

1 Introduction

Air pollution is a major environmental and health problem affecting developed and developing countries around the world (Akimoto, 2003). Increasing amounts of potentially harmful gases and particles are being emitted into the atmosphere on a global scale, resulting in damage to human health and the environment and reducing the resources needed for the long-term sustainable development of the planet (Baldasano *et al.*, 2003). Urban growth and industrial development have caused serious problems of air pollution in the last decades. The atmosphere has become a massive chemical reactor where pollutants such as volatile organic compounds (VOCs) and nitrogen oxides (NO_x) react in the presence of solar radiation to yield a variety of pollutants. In the second half of the XXth century, large cities began to experience a new pollution problem, which had been unknown until then. This condition is called *photochemical smog* because it contains an increased concentration of ozone (O_3) in the lower atmosphere (troposphere) formed by the interaction of nitrogen oxides, volatile organic compounds and solar radiation. The best-known and most studied case is that of Los Angeles, USA (Figure 1.1), which was identified by Hagen-Smith *et al.* (1951) by recognizing symptoms of damage to plants.



Figure 1.1. First registered photo of photochemical smog in Los Angeles (1943).

Already in the decade of the eighties of the last century, it became clear that the changing composition of the earth's atmosphere was becoming a problem going beyond local and regional scale and spreading to entire continents through what is known as acid rain. It was caused by the intense use of fossil fuels with high sulfur content to generate electric energy in classic thermal power plants. Finally, the issue took on a global scale, far greater than the classical concept of air pollution and began to threaten the basic workings of the planetary system, particularly in a fundamental area: the atmosphere.

Today, the majority of large cities in the world have problems related to air quality, not only in developed countries (North America, Europe or Japan) but also in cities of developing areas such as Mexico City, Santiago de Chile, Cairo, Bangkok, etc. (Figure 1.2).

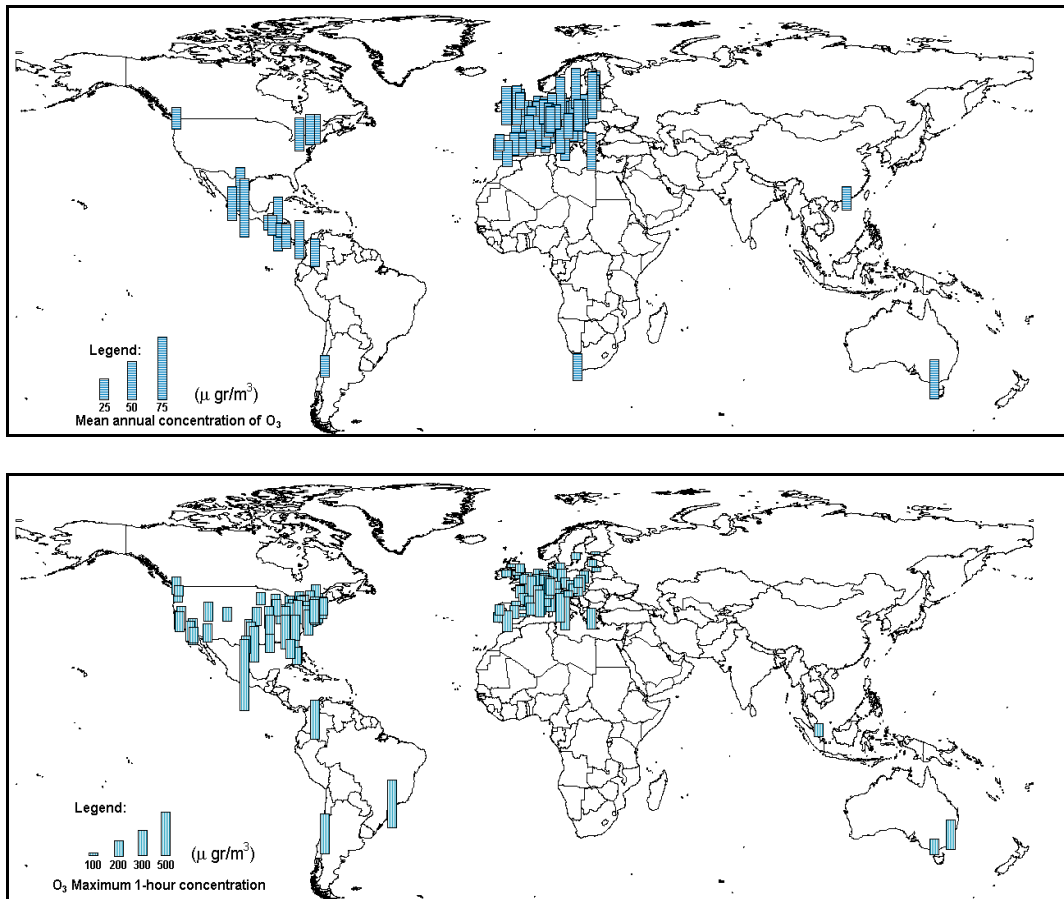


Figure 1.2. Average annual (up) and maximum 1-hour concentration (down) of ground-level ozone (Baldasano *et al.*, 2003).

Air pollutants are usually classified into suspended particulate matter (dusts, fumes, mists and smokes), gaseous pollutants (gases and vapors) and odors. Particulate matter suspended in air includes total suspended particles (TSP), PM₁₀ (particulate matter with median aerodynamic diameter less than 10 µm), PM_{2.5} (particles with median aerodynamic diameter less than 2.5 µm), fine and ultra fine particles, diesel exhaust, coal fly-ash, mineral dusts (e.g. coal, limestone, cement), metal dusts and fumes (e.g. zinc, copper, iron, lead), acid mists (e.g. sulfuric acid), fluoride particles, paint pigments, pesticide mists, carbon black, oil smoke and many others.

Gaseous pollutants include sulfur compounds: e.g. sulfur dioxide (SO₂) and sulfur trioxide (SO₃), carbon monoxide (CO), nitrogen compounds: e.g. nitric oxide (NO), nitrogen dioxide (NO₂), ammonia (NH₃), organic compounds: e.g. hydrocarbons (HC), volatile organic compounds

(VOCs), halogen compounds (HF and HCl), etc. Referring to odors, while some are known to be caused by specific chemical agents such as hydrogen sulfide (H₂S), carbon disulfide (CS₂) and mercaptans (R-SH, R₁-S-R₂), others are difficult to define chemically.

Secondary pollutants may be formed by thermal, chemical or photochemical reactions. For example, photochemical reactions between NO_x and reactive hydrocarbons can produce O₃, giving rise in urbanized zones to the formation of photochemical smog. The emission of primary pollutants (SO₂, particulate matter, NO_x, etc.) to the atmosphere contributes to the production of secondary ones that highly increment air pollution. However, the impact that occurs in a specific region depends not only on its own atmospheric emissions, but also on a complex relation between transport, dispersion, reaction and deposition mechanisms that comprise all the atmospheric processes. Consequently, the study of air pollution has several approaches, depending on the mechanism to analyze.

1.1 Air Pollution at the Beginning of the XXIst Century

Nowadays, one of the main environmental problems derives from the increment in air pollutants' concentration. As an example, tropospheric ozone levels today are higher than those measured in the pre-industrial age, as a result of the increase in emissions of nitrogen dioxide and volatile organic compounds proceeding from industry and vehicles since 1950s. Regional model simulations also clearly indicate that there would be lower levels of photooxidant species in the unpolluted boundary layer over Europe, if anthropogenic emissions were excluded (Ebel *et al.*, 1991).

According to De Leeuw *et al.* (2001a), the most serious problems in Europe are related with particulate matter with a diameter under 10 micrometers (PM₁₀), nitrogen dioxide and ozone. The objectives proposed by the EU related to air quality for year 2010 are less well attained in southern Europe than in the more northern cities. Partly this will be caused by better dispersion conditions in northern cities.

Baldasano *et al.* (2003) compiled information about air quality in the principal cities of the world, both in developed and developing countries, and made an evaluation of the tendencies that emerged at the end of the XXth and the beginning of the XXIst century. As seen on Figure 1.3, there is a clear downward tendency in the values of particulate matter, sulfur dioxide and nitrogen dioxide, although these levels are evidently above the various thresholds and guideline values established.

If data is analyzed by grouping countries according to zone (Table 1.1), it is found out that occidental, high-income countries do not have problems related to SO₂. Nitrogen oxides reach high values all around the world, due to the intensive automobile use. On the other side, cities in zones with low income have low averages for suspended particles. Ozone shows important

average values in all of the regions except Europe, which also shows a high value. This situation illustrates that the ground-level ozone is a global problem.

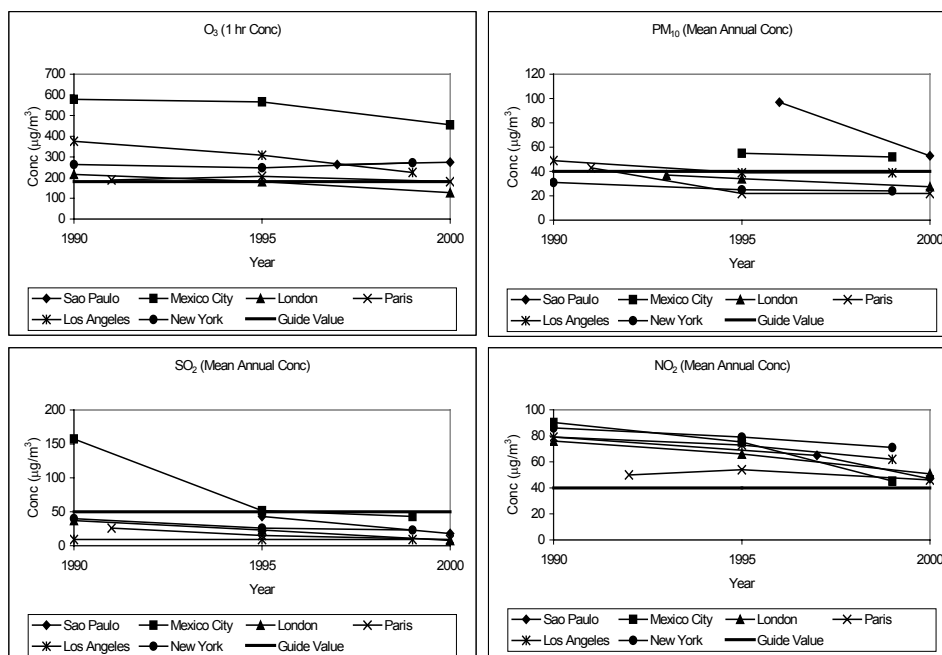


Figure 1.3. Air quality trends in mega-cities (Baldasano *et al.*, 2003).

Table 1.1. Concentrations of air pollutant by zone (Baldasano *et al.*, 2003).

Zone	SO ₂	NO ₂	Particulate matter		Ozone	
	µg/m ³	µg/m ³	TSP µg/m ³	PM ₁₀ µg/m ³	Annual (µg/m ³)	Max 1 hr (µg/m ³)
Africa	35	44	89		37	
Europe	12	42	58	28	39	176
North America	13	39	21	25	39	229
Latin America	41	46	187	66	42	412
Asia	74	51	251	43	32	181
Oceania	4	18	43	17	51	237

1.1.1 Trends of Photooxidant Concentrations and Precursors

Trend studies attempt to establish the evolution on the concentration of pollutants during the last decades. Analyses of available records have suggested that ozone concentrations in the 1990s were higher than what they were around the beginning of the XXth century. For example, Marengo *et al.* (1994) and Vingarzan (2004) found out that tropospheric ozone concentrations have increased in a factor of five since the final years of nineteenth century (Figure 1.4).

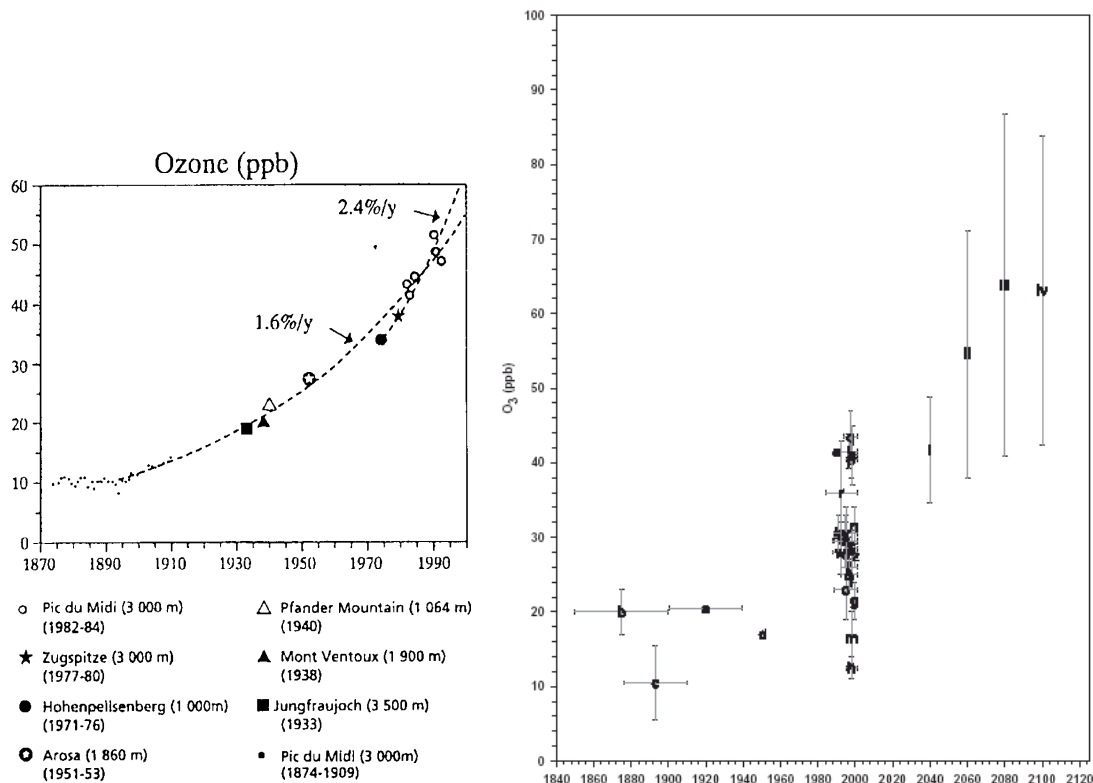


Figure 1.4. Evolution of tropospheric ozone (ppb) in Europe above the PBL during XXth century (left, Marenco *et al.*, 1994); and (right) historical, current and projected background surface ozone annual concentrations in the PBL (a. Athens, Greece; b. Europe; c. Montsouris, France; d. and e. Arosa, Switzerland; f. Pt. Barrow, Alaska; g. US Virgin Islands; h. American Samoa; i. South Pole, Antarctica; j. Arrival Heights, Antarctica; k. Svalbard, Norway; l. Mauna Loa, Hawaii; m. Mount Rainier National Park, Washington; n. Denali National Park, Alaska; o. Glacier National Park, Montana; p. Lassen National Park, California; q. Rocky Mountain National Park, Colorado; r. Theodore Roosevelt National Park, North Dakota; s. Yellowstone National Park, Wyoming; t. Nova Scotia; u. Quebec; v. Algoma, Ontario; w. Chalk River, Ontario; x. Egbert, Ontario; y. Experimental Lakes Area, Ontario; z. Saskatchewan; \$. Alberta; &. British Columbia; i. Range of surface O₃ projections for the 2040; ii. Range of surface O₃ projections for the 2060; iii. Range of surface O₃ projections for the 2080; iv. Range of surface O₃ projections for 2100) (Vingarzan, 2004).

Nevertheless, meteorological variation from year to year hampers the determination of tendencies in the frequency of episodes with a high ozone level. In addition, it is attributed to the raise of tropospheric ozone levels an increase in the global average radiative forcing of $0.35 \pm 0.2 \text{ W m}^{-2}$, which means that ozone is the third most important greenhouse gas, after CO₂ and CH₄ (IPCC, 2001).

1.1.2 Trends of Tropospheric Ozone

The modern tropospheric ozone measurements are mainly based on ultraviolet absorption, and were started in the 1970s at several remote coastal and high altitude sites (Scheel *et al.*, 1994).

All stations north of about 20°N exhibited a positive trend in ozone that is statistically significant. There are particularly large positive trends observed at the high elevation sites in southern Germany. On the other hand, a statistically significant negative trend of about 7% per decade is observed at the South Pole. The trends observed in the northern hemisphere are largely due to the relatively rapid ozone increase that occurred in the 1970s.

Over the last decade, no or only a small ozone increase has occurred in the free troposphere and, indeed, ozone concentrations at some locations in the polluted boundary layer have increased during the last decade (Borrell *et al.*, 1997). Free tropospheric concentrations are obtained from ozone sondes or from measurements at high altitude sites. Studies of the O₃ sonde records performed by the same authors show, on average, increases in free tropospheric Ozone at northern mid-latitudes of around 10% per decade since 1970. Guicherit and Roemer (2000) indicate that perturbations in anthropogenic emissions of reactive trace gases have caused tropospheric ozone increases, in particular in the northern hemisphere. The number of sites where surface O₃ measurements and O₃ soundings of high quality are performed are small, especially at low latitudes and throughout the southern hemisphere. The longest ozone surface measurements and sounding records are available from Europe, where an upward trend of 5±20% per decade can be observed; the increase occurred, primarily before 1985. Ozone trends for other mid-latitudinal locations are generally smaller. At high latitudes in the southern hemisphere a negative O₃ trend is due to a reduced downward flux of ozone associated with stratospheric ozone depletion.

A detailed study about ozone trends in Europe is the analysis made by de Leeuw (2000). Applying the methodology defined by him on an extended data set covering the years 1994-1999, data was analyzed for a possible trend in statistical parameters (50- and 98-percentiles) and number and severity of exceedances of threshold values. Time series are rather short but the data suggests that there might be a small increasing trend in the 50 percentile values. The peak ozone concentrations expressed as 98-percentiles or as number of exceedance days, tend to decrease in the period 1994-1999. However, these conclusions must be interpreted carefully since on the short time scales considered meteorological inter-annual variations might play an important role. The decrease in peak ozone concentrations is most likely caused by the decrease in European ozone precursor emissions since 1990. Possible explanations for the increasing 50-percentile values are an increase in tropospheric ozone background values caused by a worldwide increase in CH₄, CO and NO_x emissions and a reduced ozone titration by reduced NO_x emissions at the local scale.

Vingarzan (2004) stated that modern day annual average background ozone concentrations over the midlatitudes of the Northern Hemisphere range between approximately 20–45 ppb, with variability being a function of geographic location, elevation and extent of anthropogenic influence. Annual median ozone levels at background stations fall between 23 and 34 ppb. Comparisons of ozone levels with those measured over a century ago indicate that current levels have increased by approximately two times. Although current trends are not uniform, there is

some indication that background ozone levels over the midlatitudes of the Northern Hemisphere have continued to rise over the past three decades, and that this rise has been in the range of approximately 0.5–2% per year. Rising trends were steeper in the 1970s and 1980s compared to the 1990s, which have seen either a leveling off or a decline in the magnitude of these trends.

Last, Sudo *et al.* (2004) analyzed the time evolution of global mean tropospheric O_3 from 1850 to 2000 (Figure 1.5). They showed increases in O_3 at all altitudes toward the present-day. Global mean surface O_3 level increases from 16 ppbv in 1850 to 27 ppbv in 2000 (~+70%). More rapid O_3 increases are indicated after 1950 reflecting the higher increasing rates of O_3 precursors emissions after 1950. O_3 increases, however, appear to be reduced significantly after 1980. This can be attributed to the prescribed stratospheric O_3 depletion, which causes: (1) a decrease in O_3 input to the troposphere; and (2) a shorter photochemical lifetime of tropospheric O_3 with increased tropospheric UV radiation. O_3 of stratospheric origin, decreases after 1980 (especially in the upper troposphere: 300hPa) reflecting reduced O_3 transport from the stratosphere associated with the depleted stratospheric O_3 . In response to the stratospheric O_3 depletion, the global mean chemical lifetime of tropospheric O_3 also decreases by 5-20% in the mid-high latitudes during 1980-2000. The decreased chemical lifetime of O_3 appears to be most responsible for the reduced O_3 increases at the surface after 1980.

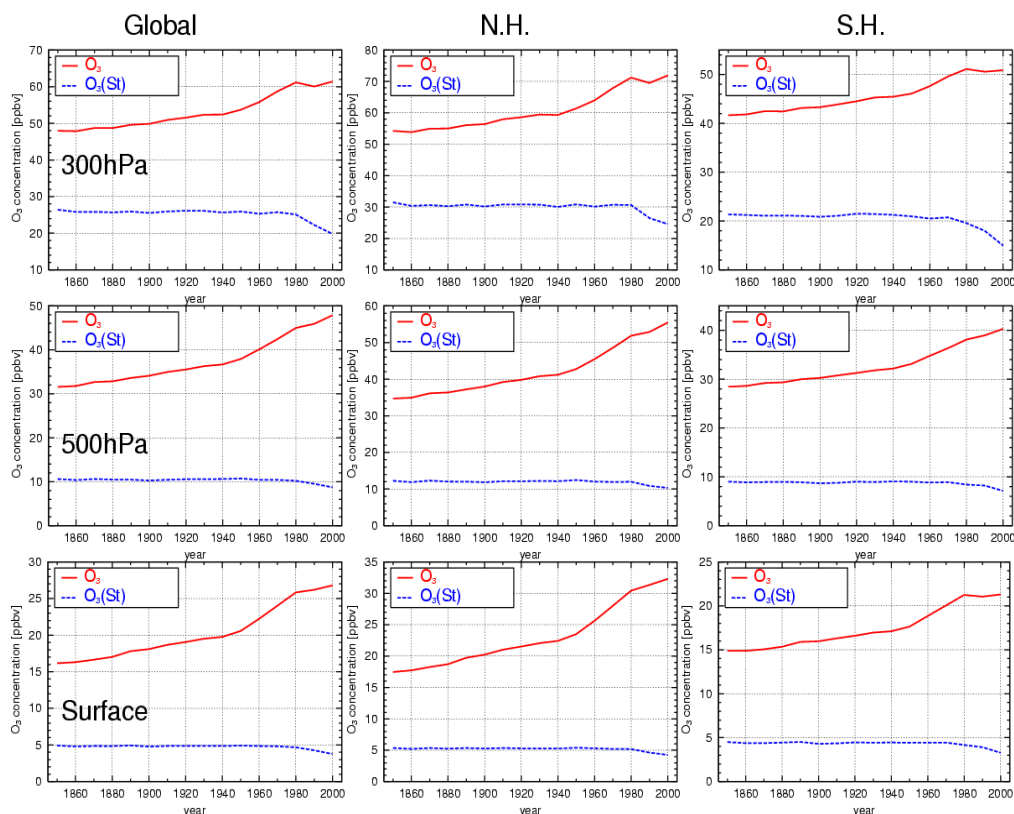


Figure 1.5. Temporal evolution (1850-2000) of global mean O_3 mixing ratios calculated at distinct altitudes (surface, 500hPa and 300hPa). Shown are net O_3 (solid lines) and O_3 from the stratosphere $O_3(s)$ (dashed lines) (Sudo *et al.*, 2004).

1.1.3 Trends of Stratospheric Ozone

About 90 percent of all ozone molecules in the atmosphere reside in the stratosphere, in a layer situated between about 15 and 30 km. Its concentration can range from 2,000 to 24,000 $\mu\text{g m}^{-3}$, since the ozone layer is a highly variable phenomenon (Jacobson, 2002). Whereas ozone molecules near the surface are harmful, the same O_3 molecules in the stratosphere shield the Earth from harmful ultraviolet radiation. Ozone absorbs virtually all-solar ultraviolet radiation between wavelengths of about 240 to 290 nm. Such radiation is lethal to simple unicellular organisms, and to the surface cells of higher plants and animals (Wayne, 2000).

It is now apparent that stratospheric ozone concentrations have been declining over at least the three past decades, and dramatic depletions of ozone over the Antarctic can only be explained in terms of anthropogenic perturbations (World Meteorological Organization, 1998). According to Harris *et al.* (1997), at mid-latitudes in the northern hemisphere the trends from 1979 to 1994 are significantly negative (up to 7% per decade), meanwhile tendencies in the southern mid-latitudes represent a reduction of 3 to 6% per decade. Staehelin *et al.* (2001; 2002) reach the same conclusions as the aforementioned study, indicating that not only long-term trends in chemical composition, but also long-term changes in the dynamical structure of the atmosphere have significantly contributed to the ozone decrease.

It is important to highlight the importance of stratosphere-troposphere exchange (STE) on ground-level ozone concentrations. The different chemical composition of tropospheric and stratospheric air allows stratospheric air masses to reach a location in the lower troposphere either via direct descent or, alternatively, by descent followed by horizontal transport (Bonasoni *et al.*, 2000). Stratospheric air mass intrusions rarely reach the ground without experiencing a significant dilution with tropospheric air, contributing with a considerable portion of ozone to the levels of ground-level O_3 .

Furthermore, global chemical transport model simulations help explaining the STE. Lelieveld and Dentener (2000) and Roelofs and Lelieveld (2000) suggest that in the free troposphere, on average, 20 to 40% of the ozone originates from the stratosphere. Borchini and Marengo (2002) apply a multivariate analysis to discriminate air masses directly linked to the STE. A possible hypothesis to explain these exchanges is the dynamics associated with strong convection situations. In the same line of investigation, Tulet *et al.* (2002) study the impact of deep convection upon the redistribution of ozone during a summer pollution episode in Europe. Convection favors large-scale downward motions and stratospheric intrusions down to the middle and lower troposphere. Finally, Lelieveld *et al.* (2002) state that in the boundary layer, about 90% of the O_3 is formed in situ, with stratospheric intrusions representing 10% of total values.

1.1.4 Trends of Other Photooxidants

Direct measurements have not been found in the bibliographic research for the analysis of the long-term trend in NO_x and hydrocarbon concentrations. The longest continuous record for individual hydrocarbons (Solberg *et al.*, 1994) is from Birkenes, near the south coast of Norway. Authors have shown that there is a statistically significant upward trend in the concentrations of acetylene, propane, butane and also in the sum of $\text{C}_2\text{-C}_5$ hydrocarbons. Indirect information on long-trends in NO_x can be obtained from the analysis of the contents of nitrate in ice cores. Nitrate is the final product of nitrogen oxides oxidation and is removed from the atmosphere by heterogeneous processes such as rainout. Therefore, changes in the concentrations of nitrate in the ice should reflect the changes in the concentration of NO_x . The onset of the increase in nitrate concentrations coincides with the start of the increase of tropospheric ozone over Europe between 1940 and 1950 (Staehelin *et al.*, 1994).

Fusco and Logan (2003) used the GEOS-CHEM model in order to analyze trends of ozone and precursors at Northern Hemisphere midlatitudes. Model results report local increases in NO_x concentrations in the period 1970-1995, which have caused most of the increases seen in lower tropospheric ozone over Europe and Japan. Increases in methane are responsible for roughly one fifth of the anthropogenically-induced increase in tropospheric ozone at northern midlatitudes.

Richter *et al.* (2004) used the eight years of available GOME data, to investigate possible trends in NO_x concentrations. In a global view, a straight line has been fitted to the annual averages of tropospheric NO_2 from 1996 to 2002. The resulting slopes are shown in Figure 1.6. In most regions of the world, the NO_2 columns have not changed significantly over these 7 years. However, two exceptions are obvious from the graph: NO_2 columns in China increased strongly while they decreased in central Europe and also the South-Eastern US. There are also some indications of increasing NO_2 in the Great Lake region and the Middle East. These observations are broadly consistent with a trend of about 17% in the NO_x emissions from 1995 to 2000. A strong increase in NO_2 of up to 10^{15} molecules cm^{-2} year^{-1} is observed over industrialized parts of China, where NO_2 columns increase mainly in winter but also in summer.

Long-term records of other photooxidants, such as hydrogen peroxide or peroxyacetyl nitrate (PAN), are sparse. For peroxyacetyl nitrate, a continuous record from the Dutch air quality networks shows an increase of almost a factor of 3 in the 1970s (Guicherit, 1988) when oxidants concentrations were increasing slightly. The PAN increase suggests that the potential for the formation of photooxidants was still increasing in the 1970s in the more heavily polluted areas of Europe. In the 1980s the concentration of PAN at Delft stabilized. The atmospheric measurements of hydrogen peroxide made in the United States and in Europe are not of a sufficient length to allow a trend assessment (Borrell *et al.*, 1997).

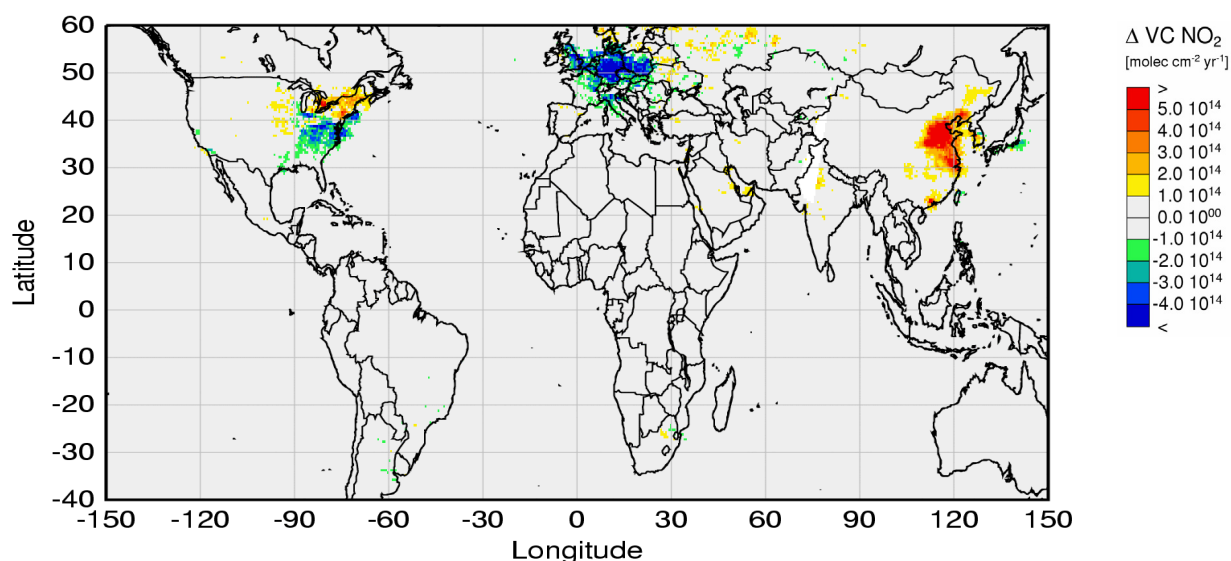


Figure 1.6. Linear trend of tropospheric NO_2 columns measured by GOME from 1996 to 2002 (Richter *et al.*, 2004). Large increases are observed over China and the northeastern US while NO_2 decreased over Europe and the southeastern US.

1.2 Tropospheric Photochemistry

The *gas-phase chemistry* of the troposphere involves the oxidation of organic molecules in the presence of oxides of nitrogen under the action of sunlight. Atmospheric oxidation proceeds via chains of radical reactions, which can be long and complex in the case of organic compounds. The predominant hydrocarbon in the atmosphere is methane, but a large number of other hydrocarbons and organic compounds with an anthropogenic and biogenic origin are present. Photochemical ozone results from the interaction of emissions of nitrogen oxides (NO_x) and non-methane organic gases. On the other side, *heterogeneous* or *aqueous-phase chemistry* involving reactions in aerosol particles and cloud droplets may affect ozone concentrations in a number of ways including production and loss of hydroxyl radicals and nitrogen oxides, direct loss of O_3 , and production of halogen radicals (Jacob, 2000).

There is a high number of chemical and photochemical reactions that drive to the formation of oxidant pollutants such as ozone and peroxyacetyl nitrate, but in this section just the most relevant processes are described, like radical formation, attack of these radicals to volatile organic compounds and transformation of nitrogen oxides.

A key process in atmospheric pollution formation is photolysis of species such as NO_2 , HCHO and HONO. Measuring photolysis rates in the atmosphere (in an indirect or a direct way) is difficult, thus their values are obtained from other parameters. To calculate photolysis rate of a chemical compound, it must be considered: the fraction of solar radiation it absorbs, the distribution of wavelengths and intensity of solar radiation. The total photolysis rate of a

substance A in the troposphere, in molecules $\text{cm}^{-3} \text{ s}^{-1}$, can be expressed in the following way (Roselle *et al.*, 1999):

$$K_c = \int_{\lambda=290\text{nm}}^{\lambda_i} \sigma(\lambda) \cdot J(\lambda) \cdot \phi(\lambda) \cdot [A] \cdot d\lambda \quad (1.1)$$

where

λ : wavelength (nm).

$J(\lambda)$: actinic flux ($\text{photons cm}^{-2} \text{ nm}^{-1} \text{ s}^{-1}$).

$\sigma(\lambda)$: absorption cross-section in base e ($\text{cm}^2 \text{ molecules}^{-1}$).

$\phi(\lambda)$: primary quantum yield of A ($\text{molecules photons}^{-1}$).

[A]: concentration of A.

This rate can be considered as a first-order rate constant: $K_c = K_a [A]$, and the integral can be substituted by a summatory in an interval of wavelengths, where a mean value is had as the variables value within that interval. Absorption cross-sections and quantum yields are function of wavelength, and may also be function of temperature and pressure; they are unique to species and reactions (Jacobson, 1999). The actinic flux is usually estimated with radiative transference models (Roselle *et al.*, 1999), depending on solar zenith angle. Photolysis of a molecule may produce one or more sets of products, and the probability of each set of products is embodied in the quantum yield.

1.2.1 Background Gas-Phase Chemistry

The troposphere behaves as a giant chemical reactor where pollutants react under the influence of sunlight radiation to generate a wide variety of products. The gas-phase chemistry of the troposphere involves the oxidation of organic molecules in the presence of oxides of nitrogen under the action of sunlight, to generate ozone, which can be considered as the main product of tropospheric chemistry.

NO_2 photolysis can drive to ozone formation when NO and NO_2 are present in sunlight. Ozone formation occurs as a result of the photolysis of NO_2 at wavelengths $< 424 \text{ nm}$ (Jacobson, 1999; Atkinson, 2000):



where M represents another third body that removes energy of the reaction and stabilizes ozone. Once formed, ozone reacts with NO to regenerate NO_2 .



The above three reactions occur rapidly, establishing a steady-state ozone concentration:

$$[\text{O}_3] = \frac{J[\text{NO}_2]}{k[\text{NO}]} \quad (1.5)$$

where k is the rate constant for reaction 1.4, and $J[\text{NO}_2]$ is the photolysis rate of NO_2 . There is a reaction path that converts NO to NO_2 without consuming ozone, and allows O_3 to accumulate (Figure 1.7).

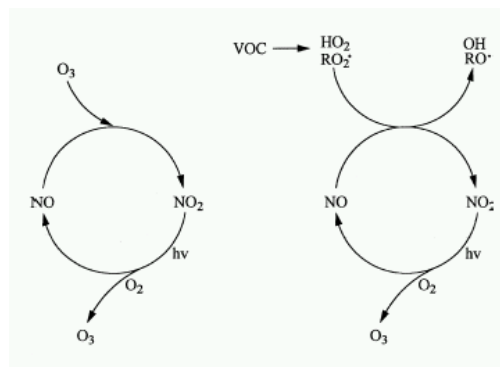
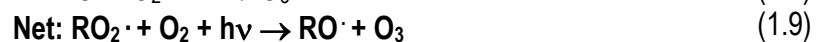
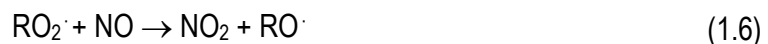


Figure 1.7. Schematics of the reactions involved in NO -to- NO_2 conversion and ozone formation, in absence of VOCs (left) and in the presence of VOCs (right) (Atkinson, 2000).

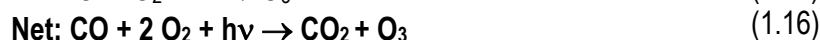
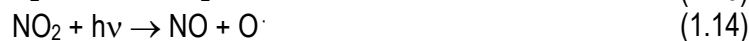
That path is conditioned by the presence of hydrocarbons, in particular, peroxy radicals (RO_2). Generation of the organic peroxy radicals occurs largely by the attack of the hydroxyl radical ($\text{OH}\cdot$) on hydrocarbons.



The atmospheric chemistry of **carbon monoxide** exhibits some of the essential elements of hydroxyl radical attack, formation of the hydroperoxyl radical and conversion of NO to NO_2 . Ozone photolysis produces an excited singlet $\text{O}(^1\text{D})$ oxygen atom that reacts with water vapor to form hydroxyl radicals (Wayne, 2000):



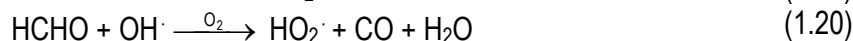
The atmospheric oxidation of CO in presence of the hydroxyl radical can be summarized as follows:



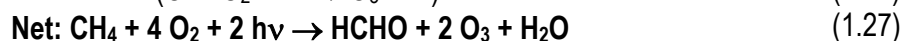
Neither $\text{OH}\cdot$ nor $\text{HO}_2\cdot$ are consumed in this reaction cycle, which can be viewed as a catalytic oxidation of CO to CO_2 . This cycle occurs until one of the molecules is removed in a termination reaction, generally $\text{OH}\cdot$ that is eliminated in the reaction with NO_2 to form gaseous nitric acid:



Formaldehyde reactions may be concisely written as (Seinfeld and Pandis, 1998):



The overall **methane** oxidation process, leading to ozone formation, may be summarized as follows (Seinfeld and Pandis, 1998; Wayne, 2000):



Radicals have a decisive role in tropospheric chemistry because they are very reactive species that rapidly attack lots of atmospheric pollutants, since they own a free electron in their structure that can be transferred to other species in chemical reactions. Most important radicals are oxygen atoms ($\text{O}\cdot$), hydroxyl ($\text{OH}\cdot$), hydroperoxyl ($\text{HO}_2\cdot$), peroxyalkyl ($\text{RO}_2\cdot$), alkyl (RC H_2) and alcoxy ($\text{RO}\cdot$). Hydroxyl radical dominates atmospheric photochemistry, both in a polluted or clean troposphere, initiating chain reactions when attacking VOCs and CO .

Hydroxyl radical ($\text{OH}\cdot$) is the most important reactive species in the troposphere. Indeed, it reacts with most trace species, and its importance derives from both its high reactivity toward other molecules and its relatively high concentration. When reacting with atmospheric trace gases, $\text{OH}\cdot$ is generated in catalytic cycles, leading to sustained concentrations on the order of 10^6 molecules cm^{-3} during daylight hours (Seinfeld and Pandis, 1998). There are three principal sources of hydroxyl radicals in the atmosphere (Seinfeld, 1989; Atkinson, 2000):

1. Photochemical dissociation of ozone: at wavelengths of less than 335 nm O_3 dissociates to yield, in part, electronically excited oxygen atoms, $O(^1D)$, by reaction 1.10. Most of the excited $O(^1D)$ is quenched by N_2 and O_2 back to the ground state $O(^3P)$. A small fraction of $O(^1D)$ reacts with water vapor to produce OH^\cdot radicals:



2. Reaction of HO_2^\cdot radicals with NO : when NO is present, the most important atmospheric reaction that the hydroperoxyl radical undergoes is with NO



3. Photochemical dissociation of nitrous acid ($HONO$): $HONO$ is rapidly photolyzed at wavelengths ≤ 400 nm during daytime hours to yield OH^\cdot radicals. Since the principal removal process of nitrous acid is photodecomposition, nitrous acid achieves its maximum concentrations during nighttime:



Hydroperoxyl radical (HO_2^\cdot) is intrinsically related to OH^\cdot chemistry. Hydroperoxyl radicals take part mainly at night, when OH^\cdot concentration decreases because of the lack of solar radiation (Stockwell, 1995). The most important source of HO_2^\cdot in the non-polluted troposphere is the reaction of hydrogen atoms with molecular oxygen. During daytime, hydroperoxyl radicals are created through reactions (Finlayson-Pitts and Pitts, 2000):



Formaldehyde is a major source of HO_2^\cdot during the day. The reactions of some alkoxy radicals generated in the VOCs oxidation sequence, with O_2 also generate HO_2^\cdot :



Hydrogen peroxide (H_2O_2) is a photochemical product that plays a fundamental role as precursors of odd-oxygen as well as reservoirs of odd-hydrogen radicals. The generation of these products is affected by the levels of chemical components such as NO_x , CO , methane and non-methane hydrocarbons (Lee *et al.*, 2000). Hydrogen peroxide is formed from addition of

molecular oxygen to active hydrogen to produce a hydroperoxyl radical (reaction 1.35), followed by HO₂[·] self-reaction:



The major gas-phase destruction pathways for H₂O₂ are its reaction with OH[·] and its photolysis:

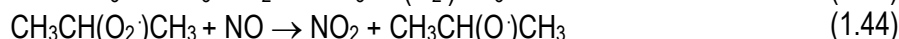
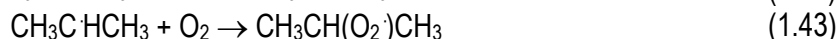
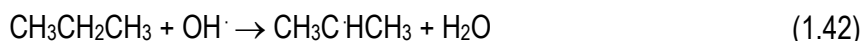


1.2.2 Chemistry of Non-Methane Organic Compounds in the Troposphere

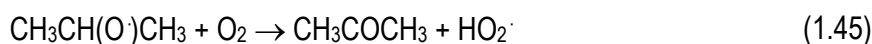
In the lower troposphere, chemical reactions of anthropogenic and biogenic VOCs and anthropogenic NO_x emissions dominate over those of methane and its degradation products. Chemistry of the troposphere is significantly complicated because of the presence of many organic compounds of various classes (e.g. alkanes, alkenes, aromatics, etc.) and the complexity in the chemistry of these organic species.

Alkanes, alkenes and alkynes constitute a major class of anthropogenic hydrocarbon emissions. Alkanes react with OH[·] radicals during daylight hours and with the NO₃[·] at night (Finlayson-Pitts and Pitts, 2000), with the latter process being of minor importance (less than 10%) to the total alkane consumption. The reactions of alkenes and alkynes are similar to those of alkanes, but the rates of reaction of alkenes with OH[·] radicals are significantly higher than those of the corresponding alkanes. Because of their high reactivity with respect to ozone formation, alkenes are important contributors to overall ozone formation. Alkenes react with the hydroxyl radical. Because of the double bonded carbon atoms in alkene molecules, they will also react with ozone, the NO₃[·] radical and atomic oxygen (Atkinson, 2000).

Reactions of alkanes with hydroxyl radicals proceed by H-atom abstraction from C-H bonds. The resulting alkyl (R[·]) radical reacts rapidly, and exclusively, with O₂ to yield an alkyl peroxy radical (RO₂[·]). For propane, for example:



The alkoxy (RO[·]) radicals react by unimolecular decomposition, unimolecular isomerization, or with O₂ to produce HO₂[·] radicals



The result is: NO_2 and acetone (CH_3COCH_3) are formed from NO . If we consider that hydroperoxy radical (HO_2^\cdot) reacts with NO to produce NO_2 and OH^\cdot ; then hydroxyl radical is regenerated. Under tropospheric conditions, these alkyl peroxy radicals react with NO by two pathways:



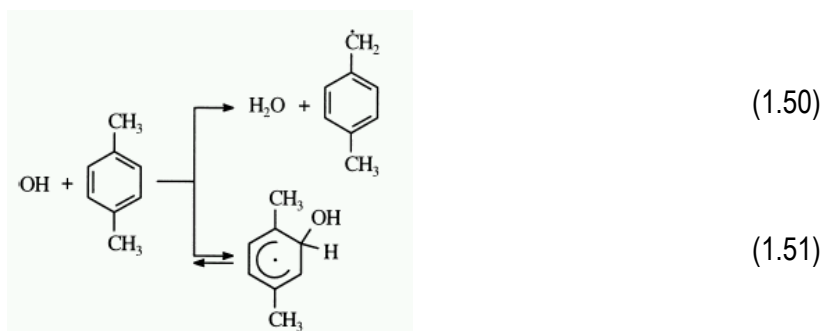
with HO_2^\cdot radicals



At NO concentrations above 30 parts per trillion (ppt), reaction with NO is the dominant reaction pathway for RO_2^\cdot radicals. The yield of the alkyl nitrate (RONO_2) is increased with the number of carbon atoms in RO_2^\cdot . HO_2^\cdot radicals are consumed, mainly through the reaction with nitrogen oxide:



Aromatic organic compounds are a major class of organics associated mainly with the urban environment. The monocyclic aromatic hydrocarbons react solely with the OH^\cdot radical, a reaction that can proceed by two pathways (Atkinson, 2000): (1) H-atom abstraction of alkyl H-atoms for alkyl-substituted aromatics from the alkyl-substituent groups, and (2) OH^\cdot radical addition to the aromatic ring.

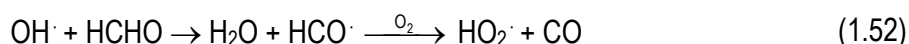


The H-atom abstraction path leads to the formation of aromatic aldehydes, such as benzaldehyde, with subsequent reactions of these aldehydes leading to the production of peroxyacyl nitrates and nitrophenols. This H-atom abstraction path accounts for less than 10% of the overall OH^\cdot radical reaction for benzene and the alkyl-substituted aromatic hydrocarbons.

The H-atom abstraction by oxygen from the OH^\cdot -aromatic adduct to yield phenolic compounds has been shown to be relatively minor, accounting for about 16% of the overall OH^\cdot radical products of toluene. The major reaction pathway is thought to be that involving ring cleavage of the OH^\cdot -aromatic- O_2 adduct. The α -dicarbonyls, glyoxal, methylglyoxal and biacetyl, with have

been identified as products from benzene and the methyl-substituted benzenes, are indications of ring cleavage. The uncertainties in atmospheric chemistry of aromatics are major (Seinfeld and Pandis, 1998): (1) ring-opening versus ring-conserving pathways; (2) nature and yield of all products in ring-opening and (3) phenol distribution and subsequent reactions of ring-conserving paths.

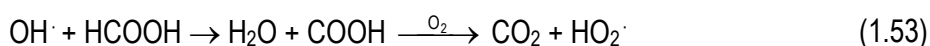
Aldehydes undergo photolysis and reaction with $\text{OH}\cdot$ and $\text{NO}_3\cdot$ radicals, the first two being the major loss processes (Seinfeld, 1989). The formaldehyde- $\text{OH}\cdot$ reaction yields the formyl ($\text{HCO}\cdot$) radical, which subsequently reacts with O_2 to form $\text{HO}_2\cdot$ and CO :



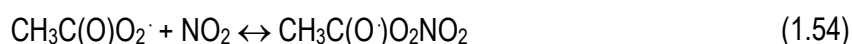
For the higher aldehydes, the acyl ($\text{RCO}\cdot$) radical initially formed rapidly adds oxygen to yield a peroxyacyl radical $[\text{RC(O)OO}\cdot]$. The peroxyacyl radical can react with NO or NO_2 , the latter reaction leading to the peroxyacyl nitrates. It is estimated that 80 to 90% of the formaldehyde in the urban atmosphere results from the photooxidation of other organics and only about 10% to 20% from direct emission.

Ketones are exemplified by acetone and its higher homologues. Photolysis and $\text{OH}\cdot$ reaction are the major atmospheric loss processes, although, with the exception of acetone, photolysis is probably of minor importance. The major reaction products from the atmospheric reactions of ketones are aldehydes and PAN precursors, and bifunctional oxygen-containing compounds may be formed in small yield. The most important uncertainties in carbonyl chemistry involve photolysis rates and quantum yields, the fate of hydrocarbonyls, and the existence of nitrate carbonyls resulting from higher alkanes. Because carbonyl photolysis is such an important source of free radicals, uncertainties in photolysis rate translate into uncertainties in ozone formation rates.

Carboxylic acids such as formic and acetic acid react with the $\text{OH}\cdot$ radical through the formation of an addition complex. For example, for formic acid:



Peroxyacetyl nitrate (PAN) has long been known to be an important atmospheric species as a reservoir for NO_x and acetyl peroxy radicals (Stockwell *et al.*, 1995). PAN and analogues are formed during degradation of aldehydes, by the reaction of alkyl and acyl peroxy radicals with NO_2 . The PAN molecule serves as a temporary reservoir for peroxyacetyl radical and NO_2 , because the formation reaction reverses thermally, having PAN molecule a lifetime of 45 minutes at 298 K.



Photochemical dissociation of aldehydes (RCHO) leads to the formation of radicals that through a rapid series of reactions lead ultimately to the formation of OH \cdot :



Because the formation of ozone and other secondary species is not instantaneous following the emission of hydrocarbons and nitrogen oxides, significant transport and mixing occur simultaneously to the reaction. The thermal decomposition of PAN leads to CO $_2$, NO $_2$ and peroxy radicals. In turn, the reactions of peroxy radicals finally lead to HO $_2\cdot$ and formaldehyde, which contribute to photochemical reactions including ozone formation (Grosjean *et al.*, 2001).

In the case of **alcohols**, the atmospheric reaction of the simple aliphatic alcohols involves OH \cdot attack. For example, for methanol (Seinfeld, 1989):



The first path accounts for about 85% of the overall reaction pathway at 298 K. Both the C \cdot H $_2$ OH and CH $_3$ O \cdot radicals react with O $_2$ to give formaldehyde and HO $_2\cdot$. Thus, the overall methanol-OH \cdot reaction may be written as:



1.2.3 Atmospheric Chemistry of Biogenic Volatile Organic Compounds

Earth's troposphere contains an amazing mixture of biogenic volatile compounds (BVOCs), which are often hydrocarbons. These biogenic-origin compounds play an important role in: (1) shaping global tropospheric chemistry; (2) regional photochemical oxidant formation; (3) balancing the global carbon cycle; and (4) production of organic acids which contribute to acidic deposition in rural areas (Fehsenfeld *et al.*, 1992). In addition, non-methane hydrocarbons with a biogenic origin from terrestrial vegetation are one of the main sources of non-anthropogenic aerosols in the troposphere, and therefore, play an important role in ozone chemistry and climate (Andreae and Crutzen, 1997). The volatile olefinic compounds, such as isoprene and the terpenes, are thought to constitute the bulk of these emissions. However, it is becoming increasingly clear that a variety of partially oxidized hydrocarbons, principally alcohols, are also emitted. Because of the presence of C=C double bonds, these molecules are very reactive with OH \cdot , ozone, NO $_3\cdot$ and Cl atoms (Finlayson-Pitts and Pitts, 2000). In addition, as they are quite large and of relatively low volatility, their polar oxidation products are even less volatile. Smaller quantities of partially oxidized VOCs, such as alcohols, aldehydes, ketones, and acids are also released as reaction

products. These compounds may also be formed *in situ* in the atmosphere as intermediates in the oxidation of the primary biogenic releases. Sulfur compounds and some halogenated hydrocarbons are further components of the inventory of natural organic chemicals. Of the biogenic hydrocarbons, terpenes and specially isoprene are, by the far, the most important. Chemistry is generally analogous to that of alkenes, so, just a short description is made in this section for these two species.

Terpenes are organic compounds of biogenic origin whose structure may be divided into isoprene units. The more volatile mono- (C₁₀) and sesquiterpenes (C₁₅) are emitted in large quantities from the vegetation (Calogirou *et al.*, 1999). The products and mechanisms of the atmospherically important reactions of the terpenes in the troposphere are not well understood, at least in part because of the complexity of the products. Commonly, terpenes are oxidized in the atmosphere during the day by both OH· radicals and ozone, at night by NO₃· radicals and ozone, while the reaction with O₃ leads to the formation of additional OH· radicals (Aschmann *et al.*, 2002). Koch *et al.* (2000) observed particle formation in the chemistry of terpenes, revealing that the mass-based aerosol yields were strongly dependent on the structure of the hydrocarbon, the initial hydrocarbon-to-NO_x ratio and the amount of seed aerosol initially present. Isoprene is much more reactive in the atmosphere than methane and other alkenes; the high reactivity also means that this biogenic species make a significant contribution to atmospheric chemistry. Table 1.2 summarizes the products observed for isoprene when reacting as an alkene, with OH· radical, NO₃· radical and ozone.

Table 1.2. Products observed from the atmospheric reactions of isoprene (adapted from Atkinson, 1997; Atkinson and Arey, 1998).

<i>Product</i>	<i>Yield (%)</i>
<i>OH· radical reaction (in the presence of NO)</i>	
methyl vinyl ketone + HCHO	32
methacrolein + HCHO	23
3-methylfuran	4-5
HOCH ₂ C(CH ₃)=CHCHO and/or HOCH ₂ CH=C(CH ₃)CHO	Observed
CH ₂ =C(CH ₂ OH)CHO	Observed
organic nitrates	8-14
<i>NO₃· radical reaction</i>	
methyl vinyl ketone	3.5
methacrolein	3.5
HCHO	11
O ₂ NOCH ₂ C(CH ₃)=CHCHO and isomers	Observed
O ₂ NOCH ₂ C(CH ₃)=CHCH ₂ OH and isomers	Observed
O ₂ NOCH ₂ C(CH ₃)=CHCH ₂ OOH and isomers	Observed
<i>O₃ reaction</i>	
methyl vinyl ketone	16
methacrolein	39
HCHO	90
epoxides	5
OH·	27
O(³ P)	<10

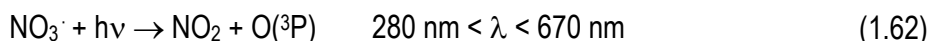
1.2.4 NO_x Transformation Chemistry

Most of the NO_x emitted to the atmosphere has an anthropogenic origin (combustion processes), and is released mainly as nitrogen oxide (NO). It plays a fundamental role in air quality issues, and could influence in other environments as water. In the troposphere, NO reacts rapidly with ozone to generate NO_2 , but as commented before, in the presence of sunlight this reaction has the competence of other chemical reactions. NO can also react with peroxyalkyl (RO_2) produced through the attack of hydroxyl radical to some VOC or with hydroperoxy radical.

In the existence of sunlight, nitrogen dioxide reacts mainly with $\text{OH}\cdot$ to produce nitric acid (Atkinson, 2000):



During daylight, $\text{NO}_3\cdot$ undergoes a quick photolysis by absorption of visible light, so daytime concentrations are negligible.



In urban environments, with intense photochemical activity, NO_2 can react with a peroxyacyl radical, like $\text{CH}_3\text{C}(\text{O})\text{O}\cdot$ resultant of the photodecomposition of aldehydes and ketones, with formation of PAN and other nitrous organic compounds (Wayne, 2000):



Thermal decomposition of PAN depends on temperature, being a stable compound at low temperatures. PAN is probably the most important nitrogen source in the high layers of the troposphere, where temperatures are lower, depending NO_2 when air descends and heats.

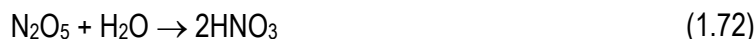
The key differences between day and night chemistry can be summarized like this: (1) absence of photolytic reactions, and (2) accumulation of nitrate free radical, $\text{NO}_3\cdot$; which is rapidly photolyzed during the day, so its daytime concentration is negligible. During the night, the process that occurs is:



NO_3 can be reconverted to NO_2 or thermally decompose:



Finally, N_2O_5 is irreversibly converted to nitric acid in the presence of water vapor:

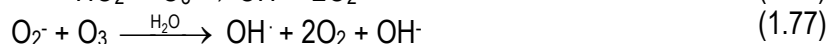
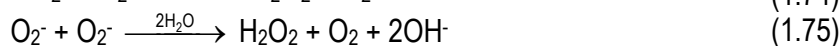
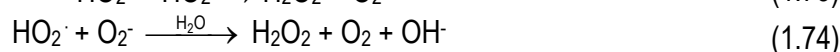


As seen from above, nitrogen oxides are converted into nitric acid by a route not involving OH· radicals.

1.2.5 Tropospheric Heterogeneous Chemistry

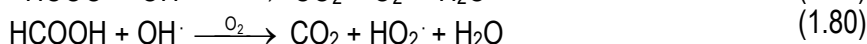
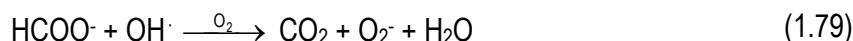
It is a common practice in the atmospheric chemistry literature to refer to heterogeneous chemistry as the ensemble of chemical processes involving aerosol phases (liquid and solid particles) in the atmosphere. Condensed water is the predominant form of suspended matter in the troposphere, and clouds the most abundant form of condensed water (Wayne, 2000). Because of that, much of the literature on heterogeneous chemistry in the troposphere has focused on clouds. Models investigating chemical processes in aqueous aerosols and clouds generally include detailed gas-phase and aqueous-phase chemical mechanisms coupled by gas-droplet transfer (Sander and Crutzen, 1996). We briefly describe below the main processes that are associated with heterogeneous chemistry, according to Ravishankara (1997), Finlayson-Pitts and Pitts (2000), Wayne (2000) and Jacob (2000).

Reactions 1.73 through 1.77 summarize the major processes affecting $\text{HO}_2\cdot$. The $\text{HO}_2\cdot$ radical is efficiently scavenged by cloud droplets because of acid-base dissociation $\text{HO}_2\cdot(\text{aq})/\text{O}_2^-$ followed by electron transfer O_2^- to $\text{HO}_2\cdot(\text{aq})$ to produce H_2O_2 .

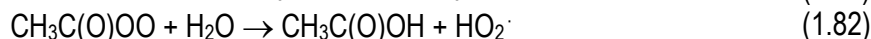
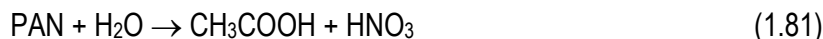


The OH^- produced in the formerly mentioned reactions is recycled to $\text{HO}_2\cdot(\text{aq})/\text{O}_2^-$ by oxidation of organic molecules including hydrated formaldehyde. Reactions 1.77, 1.78 and 1.79 constitute a cycle catalyzed by HO_x that destructs O_3 in the aqueous phase. The efficiency of the cycle is limited by the aqueous-phase HO_x sink from reaction 1.74.

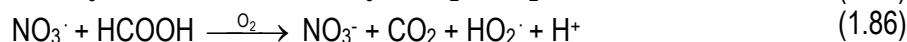
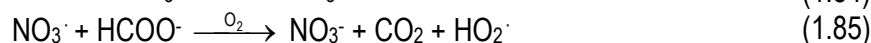




Irreversible loss of gas-phase $\text{CH}_3\text{C}(\text{O})\text{OO}^\cdot$ to pure liquid water surface occurs due to rapid hydrolysis of $\text{CH}_3\text{C}(\text{O})\text{OO}^\cdot$ in the aqueous phase. Decomposition of PAN followed by reaction 1.82 could represent a small nighttime source of $\text{HO}_{x(\text{aq})}$ in polluted clouds with elevated PAN; it would be insignificant in the daytime.



Uptake of NO_3^\cdot by aqueous aerosols is limited, with a NO_3^\cdot lifetime of the order of hours against uptake by aerosols. Therefore, heterogeneous-chemistry sinks of NO_3^\cdot is negligible compared to gas-phase reactions with NO_2 and organic compounds.



1.3 Air Quality Modeling

Air quality models (AQMs) are computerized representations of the atmospheric processes responsible for air pollution, including ozone formation. Models simulate the atmosphere in varying degree of detail by mathematically representing emissions; initial and boundary concentrations of chemical species; the chemical reactions of the emitted species and their products; and the local meteorology such as sunlight, wind, and temperature. In this way, an understanding of atmospheric chemistry and meteorology is combined with estimates of source emissions to predict possible control strategy effects. AQMs are also an important tool in gaining understanding about the behavior of various compounds in the atmosphere, such as the reactivity of volatile organic compounds. Therefore, the components of an air quality model (Figure 1.8) could be divided into three different modules (Russell and Dennis, 2000): (1) meteorological models; (2) emission models and (3) chemical transport models (CTMs). Some authors consider a fourth module corresponding to visualization and analysis, which helps to the decision support system; but this module is usually isolated from the rest of the air quality model.

1.3.1 Meteorological Models

Meteorological models provide the necessary information about the atmospheric state to the chemical transport model. Depending on the necessities of the chemical transport model, the information needed will be better defined. Atmospheric pollutant dispersion is based on the

advection transport, mixing by eddy diffusion and dry or wet deposition. These phenomena depend on the meteorological state of the atmosphere; in this way, chemical transport models need at least information of the wind pattern and some information about the atmospheric turbulence.

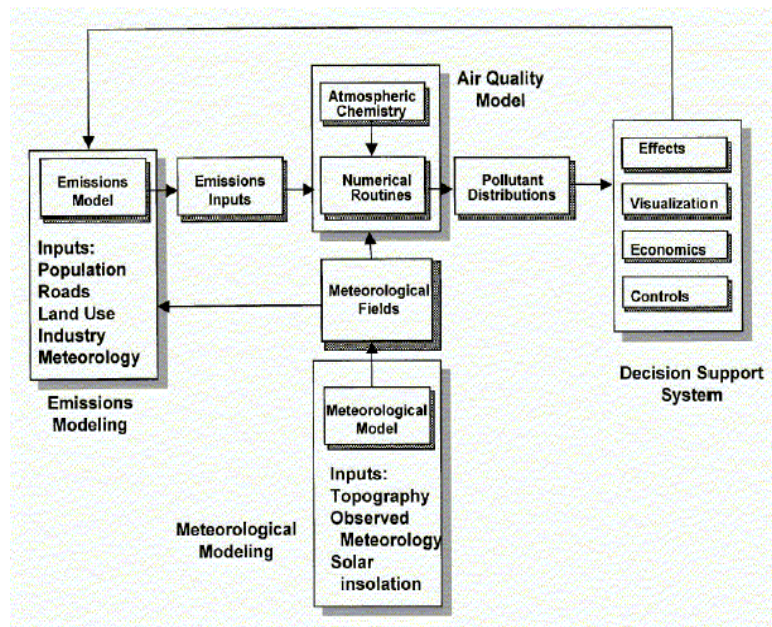


Figure 1.8. Structure of an air quality model and related modeling tools (Russell and Dennis, 2000).

Meteorological models can be classified as *prognostic* or *diagnostic* models. Prognostic models are based on the solution of time-dependent hydrodynamic and thermodynamic equations, appropriately modified to apply into the atmosphere. These models are also called *dynamic* or *primitive equation* models (Pielke, 1984). They provide a forecast forward in time of the atmospheric state evolution. Diagnostic models provide information of the wind field, or other meteorological variable, by satisfying some physical constraints. In case of impose the continuity equation to the wind measurement information, assuring mass conservation, the wind model is defined *mass consistent* (Ratto *et al.*, 1994). These models do not produce a forecast forward in time; they describe the state of the field of interest in the same time of the initialization data, providing a diagnostic of the variable. These models are also called *kinematic* models.

The actual tendency in air quality modeling evolves towards the use of prognostic models as pre-processor meteorological package. Prognostic models used in photochemical modeling present the same characteristics of weather prediction models. This type of models is commonly named Numerical Weather Prediction (NWP) models. The main differences between meteorological models that produce inputs for CTMs and a model for the weather prediction lay in the meteorological scale of study. Usually, chemical transport models are applied over regions with dimensions lower than 1,000 km of extension (mesoscale) with a spatial resolution of a few

kilometers. Nevertheless, models used for the weather prediction work on more extensive regions (macroscale). Both models are based on the same primitive equations to resolve the physics of the atmosphere (Seaman, 2000).

1.3.2 Emission Models

An atmospheric emission inventory is a compilation of the estimations of pollutant emissions towards atmosphere that are produced in a determined geographical zone, during an established period of time. Theoretically, emissions generated in a region could be quantified by measuring the amount of emitted substances from all sources, during the period of interest. It is not possible to measure emissions from all of the individual sources or, in the short term, from all the different source types. So, in practice, atmospheric emissions are estimated on the basis of measurements made at selected or representative samples of the main sources and source types. Models can also be used to relate the activity in that source with the amount and kind of substances that are emitted to the atmosphere.

The basic model for an emission estimate is the product of, at least, two variables: (1) an activity statistic and a typical average emission factor for the activity, or (2) an emission measurement over a period of time and the number of such periods emissions occurred in the required estimation period. Emission estimates are collected together into inventories or databases which usually also contain supporting data on, for example: the locations of the sources of emissions; emission measurements where available; emission factors; capacity, production or activity rates in the various source sectors; operating conditions; methods of measurement or estimation, etc.

An *atmospheric emission model* can be defined as a set of mathematical submodels of different degree of complexity that are integrated and are useful for estimating emissions to the atmosphere, from different sources located in a determined geographical area, in an established period of time (Baldasano, 1998). The use of estimations obtained with the model determines the way the results are reported. So, it could be enough with resume tables specifying the type of pollutant and nature of the source. Sometimes, it is essential to report files that are going to be the inputs of chemical transport models. In this case, the emission model gives information about quantity and kind of pollutant in the different cells that divide the zone under study.

Fundamentally, there are two approaches in the development of emission inventories (Costa and Baldasano, 1996):

1. *Top-down approach*: it estimates total emissions for the geographical area under study and then prorates those emissions in the different cells that constitute the spatial ambit of analysis (spatial disintegration), through parameters such as traffic, population and industrial density.

2. *Bottom-up approach*: it estimates emissions for all cells in which geographical area has been dividing, by means of establishing every parameter for each cell in particular. Total emission value is obtained by aggregation of estimations carried out for every single cell.

1.3.3 Chemical Transport Models

The principal objective of a chemical transport model is to mathematically reproduce the phenomena of air pollution. Therefore, CTMs could be used to simulate air quality (concentration of each pollutant) in different times and places. However, a combination of air quality measurements and chemical transport models should be used in order to assess air quality (de Leeuw *et al.*, 2001b). To use these models, some information intrinsic to the chemical transport model is needed, such as grid structure, resolution and initial and boundary conditions. Inputs to CTMs can be broadly grouped as those dealing with meteorology and emissions; inputs are specified at for each computational cell in the model domain (Russell and Dennis, 2000):

1. *Meteorological inputs*: CTMs require hourly, vertically and horizontally resolved wind fields, as well as hourly temperature, humidity, mixing depth and solar insolation fields. Some also use the vertical diffusivities, cloud characteristics and rainfall developed from meteorological models. Meteorological inputs are typically developed decoupled from the chemical transport model. Air quality models find it desirable to use dynamic or prognostic meteorological models because of the sparse data.
2. *Emissions*: a key use in CTMs is to determine how pollutant concentrations respond to changes in emissions inputs, and accurate emissions inputs are key to good model performance. Emissions inputs are developed to be compatible with the chemical mechanism used in the model, and with the model resolution (both vertically and horizontally). Detailed, speciated VOCs emissions are lumped into the appropriate chemical mechanism categories. Typically, this would include hourly, spatially gridded estimates of the emissions of CO, NO_x, SO₂ and various primary VOCs in the mechanism. For particulate matter modeling, one would add primary emissions of SO₃, NH₃, PM_{2.5} and PM₁₀.

Related to the coordinate system, CTMs can be classified into *Lagrangian* or *Eulerian* models. Lagrangian models consider a mobile coordinate system that, in the case of atmospheric phenomena, goes following a defined air parcel. In Eulerians, on the contrary, the coordinate system is fixed.

Box models are the simplest air pollution models, and a particular case of Eulerian photochemical dispersion models. They are based on the mass conservation of a pollutant inside a single cell, or box, where emissions are considered homogeneous (Jacobson, 1999). The ground bounds this cell on the bottom, the inversion base (or some other upper limit to mixing) on the top, and the

east-west and north-south boundaries on the sides. Box models can be applied for both inert and reactive pollutants. Fundamental to the model concept is the assumption that pollutant concentrations in a volume of air are spatially homogeneous and instantaneously mixed. Under this condition, pollutant concentrations can be described by a simple balance among the rates at which they are transported in and out the air volume, their rates of emission from sources within the volume, the rate at which the volume expands or contracts, the rates at which pollutants flow out the top of the volume, and the rates at which pollutants react chemically or decay.

Trajectory models use a moving-coordinate approach to describe the atmospheric diffusion and pollutant transport. A hypothetical column of air is defined, bounded on the bottom by the ground and on the top by inversion base, which varies with time. Given a specified starting point, the column moves under the influence of the prevailing winds, passing over emission sources, which inject primary pollutant species in the column (Seinfeld, 1988). Chemical reactions may be simulated in the column. Some trajectory models allow the column to be partitioned horizontally or vertically into several layers, or cells. The formulation employed by trajectory models to describe atmospheric dynamics represents an attempt to solve the mass conservation, or atmospheric diffusion equation in a moving coordinate system. The air parcel of interest is assumed to travel solely with the horizontal wind.

Grid models employ a fixed Cartesian reference system within which to describe atmospheric dynamics. The region to be modeled is bounded on the bottom by the ground, on the top usually by the inversion base or some other maximum height, and on the sides by the desired east-west and north-south boundaries. This space is then subdivided into a two- or three-dimensional array of grid cells (Figure 1.9).

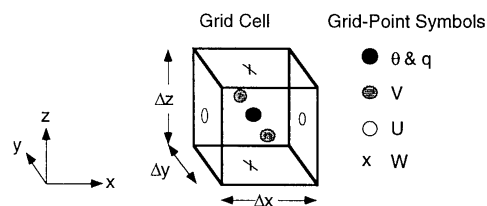


Figure 1.9. Grid of an Eulerian Model (Stull, 2000).

Some grid models assume only a single, well-mixed cell extending from the ground to the inversion base: others subdivide the modeled region into a number of vertical layers. The basis for grid models is the solution of the atmospheric reaction diffusion equation using an Eulerian coordinate system (Dabdub and Manohar, 1997). Most common applications of grid models to date have been related to photochemical ozone and aerosol dynamics, because grid models provide the only means to predict three-dimensional concentration distributions over a region. Their limitations derive principally from the considerable database needed as input (Seinfeld, 1988).

One of the most important components of chemical transport models is the photochemical mechanism. A chemical mechanism for troposphere is a mathematical description of photochemical processes of low atmosphere through a series of chemical reactions involving primary and secondary pollutants. Divergence points between different chemical schemes are (Kuhn *et al.*, 1998): (1) formulation of the reaction mechanism, (2) rate constants for the reactions and their temperature and pressure dependencies, and (3) temporal integration of the reaction rates by a chemical solver. Chemicals considered in a photochemical mechanism distinguish between inorganic compounds (NO_x , O_x , HO_x , and SO_x) and organic compounds, mainly volatile organic compounds. The variety of VOCs emitted to the atmosphere is wide, and its speciation and determination in gas emission inventories is very complicated. A more detailed analysis of this issue will be depicted in Chapter 3.

1.3.4 Previous Research in Air Quality Modeling in the Northeastern Iberian Peninsula

This investigation is in keeping with a line of research started in the Environmental Modeling Laboratory under the supervision of Dr. José M. Baldasano, in order to study and understand atmospheric behavior in very complex terrains. Therefore, a short review of photochemical modeling studies in the northeastern Iberian Peninsula is depicted below.

The first experience with photochemical modeling in the northeastern Iberian Peninsula, the *Barcelona Project*, started to be developed in 1991. Its objective was to understand transport and transformation processes for explaining circulatory and dispersion behavior of the atmosphere, as well as tropospheric ozone pollution in the geographical area of Barcelona. To achieve that purpose, it was used a methodology of numerical experimentation complemented with on-site campaigns and data from a web of air quality stations. In a first stage, mesoscale meteorological model MEMO and photochemical dispersion model MARS (Moussiopoulos, 1994) were applied, using as an inventory model a preliminary version of actual EIM-LEM (Costa and Baldasano, 1996).

Considering meteorological modeling, Calbó and Baldasano (1995) developed the hydrostatic mesoscale meteorological model PROMETEO. That model allowed describing temporal evolution of a number of atmospheric variables, like winds, temperature or kinetic energy, through the resolution of a set of equations that were used in the description of the atmosphere: mass conservation, momentum conservation, energy conservation and ideal-gases law. Some meteorological parameters, such as air moisture, were simplified; meanwhile others were reproduced with detail, as turbulence (treated with a second-order closure scheme). Model also incorporated a detailed treatment of radiation, as well as an energy balance in the surface.

Soriano *et al.* (2001) studied atmospheric circulations in the area of Barcelona for a typical summertime situation, basing in lidar measurements and simulations with MEMO mesoscale

model. This technique allowed establishing a circulatory pattern of atmospheric pollutants in a breeze situation for this geographical area.

Finally, Jorba *et al.* (2003) used the fifth generation Pennsylvania State University/NCAR Mesoscale Model MM5 in order to simulate a summertime low pressure gradient (13 August to 16 August, 2000) over the East coast of the Iberian Peninsula, to describe the circulatory patterns in the Western Mediterranean coast. The numerical weather prediction model was run for synoptic situations affecting the Peninsula, and simulation outputs were compared with surface and aloft measurements in 52 surface stations located at the northeast of the Iberian Peninsula. Results of the simulation showed the importance of the orographic features of the coastal region in the development of the re-circulations of the air masses.

Respect to emission modeling, EIM-LEM emission model was developed by Costa and Baldasano (1996). It considered different emission sources, like road traffic, industries, petrol stations, domestic heating, activities in the port of Barcelona and the airport of El Prat de Llobregat, and biogenic. It allowed a spatial and temporal of emissions, and incorporates a VOCs profile, but only classified them in five groups (methane, other alkanes, alkenes, aromatic compounds and aldehydes). With emission inventory generated by EIM-LEM for 1990, the authors stated that the main source of emissions in an area of 39 x 39 km² centered in the city of Barcelona was road traffic (76% of the total amount of pollutants emitted). 70.71% of the emissions corresponded to CO, 13.91% to NO_x, 14.38% to VOCs, 0.65% to particles and 0.36% to SO₂. The authors also concluded that biogenic VOCs (BVOCs) emissions were not negligible, since they represented about 8% of the total emissions of VOCs, raising the levels of this pollutant in summer due to the increment of temperature.

Delgado *et al.* (2000) developed a vehicle emission model from road traffic, estimating the emissions of atmospheric pollutants in the area of Catalonia (31895 km²), with a spatial resolution of 1 km². In the whole study area, the road traffic emitted 407,309 tones year⁻¹ of air pollutants: 69.6% of the total emissions corresponded to CO, 19.11% to NO_x, 8.61% to VOCs, 1.65% to SO₂ and 1.03% to particles. Toll and Baldasano (2000) extended the area under studio considered in EIM-LEM model to a square of 80 x 80 km², as well centered in Barcelona. They obtained highly disaggregated anthropogenic and biogenic emissions in the zone considered. Major sources of VOCs were road traffic (51%) and vegetation (34%), while NO_x were mostly emitted by road traffic (88%).

Parra (2004) developed the high resolution (1h and 1km²) EMICAT2000 emission model, in order to estimate the emission of primary pollutants in Catalonia; and to provide the basis for further work in air quality modeling using chemical transport models. This emission model includes the emissions from vegetation (Parra *et al.*, 2004), on-road traffic (Parra and Baldasano, 2004), industries and emissions by fossil fuel consumption and domestic-commercial solvent use. A further description of this emission model is presented in Section 2.2.2.

The two elements previously commented (meteorological and emission models) are essential for the study of atmospheric pollution in zones with complex terrain and spatial and temporal distribution of emissions, as the case of the northeastern Iberian Peninsula. In this sense, Baldasano *et al.* (1994) described the transport processes of air pollutants that take place over the Barcelona geographical area during summer days. The study was based on the results of a numerical simulation made by the three-dimensional non-hydrostatic model MEMO. Experimental data from a miniature lidar were also available. Results revealed a multilayer arrangement of aerosols in the atmosphere over Barcelona. Baldasano *et al.* (1995) made a modeling study of carbon monoxide dispersion, a very little reactive pollutant, whose objective was to simulate the behavior of atmospheric transport in the air basin of Barcelona, and its influence in the dispersion of pollutants.

Toll (1999) and Toll and Baldasano (2000) stated that ozone levels in the Barcelona geographical area could reach high values. They simulated an episode of ozone pollution that took place between the 3-5 August, 1990, using the non-hydrostatic meteorological model MEMO and the photochemical model MARS, a three-dimensional chemical transport model, coupled with a highly disaggregated emission inventory. The combination of mesoscale circulations (such as sea and land breeze, convection cells and topographic injections) and local emissions strongly influenced the production and spatial distribution of ozone in the region. Ozone was formed over vegetated areas, where biogenic VOCs were emitted, due to the inland advection of NO_x from traffic emissions with the sea breeze flow. Part of the O₃ air concentrations found inland was due to the domain's Eastern lateral boundary concentrations. Geostrophic wind played an important role in upper air layers when there was no solar radiation or when its intensity was low because of the lower mesoscale effects on winds flow, transporting external precursors inland.

Jiménez and Baldasano (2002) developed a semiempirical ozone model to relate the ratio *R* non-methane organic gases/nitrogen oxides (NMOG/NO_x) with the tropospheric ozone levels reached in the northeastern Iberian Peninsula. Data used to calibrate the model responded to episodes of ozone that took place in 14-15 August, 2000 and 13-16 August, 2001. Peak levels of ozone are in the range of 0-160 µg m⁻³, while NO_x and NMOG concentrations attain 135 µg m⁻³ and 1.2 ppm, respectively. The model works better in NMOG-rich regime than in low values of NMOG/NO_x ratios, so the fit of the model to real data is higher in non-urban stations than in those placed in populated area where the emissions of NO_x are higher, hence *R* values are lower. Authors concluded that the model is a reasonably effective tool to rapidly predict tropospheric ozone peaks and the range of concentrations that are going to be reached in the northeastern Iberian Peninsula.

Barros *et al.* (2003) conducted numerical simulations with photochemical transport models for two domains situated in the Iberian Peninsula covering the Lisbon and Barcelona airsheds, by using the grid-based chemical transport models MAR IV and MARS, respectively, in order to compare the diverse circulation patterns between the most important coastal cities in the Iberian Peninsula.

Ozone concentration recorded in both cities had a similar level. Nevertheless, O_x values on Barcelona were higher than those of Lisbon, which may, at a first glance, indicate an apparently more oxidant atmosphere in Barcelona. Photochemical modeling for the two cities showed a rather different behavior of the circulatory patterns in both urban areas, which mainly have to do with the different strength of the sea breeze and topography, inducing an important offshore vertical layered dimension of pollutants transport in Barcelona versus an important inland horizontal transport in the case of Lisbon.

1.4 Objectives of this Dissertation

The high levels of air pollutants over the northeastern Iberian Peninsula in summer have a strong influence both on ecosystems and human health. Owing to cloud-free conditions and high solar radiation intensity, the region is particularly sensitive to air pollution. In addition, its complex topography induces an extremely complicated structure of the flow that has important effects in the transport and transformation of pollutants that lead to the necessity of a deep and rigorous analysis of dynamics of photochemical pollutants over the area. Despite of its complexity, the utilization of multiscale-nested air quality models has revealed as a useful tool to assess air quality issues in very complex terrains.

Following the lines of research reviewed in Section 1.3.4, the main objectives set in this Dissertation may be summarized as:

1. Development and application of MM5-EMICAT2000-CMAQ air quality model, in order to provide a powerful and flexible tool to assess quality issues in a very complex terrain with a high spatial and temporal resolution.
2. Analysis and interpretation of air pollutants dynamics and multiscale physic-chemical processes that affect the concentrations of ozone and other photochemical pollutants over the air basin of the northeastern Iberian Peninsula.

In order to achieve these objectives, some tasks or secondary objectives may be derived, as:

1. Couple the MM5 meteorological model and EMICAT2000 emission model within Models-3/CMAQ framework, with enough flexibility to allow multiple choices of cases of study, resolution and parameterizations.
2. Select and implement an accurate photochemical mechanism representative of the state-of-the-science of air chemistry within the chemical transport model of CMAQ.

3. Provide a methodology to generate initial and boundary conditions for the domain of the northeastern Iberian Peninsula, in order to minimize the errors or deviations derived from the initialization process of the MM5-EMICAT2000-CMAQ model.
4. Study the needed resolution, both horizontal and vertical, to appropriately describe the air pollution dynamics over the air basin of the northeastern Iberian Peninsula.
5. Analyze the sensitivity of ozone to emissions in the domain of study, in order to deepen in the knowledge of the chemical regimes in most problematic areas of the northeastern Iberian Peninsula; and to establish control policies for the control of ozone and other photooxidants in zones where high levels of these pollutants are achieved.
6. Explain, through the application of air quality modeling, the causes of the ozone weekend effect observed from ambient measurements in the area of study.
7. Evaluate the performance of the high-resolution simulations with MM5-EMICAT2000-CMAQ against air quality data for the northeastern Iberian Peninsula, by using both discrete and categorical statistical analysis.

1.4.1 Structure of the Document

Chapter 1 has provided a short introduction to nowadays air quality problems and the evolution in the trends of photochemical pollutants. The interactions of the pollutants in the low atmosphere have been indicated by reporting the most important chemical photochemical reactions occurring in the troposphere. In addition, this Chapter has provided an approach to air quality issues and studies through the utilization of air quality models, as well as the most important applications of photochemical modeling in the area of the northeastern Iberian Peninsula. According to all this information, the objectives to be achieved within this Dissertation have been stated.

As was discussed in the Ph.D. Dissertation Proposal, modeling was conducted for the photochemical pollution event covering the entire Western Mediterranean Basin that took place from 13-16 August, 2000. The description of this case study is summarized in **Chapter 2**. The domain of study (a squared area of 272 x 272 km² centered in Catalonia, located in the northeastern Iberian Peninsula) is also defined. This domain is conditioned by the presence of the Pyrenees mountain range (with altitudes over 3000m), the influence of the Mediterranean Sea and the large valley canalization of Ebro River; and its high complexity leads to the utilization of multiscale-nested models with very high resolution, as this is the case for MM5-EMICAT2000-CMAQ, whose parameterizations are also defined in Chapter 2.

The first step in every atmospheric modeling exercise, once the air quality model has been defined, should be the selection of a photochemical mechanism and the definition of its reactions.

Hence, photochemical mechanisms are a critical module of air quality models. In the past twenty years, several mechanisms have been developed to study the chemistry of the troposphere. **Chapter 3** compares several state-of-the-science photochemical mechanisms (including LCC, CBM-IV, RADM2, EMEP, RACM, SAPRC99, and CACM, which has never been compared before in other studies). Concise descriptions of the chemical schemes are also included in order to characterize their performance respect to an average behavior.

A three-dimensional air quality model contains a set of stiff differential equations, which describe the time evolution of chemical species in the atmosphere. Initial and boundary conditions are required in order to solve these equations. **Chapter 4** describes the process of initialization and generation of boundary conditions for MM5-EMICAT2000-CMAQ through performing multiscale-nested simulations in the entire Iberian Peninsula, that provide the boundaries for the inner domain described in Chapter 2. Furthermore, an analysis of the influences of initial and boundary conditions and their sensitivity is presented, indicating the necessity of a correct initialization of the model and the availability of good-quality boundary information when performing simulations in very complex terrains.

The study of photochemical pollution in very complex terrains, as the northeastern Iberian Peninsula, is primarily influenced by local topography and demands a high spatial resolution. In order to illustrate the influence of the grid resolution on tropospheric ozone levels and the necessity of fine grids to simulate the dynamics of photochemical pollutants, **Chapter 5** shows the results of several simulations carried out with MM5-EMICAT2000-CMAQ model using horizontal resolutions ranging from 8, 4 and 2 km for horizontal resolution and with 6 or 16 vertical layers.

After the definition of the model, the chemical mechanism implemented, initialization processes and choosing the resolution to analyze ozone-related issues, Chapters 6 to 9 report different studies of air pollutants dynamics and physic-chemical processes occurring in the northeastern Iberian Peninsula. **Chapter 6** combines the application of the global climate-chemistry model ECHAM5/MESSy and the regional model MM5-EMICAT2000-CMAQ in order to analyze the high levels of photochemical pollutants over the Western Mediterranean Basin and the northeastern Iberian Peninsula during the episode of air pollution from 13-16 August, 2000. Those models represent a useful tool to investigate the diurnal cycle of air pollutants at a high resolution, and therefore, they help understanding the relative importance of processes involved.

The kinetics of ozone (O_3) chemistry and its two main precursors, nitrogen oxides (NO_x) and volatile organic compounds (VOCs), represents an important field of uncertainty in atmospheric chemistry and photochemical modeling. This uncertainty affects the design of control strategies to reduce tropospheric O_3 production. **Chapter 7** depicts the assessment of controlling ozone precursors on sensitivity regimes by performing simulations of ozone formation with MM5-EMICAT2000-CMAQ model. Methodology presented uses photochemical indicators to represent chemical sensitivity regimes in the northeastern Iberian Peninsula with baseline emission rates

for VOCs and NO_x, and reducing anthropogenic VOCs and NO_x emissions on a 35%. Three different scenarios were considered in order to assess chemical sensitivity in urban, industrial and background domains. This sensitivity analysis provides a tool for establishing hypothetical control policies for O₃-precursor emissions through a comparison of simulated correlation between different species.

Chapter 8 shows the results obtained through the utilization of multiscale-nested air quality model MM5-EMICAT2000-CMAQ for different hypothetical scenarios of emission controls, relating the chemical sensitivity regimes in an area of high complexity as the industrial area of Tarragona. Air pollution studies in very complex terrains require high-resolution modeling for resolving the very complex dynamics of flows. As stated in Chapter 4, in order to deal with the influence of larger scale transport, high-resolution models have to be nested in larger models in order to generate appropriate initial and boundary conditions for the finer resolution domains. The aforementioned model was applied with high temporal (1h) and spatial resolution (cells of 24km, 2km and 1km for different nested domains) to represent the chemistry and transport of tropospheric O₃ and other photochemical species respect to different scenarios of emission controls; and to quantify the influence of emitter sources in the industrial area. This analysis provides an assessment of the effectiveness of policies for the control of emission of precursors by comparing modeled results for different scenarios.

Chapter 9 presents a study on the ozone weekend effect. Ambient ozone concentrations tend to be higher on weekends than on weekdays in urban upwind areas. Nevertheless, its downwind influence could be diverse. Day-of-week emission inventories are needed to support air quality models that simulate the ozone weekend effect. A day-specific hourly emissions inventory considering day-to-week variations in emissions is used for stationary, area and on-road sources has been developed in the framework of EMICAT2000 emission model. The MM5-EMICAT2000-CMAQ model has been used to assess the causes of weekday/weekend O₃ differences in the northeastern Iberian Peninsula during 13-16 August, 2000, where there are two labor (14 and 16 August) and two non-labor days (13 and 15 August) with different emission patterns. Dynamic simulations were used to compare and contrast the effects of periodic emission reductions on weekends. This work also helps identifying the major causes of the weekend effect in the considered domain, as the ground-level and aloft carryover, changing in mass and time of precursors emissions.

Last, **Chapter 10** portrays a general summary of the most important tasks performed during the progress of the works compiled in the Dissertation, analyzing the advantages of the proposed methodology and its limitations attending to its state-of-the-science. Furthermore, the general conclusions concerning to air pollution studies in the northeastern Iberian Peninsula are depicted; and also a suggestion of possible tasks and investigations that may be derived from the continuation of the line of research developed within this work.

1.5 References

- Akimoto, H., 2003. Global air quality and pollution. *Science*, **302**, 1716-1719.
- Andreae, M.O., Crutzen, P.J., 1997. Atmospheric aerosols: biogeochemical sources and role in atmospheric chemistry. *Science*, **276**, 1052-1058.
- Aschmann, S.M., Arey, J., Atkinson, R., 2002. OH radical formation from the gas-phase reactions of O₃ with a series of terpenes. *Atmospheric Environment*, **36**, 4347-4355.
- Atkinson, R., 1997. Gas-phase tropospheric chemistry of volatile organic compounds: 1. Alkanes and alkenes. *Journal of Physical and Chemical Reference Data*, **26**, 215-290.
- Atkinson, R., Arey, J., 1998. Atmospheric chemistry of biogenic organic compounds. *Accounts of Chemical Research*, **31**, 574-583.
- Atkinson, R., 2000. Atmospheric chemistry of VOCs and NO_x. *Atmospheric Environment*, **34**, 2063-2101.
- Baldasano, J.M., Cremades, L., Soriano, C., 1994. Circulation of air pollutants over the Barcelona geographical area in summer. Proceedings of Sixth European Symposium Physico-Chemical Behavior of Atmospheric Pollutants. Varese (Italy), 18-22 October, 1993. Report EUR 15609/1 EN: 474-479.
- Baldasano, J.M., Calbó, J., Costa, M., 1995. Importance of atmospheric transport processes on the urban air quality: the case of Barcelona. In: *Urban Air Pollution II*, Chapter 2, Ed. N. Moussiopoulos *et al.* Computational Mechanics Publications, Southampton, UK, 41-68.
- Baldasano, J.M., 1998. Guidelines and formulation of an upgrade source emission model for atmospheric pollutants. In: *Air Pollution Emissions Inventory*, Volume 3. Power, H., Baldasano, J.M. (Eds). Computational Mechanics Publications, Southampton (UK), 238 pp.
- Baldasano, J.M., Valera, E., Jiménez, P., 2003. Air quality data from large cities. *The Science of the Total Environment*, **307**(1-3), 141-165.
- Barros, N., Toll, I., Soriano, C., Jiménez, P., Borrego, C., Baldasano, J.M., 2003. Urban Photochemical Pollution in the Iberian Peninsula: the Lisbon and Barcelona Airsheds. *Journal of the Air & Waste Management Association*, **53**, 347-359.
- Bonasoni, P., Evangelisti, F., Bonafe, U., Ravegnani, F., Calzolari, F., Stohl, A., Tossiti, L., Tubertini, O., Colombo, T., 2000. Stratospheric ozone intrusion episodes recorded at Mt. Cimone during the VOTALP project: case studies. *Atmospheric Environment*, **34**, 1355-1465.
- Borchi, F., Marengo, A., 2002. Discrimination of air masses near the extratropical tropopause by multivariate analyses from MOZAIC data. *Atmospheric Environment*, **36**, 1123-1135.
- Borrell, P., Builtjes, P., Grennfelt, P., Hov, O., 1997. Photooxidants, Acidification and Tools: Policy Applications of EUROTRAC Results. Ed. Springer-Verlag. Germany.
- Calbó, J., Baldasano, J.M., 1995. PROMETEO: an hydrostatic mesoscale model applied to the simulation of land-sea breeze in the Barcelona area. *Environmental Software*, **10**, 3, 139-155.
- Calogirou, A., Larsen, B.R., Kotzias, D., 1999. Gas-phase terpene oxidation products: a review. *Atmospheric Environment*, **33**, 1423-1439.
- Costa, M., Baldasano, J.M., 1996. Development of a source emission model for atmospheric pollutants in the Barcelona area. *Atmospheric Environment*, **30A**, 2, 309-318.
- Dabdub, D., Manohar, R., 1997. Performance and portability of an air quality model. *Parallel computing*, **23**, 2187-2200.

- De Leeuw, F., 2000. Trends in ground level ozone concentrations in the European Union. *Environmental Science and Policy*, **3**, 189-199.
- De Leeuw, F., Sluyter, R., van Breugel, P., Bogman, F., 2001a. Air Pollution by ozone in Europe in 1999 and the summer of 2000. European Environmental Agency Topic Report number 1/2001. EEA, Copenhagen, Denmark.
- De Leeuw, F., Moussiopoulos, N., Sahm, P., Bartonova, A., 2001b. Urban air quality in larger conurbations in the European Union. *Environmental Modelling and Software*, **16**, 399-414.
- Delgado, R., Toll, I., Soriano, C., Baldasano, J.M., 2000. Vehicle emission model of air pollutants from road traffic. Application to Catalonia (Spain) for 1994. In: *Air Pollution VIII*, section 4. Edited by J.W.S. Longhurst, C.A. Brebbia and H. Power. Wit Press, UK, 379-388.
- Ebel, A., Haas, H., Jakobs, H.J., Laube, M., Memmesheimer, M., Oberreuter, A., Geiss, H., Kuo, Y-H., 1991. Simulation of the ozone intrusion caused by a tropopause fold and cut-off low. *Atmospheric Environment*, **25A**, 2121-2144.
- Fehsenfeld, F., Clavert, J., Fall, R., Goldan, P., Guenther, A.B., Hewitt, C.N., Lamb, B., Liu, S., Trainer, M., Westberg, H., Zimmerman, P., 1992. Emissions of volatile organic compounds from vegetation and the implications for atmospheric chemistry. *Global Biogeochemical Cycles*, **6**, 4, 389-430.
- Finlayson-Pitts, B.J., Pitts, J.N., 2000. *Chemistry of the upper and lower atmosphere. Theory, experiments and applications*. Academic Press, UK, 969 pp.
- Fusco, A.C., Logan, J.A., 2003. Analysis of 1970-1995 trends in tropospheric ozone at Northern Hemisphere Midlatitudes with the GEOS-CHEM model. *Journal of Geophysical Research*, **108**(D15), 4449, doi: 10.1029/2002JD002742, 2003.
- Grosjean, E., Grosjean, D., Woodhouse, L.F., 2001. Peroxyacetyl nitrate and peroxypropionyl nitrate during SCOS 97-NARSTO. *Environmental Science and Technology*, **35**, 4007-4014.
- Guicherit, R., 1988. Ozone on an urban and regional scale – with special reference to the situation in the Netherlands. In: I.S.A Isaksen (Ed.), *Tropospheric Ozone*, Reidel Publ., 49-62.
- Guicherit, R., Roemer, M., 2000. Tropospheric ozone trends. *Chemosphere – Global Change Science*, **2**, 167-183.
- Hagen-Smith, A.J., Darley, E.F., Zaitlin, M., Hull, H., Nobel, W., 1951. Investigation on injury to plants from air pollution in the Los Angeles area. *Plant Physiology*, **27**, 18.
- Harris, N.R.P., Ancellet, G., Bishop, L., Hofmann, D.J., Kerr, J.B., McPeters, R.D., Prendez, M., Randel, W.J., Staehelin, J., Subbaraya, B.H., Volz-Thomas, A., Zawodny, J., Zerefos, C.S., 1997. Trends in stratospheric and free tropospheric ozone. *Journal of Geophysical Research*, **102**, 1571-1590.
- IPCC, 2001. *IPCC Third Assessment Report: Climate Change 2001*. Geneva (Switzerland).
- Jacob, D.J., 2000. Heterogeneous chemistry and tropospheric ozone. *Atmospheric Environment*, **34**, 2131-2159.
- Jacobson, M.Z., 1999. *Fundamentals of atmospheric modeling*. Cambridge University Press, UK, 656 pp.
- Jacobson, M.Z., 2002. *Atmospheric pollution. History, science and regulation*. Cambridge University Press, UK, 399 pp.
- Jiménez, P., Baldasano, J.M., 2002. Validation of a semiempirical ozone model. In: *Air Pollution 2002*. Edited by C.A. Brebbia and J.F. Martín-Duque. Wit Press, UK, 3-13.
- Jorba, O., Gassó, S., Baldasano, J.M., 2003. Regional circulations within the Iberian Peninsula east coast. In: *26th NATO/CCMS International Technical Meeting on Air Pollution Modelling and Its Application*. Kluwer Academic/Plenum Publishers, 388-395.

- Koch, S., Winterhalter, R., Uherek, E., Kolloff, A., Neeb, P., Moortgat, K., 2000. Formation of new particles in the gas-phase ozonolysis of monoterpenes. *Atmospheric Environment*, **34**, 4031-4042.
- Kuhn, M., Builtjes, P.J.H., Poppe, D., Simpson, D., Stockwell, W.R., Andersson-Skold, Y., Baart, A., Das, M., Fiedler, F., Hov, O., Kirchner, F., Makar, P.A., Milford, J.B., Roemer, M.G.M., Ruhnke, R., Strand, A., Vogel, B., Vogel, H., 1998. Intercomparison of the gas-phase chemistry in several chemistry and transport models. *Atmospheric Environment*, **32**, 693-709.
- Lelieveld, J., Dentener, F.J., 2000. What controls tropospheric ozone? *Journal of Geophysical Research*, **105**, 3531-3551.
- Lelieveld, J., Berresheim H., Borrmann, S., Crutzen, P.J., Dentener, F.J., Fischer, H., Feichter, J., Flatau, P.J., Heland, J., Holzinger, R., Kormann, R., Lawrence, M.G., Levin, Z., Markowicz, K.M., Mihalopoulos, N., Minikin, A., Ramanathan, V., de Reus, M., Roelofs, G.J., Scheeren, H.A., Sciare, J., Schlager, H., Schultz, M., Siegmund, P., Steil, B., Stephanou, E.G., Stier, P., Traub, M., Warneke, C., Williams, J., Zieris, H., 2002. Global air pollution crossroads over the Mediterranean. *Science*, **298**, 794-799.
- Lee, M., Heikes, B.G., O'Sullivan, D.W., 2000. Hydrogen peroxide and organic hydroperoxide in the troposphere: a review. *Atmospheric Environment*, **34**, 3475-3494.
- Marenco, A., Gouget, H., Nedelec, P., Pages, J.-P., 1994. Evidence of a long term increase in tropospheric ozone from Pic du Midi data series: Consequences: positive radiative forcing. *Journal of Geophysical Research*, **99**(16), 617-632.
- Moussiopoulos, N., 1994. MARS – Model for the Atmospheric dispersion of Reactive Species. In: The EUMAC Zooming Model. Model Structure and applications. Edited by N. Moussiopoulos, EUROTRAC, Garmisch-Partenkirchen (Germany).
- Parra, R., 2004. Development of the EMICAT2000 model for the estimation of air pollutants emissions in Catalonia and its use in photochemical dispersion models. Ph.D. Dissertation (in Spanish), Polytechnic University of Catalonia (Spain).
- Parra R., Baldasano, J.M., 2004. Modelling the on-road traffic emissions from Catalonia (Spain) for photochemical air pollution research. Weekday – weekend differences. In: 12th International Conference on Air Pollution (AP'2004), Rhodes (Greece).
- Parra, R., Gassó, S., Baldasano, J.M., 2004. Estimating the biogenic emissions of non-methane volatile organic compounds from the North western Mediterranean vegetation of Catalonia, Spain. *The Science of the Total Environment*, **329**, 241-259.
- Pielke, R.A., 1984. *Mesoscale Meteorological Modeling*. Academic Press, Orlando, 611 pp.
- Ratto, C.F., Festa, R., Romeo, C., Frumento, O.A., Galluzzi, M., 1994. Mass-consistent models for wind fields over complex terrain: the state of the art. *Environmental Software*, **9**, 247-268.
- Ravishankara, A.R., 1997. Heterogeneous and multiphase chemistry in the troposphere. *Science*, **276**, 1058-1065.
- Richter, A., Nüß, H., Burrows, J.P., Granier, C., Niemeier, U., 2004. Long-term measurements of NO₂ and other tropospheric species from space. In: Quadrennial Ozone Symposium QOS 2004. Kos, Greece, 1-8 June 2004.
- Roelofs, G.J., Lelieveld, J., 2000. Tropospheric ozone simulation with a chemistry-general circulation model: influence of higher hydrocarbon chemistry. *Journal of Geophysical Research*, **105**, 22697-22712.
- Roselle, S.J., Schere, K.L., Pleim, J.E., Hanna, A.F., 1999. Photolysis rates for CMAQ. In: Byun, D.W. and Ching, J.K.S. (Eds.). *Science algorithms of the EPA Models-3 Community Multiscale Air Quality (CMAQ) Modeling System*. EPA Report N. EPA-600/R-99/030, Office of Research and Development. U.S. Environmental Protection Agency, Washington, DC.

- Russell, A., Dennis, R., 2000. NARSTO critical review of photochemical models and modeling. *Atmospheric Environment*, **34**, 2283-2324.
- Sander, R., Crutzen, P.J., 1996. Model study indicating halogen activation and ozone destruction in polluted air masses transported to the sea. *Journal of Geophysical Research*, **101**, 9121-9138.
- Scheel, H.E., Sladkovic, R., Seiler, W., 1994. Ground-based measurements of ozone and related precursors at 47°N 11°E. EUROTRAC Annual Report part 9: TOR, 104-108.
- Seaman, N.L., 2000. Meteorological modeling for air quality assessment. *Atmospheric Environment*, **34**, 2231-2259.
- Seinfeld, J.H., 1988. Ozone air quality models: a critical review. *JAPCA*, **38**, 5, 616-645.
- Seinfeld, J.H., 1989. Urban air pollution: state of the science. *Science*, **243**, 4892, 745-752.
- Seinfeld, J.H., Pandis, S.N., 1998. *Atmospheric chemistry and physics: from air pollution to climate change*. John Wiley & Sons, Inc., 1326 pp.
- Solberg, S., Stordal, F., Schmidbauer, N., Hov, O., 1994. Non-methane hydrocarbons (NMHC) at Birkenes in South Norway, 1988-1993. NILU Report 47/93.
- Soriano, C., Baldasano, J.M., Buttler, W.T., Moore, K., 2001. Circulatory patterns of air pollutants within the Barcelona air basin in a summertime situation: lidar and numerical approaches. *Boundary-Layer Meteorology*, **98** (1), 33-55.
- Staehelin, J., Thudium, J., Buehler, R., Volz-Thomas, A., Graber, W., 1994. Trends in surface ozone concentrations at Arosa (Switzerland). *Atmospheric Environment*, **28**, 75-87.
- Staehelin, J., Harris, N.R.P., Appenzeller, C., Eberhard, J., 2001. Ozone trends: a review. *Reviews of Geophysics*, **39**, 2, 231-290.
- Staehelin, J., Mäder, J., Weiss, A.K., Appenzeller, C., 2002. Long-term ozone trends in Northern mid-latitudes with special emphasis on the contribution of changes in dynamics. *Physics and Chemistry of the Earth*, **27**, 261-469.
- Stockwell, W.R., 1995. On the HO₂ + HO₂ reaction: its misapplication in atmospheric chemistry models. *Journal of Geophysical Research*, **100**, D6, 11695-11698.
- Stockwell, W.R., Milford, J.B., Gao, D., Yang, Y.J., 1995. The effect of acetyl peroxy-peroxy radical reactions on peroxyacetyl nitrate and ozone concentrations. *Atmospheric Environment*, **29**, 14, 1591-1599.
- Stull, R.B., 2000. *Meteorology today for scientists and engineers*. 2nd Edition. West Publishing Company, 502 pp.
- Sudo, K., Takahashi, M., Akimoto, H., 2004. The roles of stratospheric ozone in past and future tropospheric budgets and trends. In: Quadrennial Ozone Symposium QOS 2004. Kos, Greece, 1-8 June 2004.
- Toll, I., 1999. Modeling atmospheric photochemical pollution in the area of Barcelona (In Spanish). Ph.D. Dissertation, Universitat Politècnica de Catalunya, Barcelona, Spain.
- Toll, I., Baldasano, J.M., 2000. Modeling of photochemical air pollution in the Barcelona area with highly disaggregated anthropogenic and biogenic emissions. *Atmospheric Environment*, **34**, 19, 3060-3084.
- Tulet, P., Suhre, K., Mari, C., Solmon, F., Rosset, R., 2002. Mixing of boundary layer and upper tropospheric ozone during a deep convective event over Western Europe. *Atmospheric Environment*, **36**, 4491-4501.
- Vingarzan, R., 2004. A review of surface ozone background levels and trends. *Atmospheric Environment*, **38**, 3431-3432.
- Wayne, R.P., 2000. *Chemistry of atmospheres*. 3rd Edition. Oxford University Press, 775 pp.
- World Meteorological Organization, 1998. Scientific assessment of ozone depletion: 1998. Executive Summary. Global Ozone Research and Monitoring Project. Report No. 44, 43 pp.