

Figure 4. Meteorological situation at 1200 UTC on (left) June 8 and on (right) June 14. Solid lines shows the mean sea level pressure. The wind arrows are from model level 10, approximately 2 km.

Figure 5. Ozone levels in ppbv at 1200 UTC on (left) June 8 and (right) June 14.
loss during night than for the European continent. Consequently, quite small diurnal variations of ozone are found in both observations and model results. (Figure 7, top-left panel). During the first 6 days of the campaign the levels of calculated and measured ozone are in very good agreement. During the following week the observed concentrations of ozone slowly increased, reaching a maximum of between 70 and 80 ppbv in the afternoon, while the calculated concentrations remain at the 55–60 ppbv level without significant diurnal variations. The reason for this difference is unclear. Ozone sonde measurements, discussed above, indicate enhanced O₃ in the PBL for this period, possibly from ozone production not captured by the model. Emissions are less known around the eastern Mediterranean area compared to most other parts of the model domain. Toward the end of the period the weather pattern changed, as discussed above. In the calculations this can be seen.

Figure 6. The ozone concentration as measured by ozone sounds (solid lines) released in Thessaloniki, Greece, and as calculated by the MACHO model (solid lines with square markers.)

Figure 7. Measured versus calculated hourly averaged concentrations of the chemical components measured at Agios Efstratios. For O₃, NO₂, and PAN, calculated concentrations with estimated emissions from international shipping are also shown. Data on O₃, NO₂, and PAN courtesy of P. Fabian and B. Rappenglück, University of Munich.
as an increase in ozone, peaking at more than 75 ppbv in the afternoon on June 14. This calculated peak in ozone is also seen in the measurements. A similar peak in ozone is calculated for the Tatoi station near Athens about 8 hours later (Figure 8).

For NO and NO₂ (Figure 7, two bottom panels) and PAN (Figure 7, top-right panel) the agreement between calculations and measurements is less satisfactory than for ozone. For PAN, model calculations and measurements have a similar diurnal cycle, but the model overestimates the daytime maximum concentrations by a factor of 3-10.

Several factors contribute to the overestimation of PAN. The model underestimates the NO/NO₂ ratio, favoring PAN production. This could be because the model is unable to resolve individual plumes from ships. Second, the model calculates peak concentrations of OH of about 10⁷ molecules cm⁻³. Calculations of OH based on measurements of J(O¹D), H₂O, and key chemical species indicate that peak OH concentrations might be a factor of 2 lower [Zerefos, 1998], but these calculations should be considered as order of magnitude estimates only, as not all pathways leading to OH formation were considered. If the value based on the measurements is more correct, it implies that the model overestimates NMHC oxidation and subsequently PAN production. A third contributing factor is the design of the chemistry scheme in which also higher-order peroxy nitrates are represented as PAN. The high emission rates of NMHCs from vegetation over southeast Europe in June increase PAN production in the model, while in reality a large fraction is higher-order peroxy nitrates. As discussed in section 3.1, about 30% of the calculated PAN concentrations can be attributed to biogenic emissions. Previous applications of the chemistry scheme in a global CTM gave very good agreement between measured and modeled PAN concentrations [Jaffe et al., 1997].

For NO and NO₂, calculated concentrations are substantially lower than measured, and in particular for NO there are large peaks in the measurements not captured by the model. Furthermore, the NO peak can be higher than the corresponding peak in NO₂, indicating very fresh emissions. The station was situated in a small valley, and influence from local sources cannot be excluded. The island has a ferry connection only twice a week and is not in the direct traffic route for international shipping. However, the island could be influenced by emissions from ships farther north in the Aegean Sea. As a sensitivity test, an additional NOₓ source of 1500x10⁶ kg per year (counted as NO₂) was added at the surface level to the grid box just west of Bosporus, and 750 metric tons in three pairs of grid boxes in what we believe is the most direct shipping route from Bosporus out of the Aegean Sea. This is about 20% of the contribution from international shipping just west of Gibraltar. In Figure 7, calculated concentrations of O₃, NO₂, and PAN are shown also with this source included. Calculated concentrations

Figure 8. Measured versus calculated hourly averaged concentrations of the chemical components measured at Tatoi, Athens. Data on O₃, NOₓ, and PAN courtesy of P. Fabian and B. Rappenglück, University of Munich.
of NO₂ are now closer to the measurement. For PAN the overestimation by the model is even stronger. However, contrary to the real atmosphere, shipping emissions are evenly distributed over a 50 km grid square, not as individual plumes. This will affect the NO/NO₂ ratio locally, and possibly PAN formation. For O₃, calculated daytime concentrations are of the order of 5 ppbv higher on several days. We would like to stress that these assumptions about emissions from ships are highly uncertain.

3.2.2.2. Tatoi, Athens: During the entire measurement period, northeasterly (etesian) winds prevailed. Thus at no time did the plume from Athens intercept the station, but with a grid resolution of 50 km, modeled concentrations at Tatoi are heavily influenced by urban emissions. Rappenglück et al. [1999] found that a large fraction of the NMHC measured at Tatoi could be attributed to biogenic sources.

Compared to the measurements, concentrations of NO and NO₂ are overpredicted in the model (Figure 8), in particular, during the first 4 days and on June 13, with calculated NO₂ concentrations of more than 30 ppbv (Figure 8, bottom–left panel). High NO and NO₂ concentrations were also found in the measurements; however, the peak NO₂ concentrations were only about 10 ppbv, and for much of the period the measurements at this site were representative of background conditions. In correspondence with the calculated peaks in NOₓ, ozone is temporarily removed through the reaction

\[ \text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2. \]

To some extent, this effect is also seen in the measurements. For the rest of the period both the model and the observations seem to represent airmasses advected from the Aegean Sea by the northeasterly winds, without significant influence from local sources. For O₃ both measurements and model results show a lack of diurnal variation. The absolute concentrations are about 15 ppbv lower in the model than in the measured values. This corresponds to the difference found for Agios Efstratios and for the ozone sondes at Thessaloniki during the same period, indicating that ozone levels at Tatoi are mostly determined by a regional–scale buildup of ozone.

Calculated PAN levels at Tatoi are lower than on Agios Efstratios. On the island, calculated PAN levels represent aged airmasses, whereas at Tatoi the urban influence is considerable in the calculations, as discussed above. As for O₃, measured PAN levels at Tatoi are in general representative for a larger region (Figure 1, middle left). Measured PAN levels at Tatoi are in the same range as the calculated levels at Agios Efstratios.

3.2.3. Aerosols. The aerosol optical depth during the PAUR campaign was deduced from measurements of the direct UV spectral irradiance made both in Tatoi, Athens, and on the island of Agios Efstratios in the Aegean Sea [Kylling et al., 1998]. The aerosol optical depth at 355 nm is reproduced in Figure 9 together with the sulphate column from the MACHO model. The temporal behavior of the measured aerosol concentration and the modeled sulphate column is similar. In particular, the model reproduces the marked increase on June 13–14. This peak is removed by excluding emissions from Bulgaria. Referring to the meteorological situation on June 14 (Figure 4), sulphate is advected across the southwest Bulgarian upland into the Aegean Sea.

4. Model Sensitivity to Changes in Actinic Fluxes

Two parameters that are likely to affect the actinic fluxes in the lower troposphere are changes in the total ozone column and the abundance of aerosols. Both effects represent a possible human influence on photo-
4.1. Total Ozone Column

In the reference model run the total ozone column ranges from less than 320 Dobson units (DU) in the southern parts of the model domain to 370 DU in the northern part. During the PAUR measurement campaign the measured total ozone column at Tatoi and Agios Efstratios mostly ranged between 330 and 350 DU, but with occasional fluctuations between 310 to 370 DU [Kylling et al., 1998]. In order to test the model sensitivity, in particular with regard to ozone in the boundary layer, a model run with the total ozone column increased by 25 DU (7-8%) throughout the model domain was made. An increase in ozone decreases UV radiation and hence the photolysis rate of ozone to $O(1D)$. For solar zenith angles $0^\circ$, $30^\circ$, $60^\circ$ and $90^\circ$ the reductions in the photolysis rates are 10, 11, 13, and 15%, respectively. The changes in photolysis rates are of the same magnitude as those calculated by Fuglestvedt et al. [1994]. The effects on monthly averaged ozone in June 1996 are small (Figure 10, left). With more total ozone, levels in the lowest model layer are 0.5 ppbv or less lower in polluted areas with high NO$_2$ levels (in particular in western parts of Europe and northern Italy). In background areas, with low NO$_2$, ozone levels increase. On individual days, calculated changes relative to the base model run rarely exceed 3 ppbv. In the Aegean Sea, changes are small. Compared to the overall uncertainties in the model calculations, the effects of a 25 DU change in total ozone are relatively small. Fuglestvedt et al. [1994, 1995] find that global tropospheric ozone levels are reduced following a reduction in stratospheric ozone, but with considerable regional differences. They conclude that the relative response in tropospheric ozone is significantly smaller than the relative change in the total ozone column, in good agreement with the present study.

4.2. Effect of Aerosols

Aerosols may significantly change the actinic flux, thus potentially altering the concentration of atmospheric trace gases. Dickerson et al. [1997] reported increases in the nitrogen dioxide photolysis rate of more than 20% above and in the upper part of a 1000 m thick aerosol layer. The increased photolysis rate of nitrogen dioxide may lead to ozone production in nitrogen-rich regions. For an assumed uniformly distributed aerosol optical depth of 2, Dickerson et al. [1997] found ozone in the PBL to increase by 20–40 ppbv for a region covering the eastern United States. To estimate the effect of aerosols on the atmospheric composition during the PAUR campaign, Mie scattering calculations were performed. For these calculations the aerosols were assumed to consist of ammonium sulphate only. A lognormal size distribution was used with a geometric mean radius of 0.05 μm and a geometric standard deviation of 2. The refractive index of ammonium sulphate was taken from Toon et al. [1976], and the relative humidity was accounted for.

We assume that the aerosols are located in the lowest 2 km. This is in approximate agreement with the findings of Marenco et al. [1998] during the PAUR campaign. In Figure 11 the effects of aerosol optical depths 0.6 and 2 on the photolysis rate of NO$_2$ are shown. For a moderate optical depth of 0.6 the calculated changes in photolysis rates are small, in particular above the aerosol layer. With aerosol optical depth of 2 the changes are large. Optical depths of this magnitude will usually require a combination of high aerosol loading and high humidity. Given the dry conditions in
the work of Dickerson et al. [1997]). As illustrated for the difference in ozone is depicted for June 14. Again, made assuming an optical depth of 2 everywhere (as in small negative contributions to ozone of the order of order of 3 ppbv. An additional model run was also found downwind of Athens. In Figure 12 (left) the difference in ozone is depicted for June 14. Again, differences are small, with maximum reductions of the order of 3 ppbv. An additional model run was also made assuming an optical depth of 2 everywhere (as in the work of Dickerson et al. [1997]). As illustrated for June 14, elevated ozone levels of more than 40 ppbv compared to the base model run are found over parts of Turkey (Figure 12, right) with this assumption. These differences are of the same order of magnitude as those reported by Dickerson et al. [1997]. Elevated ozone is also found downwind of Athens.

In the Mie scattering calculations, only secondary aerosols from sulphate are included. Sulphate is likely to make up less than 50% of the dried out aerosol mass. Additional contributions may come from nitrates, sea-salt particles, elemental carbon, etc. A significant fraction of the aerosols may originate from biogenic emissions. Neither aerosol types are included in the present version of the MACHO model. Pure ammonium sulphate aerosols have a single-scattering albedo close to unity. However, the aerosol single-scattering albedo during the PAUR campaign varied between 0.83, low aerosol optical depth, and 0.97, large aerosol optical depth [Kylling et al., 1998]. This indicates that a rather large fraction of the aerosols were not ammonium sulphate, especially for small aerosol optical depths. In the Mediterranean region a significant fraction of the aerosols may originate from biogenic emissions. Also, elemental carbon may be of importance. Inclusion of both in the Mie calculations will increase the aerosol optical depth. In the work of Hegg et al. [1997] a chemical apportionment of the aerosol column optical depth is made. In the eastern part of the North Atlantic their measurements indicate that wet sulphate contributes with between 30 and 50% of the aerosol column optical depth and that carbonaceous species are likely to contribute with a large percentage.

Effects on ozone require a combination of favorable meteorological conditions, high concentrations of ozone precursors (NOx and VOC) to drive the chemistry and a high sulphate column, usually in combination with high humidity. In Europe, high NOx levels and high sulphate columns are often segregated in space (Figure 1, top right and bottom right, respectively) as high NOx levels are mostly confined to northwestern parts of Europe, whereas high sulphate columns are largely found over eastern and southern Europe.

5. Conclusions

The MACHO regional-scale photochemistry model has been described. Extensive comparisons show that the results from the MACHO model compare favorably with measurements in Europe for a number of pollutants. At the two measurement sites in Greece for the PAUR campaign the model results are less satisfactory, in particular for the nitrogen species. For Tatoi the model resolution is too coarse to resolve the urban emissions from Athens. The measurements on the Aegean island of Agios Efstratios show clear signs of contamination from nearby shipping activity. With assumed emission from international shipping in the Aegean Sea, calculated NO2 levels are much closer to the measured levels. Furthermore, daytime ozone concentrations are increased by about 5 ppbv on several days.

Whereas in the eastern part of the Mediterranean horizontal advection from north to south dominates, the circulation in the western part is dominated by convection and a compensatory subsidence over the ocean possibly leading to a buildup and “cooking” of the pollutants over several days. We believe that NOx emissions from international shipping in the Mediterranean as a whole are likely to have a marked effect on photochemical smog formation in the Mediterranean and that the largest effects will be found in the western part.

Changes in UV brought about by a moderate increase in the total ozone column are shown to have limited effects on the chemistry in the PBL. Using aerosol optical
depths inferred from the calculated sulphate column, we find only very small differences in calculated ozone concentrations compared to the reference model. Assuming an optical depth of two differences in ozone can be large for individual days.

Acknowledgments. We would like to thank Roar Skålin, now at DNMI, and Steffen Unger, GMD-FIRST, Berlin, for valuable help in parallelizing and speeding up the MACHO code. At DNMI, Jan Eiof Jonson has been partially funded by the Nordic Council of Ministers through the project “Further development and applications of multi-pollutant acid deposition and oxidant models.” Part of this work was done within the framework of the PAUR project funded by the European Commission (contract ENV4-CT95-0048). We gratefully acknowledge data on O₃, NOₓ, and PAN measured at Ágios Efstratios and Tatoi by B. Rappengliick, University of Munich.

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(Received February 26, 1999; revised November 8, 1999; accepted November 15, 1999.)