

Chapter 6

Ozone

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6.1 The oxidant formation process and its long range transport

Ozone is a secondary pollutant, which means there are no direct emissions of ozone into the atmosphere of any importance and all the ozone found there has been formed by sunlight-driven chemical reactions. These photochemical reactions involve ozone precursors: nitrogen oxides ($\text{NO}_x = \text{NO} + \text{NO}_2$) and organic compounds (sometimes called hydrocarbons (HC) or volatile organic compounds VOCs) and these are the main primary pollutants that control the ozone abundance in the atmospheric boundary layer. Figure 6.1 illustrates schematically the formation of ozone and it contains the following elements: a source region for the precursors, a region over which long range transport and photochemical ozone production occur simultaneously and a receptor region which receives secondary pollutants and may contain sensitive ecosystems or human populations.

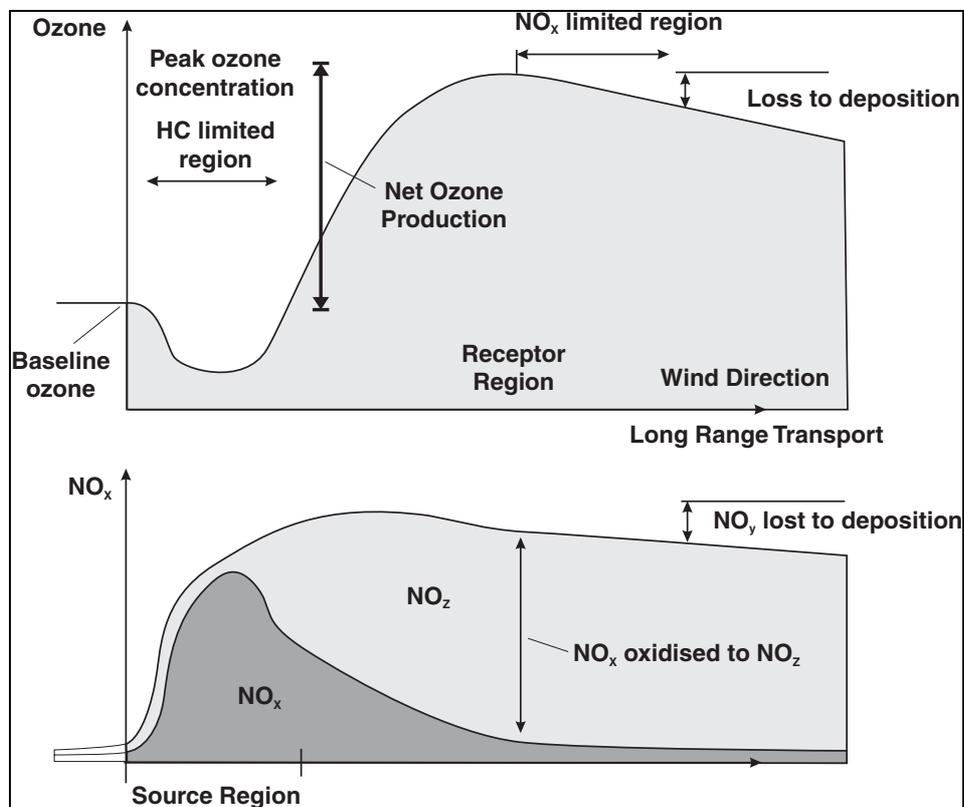


Figure 6.1 A diagrammatic representation of the relationship between net ozone production and the amount of NO_x oxidised.

Air parcels enter the source region, they contain some baseline ozone, some of which is rapidly converted into nitrogen dioxide NO_2 when the intense NO_x emissions are encountered. The photochemical reactions then get going to produce ozone and the rate of ozone production is initially limited by the availability of volatile organic compounds and it is said to be hydrocarbon limited. Because NO_2 is highly reactive, it is steadily converted to oxidised nitrogen compounds, NO_y , such as nitric acid which takes no further part in ozone formation. Air parcels become steadily depleted of NO_x and the rate of ozone production slows up. The rate of ozone production is progressively limited by the availability of NO_x and it is said to be NO_x limited. It should be noted that the above example is highly simplified, since in many parts of Europe source-regions lie very close to each other and air masses are often influenced by fresh emissions. Air may thus experience periods of alternating NO_x and VOC limitation, over many days.

The amount of ozone formed downwind of a source region depends upon the following factors: the amount of NO_x picked up over the source region(s); the amount of organic compounds picked up since their presence forces up the number of ozone molecules formed per NO_x molecule oxidised; dry deposition, since this process determines the transport distance over which ozone can be transported; atmospheric mixing since this process changes the concentration of NO_x and organic compounds and on sunlight, because the stronger the sunlight the more rapid the ozone production and the closer it is located to the source area.

6.2 Emissions of ozone precursors to the atmosphere

As noted above, ozone is not emitted, but is a secondary pollutant. The photochemical reactions generating ozone involve the oxides of nitrogen, NO_x and volatile organic compounds and these substances act as primary emitted ozone precursors. Definitions of volatile organic compounds have changed over the years and sometimes alternative names are used such as hydrocarbons, non-methane volatile organic compounds (NMVOC) and reactive organic gases. In the VOC Protocol of the Convention, VOC is defined as all organic compounds of anthropogenic nature, other than methane, that are capable of producing photochemical oxidants by reactions with nitrogen oxides in the presence of sunlight. In order to make the exclusion of CH_4 explicit, we here adopt the EMEP reporting practice of referring to NMVOC for emissions.

Some other primary-emitted species exert some influence on photochemical ozone formation on the European and hemispheric scale and a detailed modelling treatment will need to take them into account. Such species include methane and carbon monoxide because of the major role they play in controlling the long-term chemistry of the atmospheric boundary layer and troposphere. Sulphur dioxide SO_2 is important to take into account because the photochemical reactions that produce ozone also oxidise SO_2 to sulphuric acid, which can form fine particles, producing regional haze.

Emissions from biogenic sources can make important contributions to the precursor species NO_x and especially NMVOC. For NO_x , the major biogenic source is from soils, and is influenced by many factors, including the anthropogenic inputs from fertilisers and deposition of N-compounds. Estimates of source strength vary widely, with European totals ranging from around 100 Gg N/yr to 1500 Gg N/yr, depending on the chosen methodology (Simpson et al., 1999). Lightning and forest fires are estimated to account for much smaller emissions, of around 20 GgN/yr (below 7 km) and 9 GgN/yr, respectively (*ibid*).

Biogenic emissions of VOC (BVOC) are much more significant to ozone production in the European boundary layer (Simpson 1995; Vogel et al, 1995). A wide range of highly reactive species is emitted by forests, including isoprene and terpenes, such as α -pinene. Isoprene is clearly an important precursor gas for ozone formation, whereas the role of gases such as α -pinene is less clear since this gas reacts rapidly with ozone itself, as well as with OH, but its degradation

products include species with clear ozone-forming abilities. On a global scale BVOC emissions account for a large majority of total NMVOC emissions (Guenther et al., 1995). For most countries in Europe, however, the relative contribution is smaller and on an annual basis anthropogenic NMVOC emissions are estimated to be greater than BVOC emissions (Simpson et al, 1999). However, BVOC emissions have a very strong seasonal cycle, and in summertime frequently exceed man-made emissions from many countries (Simpson et al., 1995). Uncertainties in BVOC emission rates are, however, large and different estimates vary by factors of 3 or more (Guenther et al., 2003, Simpson et al, 1995, 1999; Stewart et al, 2003).

The gridded emission maps of NO_x and NMVOC in 2001 are shown in Figure 6.2. The anthropogenic emissions of nitrogen oxides and its development over time are presented in more detail in chapter 3.1. The change in the emissions of NMVOC during 1980-2001 is shown in Figure 6.3 and refers to anthropogenic releases only. The reduction between 1980 and 2001 is 33 percent, whilst the decline from the year 1988 where the emission peak to 2001, is 35 percent. The emission reduction between 1980 and 2001 for CO is 44 percent (Figure 6.4).

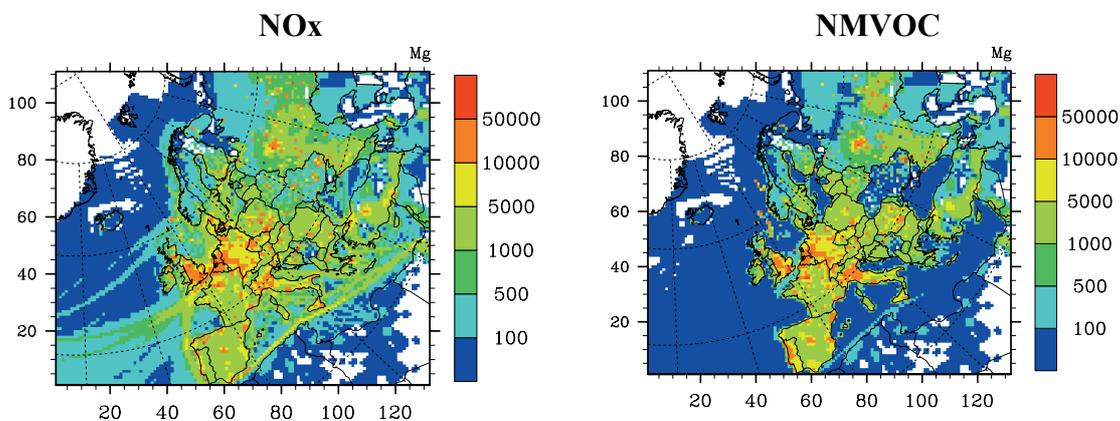


Figure 6.2 Emissions of nitrogen oxides (left) and non-methane volatile organic compounds (right) in 2001 at 50km resolution (Mg per year and grid square as NO_2 and Mg as NMVOC)

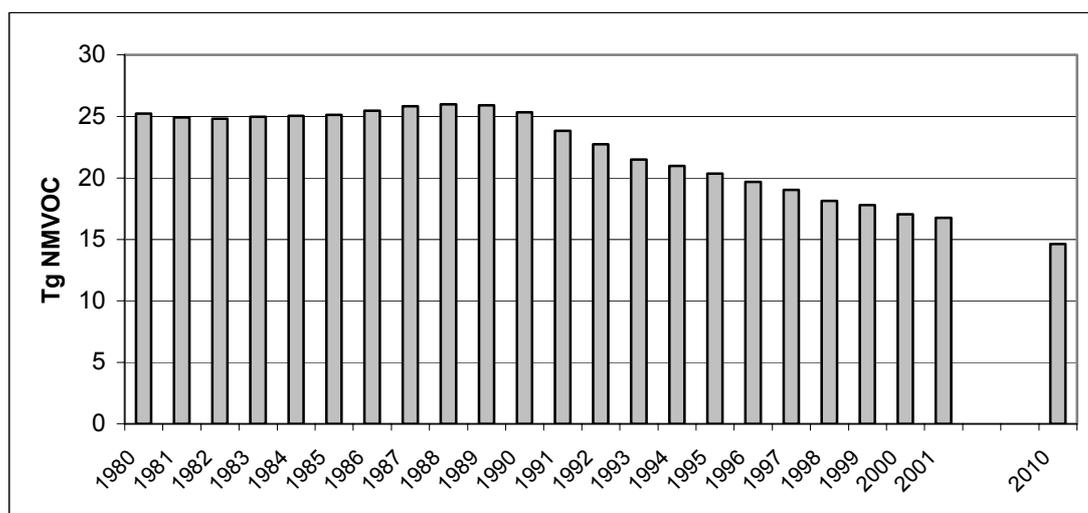


Figure 6.3. Emission of NMVOC in the EMEP area 1980-2001, and prognosis for 2010.

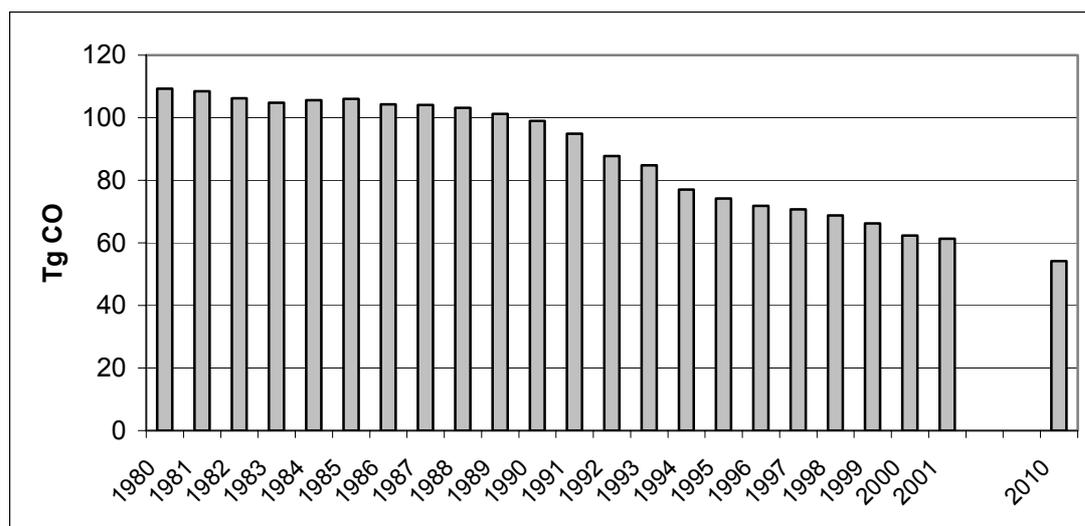


Figure 6.4 Emissions of carbon monoxide in the EMEP area 1980-2001 and prognosis for 2010.

Reporting of emissions and their trends by each Party is naturally a central issue in the work of the CLRTAP. Figure 6.5 present the percentage emission reductions for the individual countries between 1990 (the Gothenburg Protocol base year) and 2001 ($100 * (E_{1990} - E_{2001}) / E_{2001}$). Non-Signatories to the Gothenburg Protocol (UNECE, 1999) are listed to the right in the figure. The Protocol had 31 Signatories as of 3 January 2003. Increases of non-methane volatile organic compounds (Figure 6.5) have been reported by Norway, Portugal and Greece.

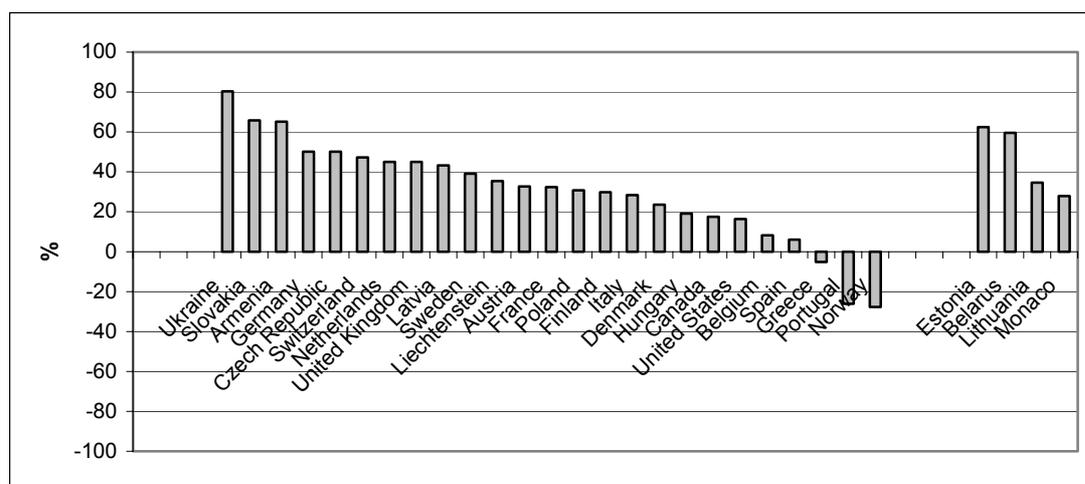


Figure 6.5 Emission reductions of volatile organic compounds in the ECE region 1990-2001. Signatories to the 1999 Gothenburg Protocol are on the left. Only countries that have reported national total emission data including main sources for both 1990 and 2001 are listed here.

Whilst reporting of national emissions of NMVOCs and NO_x are essential for testing compliance with the Protocols of the Convention on Long Range Transboundary Transport and with the National Emission Ceilings Directive of the European Union, they need to be supplemented with a substantial amount of additional information like gridded data, speciation etc. before they can be used to describe the formation and long range transport of photochemical ozone formation across Europe. This is particularly true for the emission inventories of VOCs.

The difficulty with emission inventories of VOCs is that they total together the emissions of a wide range of different individual organic compounds from a wide range of emission processes. Detailed emission inventories developed within the Task Force on Emission Inventories and Projections use a profile of speciated emissions for each emission process. In this way the total emission can be broken down into the individual emissions of up to 600 identifiable VOC species. This is important because each of these 600 VOC species exhibits a different ability to form photochemical ozone. This ability is termed reactivity. The most reactive organic compounds are the olefins: such as ethylene and propylene and the diolefins: such as 1,3-butadiene and isoprene. The least reactive are the halogenated solvents: such as methylene chloride and alkanes: such as methane and ethane. Usually, single VOC species are grouped into classes of compounds with similar chemical properties.

During the 1990s, Parties to the Convention on Long Range Transboundary Transport of Air Pollution have agreed Protocols to reduce emissions of VOCs and NO_x so as to limit ozone formation and its transboundary transport. At the time these agreements were reached, it was also expected that substantial emission reductions would be achieved by the introduction of three-way catalyst exhaust and evaporative emission controls on petrol-engined motor vehicles. The rapid implementation of these control techniques was stipulated by the so-called EURO standards in the European Community. These pollution control measures not only have steadily reduced total VOC emissions but have also tackled the most reactive VOC species. Consequently the propensity to form photochemical ozone has declined faster than would be expected based on the reduction in total VOC emissions. Equally well, modelling studies that do not take into account the declining reactivity of VOC emissions during the 1990s tend to understate the impact of VOC emission reductions.

For accurate modelling of ozone formation, not only the amount of NO_x emission has to be taken into account, but also the height of emissions. NO_x from power stations is emitted in plumes with effective heights often 100s m above the ground, whereas that from road transport is emitted at the surface and often with poor dispersion characteristics in urban areas. Since road transport NO_x is often simultaneously emitted with organic compounds, it makes a much more substantial contribution to ground-level ozone formation compared with that emitted by power stations. On the other hand, freshly emitted NO in particular from road traffic can deplete ozone locally ($\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$) and as a result urban ozone levels are often lower than levels in the surrounding suburban or rural areas. In contrast, power station NO_x emissions exert comparatively little influence on surface ozone levels in their immediate vicinity, but contribute to ozone generate at greater downwind distances.

6.3 Critical levels

Within the framework of the UN-ECE Convention on long-range transboundary air pollution, the concepts for critical levels for ozone has developed and steadily improved. Starting with the Egham, UK, and Bern, Switzerland workshops (Ashmore and Wilson, 1992, Fuhrer and Achermann, 1994), the AOT_X concept was introduced, whereby AOT_X is the accumulated amount of ozone exceeding a threshold X ppb, calculated during daylight hours over an appropriate growing season. Following small changes in Kuopio, Finland (Kärenlampi and Skärby, 1996) the AOT_{40} critical levels have been widely used for crops and for forests. The critical levels defined for these species were 3000 ppb h (accumulated over 3months) and 10 000 ppb h for forests (accumulated over 6 months), and these values were widely used.

However, some important limitations and uncertainties have been recognized for using AOT_X . In particular, the observed impacts of ozone depend on the amount of ozone which reaches the sites of damage within the leaf, whereas AOT_X -based critical levels only use the ozone concentration at the top of the canopy. The Gerzensee, Switzerland Workshop in 1999 recognized the importance

of developing an alternative critical level approach based on the flux of ozone from the exterior of the leaf through the stomatal pores to the sites of damage (stomatal flux). This approach required the development of mathematical models to estimate stomatal flux, primarily from knowledge of stomatal responses to environmental factors. It was agreed at the Gothenburg, Sweden Workshop in November 2002 (Karlsson et al., 2003) that ozone flux-effect models were sufficiently robust for the derivation of flux-based critical levels, and such critical levels should be included in the UNECE/ICP Mapping Manual for wheat, potato and provisionally for beech.

As detailed in this Manual, three approaches are now used to define critical levels for ozone:

- (a) Ozone concentrations, via AOT_x
- (b) Stomatal fluxes
- (c) Vapour-pressure-deficit modified ozone concentrations (modified AOT_x)

Each approach uses the ozone concentration at the top of the canopy and incorporates the concept that the effects of ozone are cumulative and values are summed over a defined time period. In each case, a specific threshold is used, and only ozone concentrations, vapour-pressure deficit-modified ozone concentrations or instantaneous fluxes above that threshold are summed. When the sum of the values above the threshold exceeds the critical sum defined in the relevant table for each approach and vegetation type, then the critical level for that approach & vegetation type has been exceeded.

The new procedures will give different levels of exceedance for AOT₄₀ than the old. Firstly, they use ozone concentrations at the top of the canopy. For crops the ozone concentration at this height, of about 1 m above ground level, will be significantly less than the ozone concentrations previously output from say the EMEP model (at either 1 m above crop level, or 3 m above ground level), or derived from the EMEP measurement network (usually 2-3 m above ground level). Thus the new concept will be significantly lower than previously estimated values. Conversely, ozone concentration at the top of forest canopies are often 5-10% higher than those modelled or measured, so the new estimates of AOT₄₀ for forests will be greater than previous estimates. In addition, the critical level is now reduced to 5000 ppb h for forests, a factor of two less than the previous value.

For assessing the effects on human health, an AOT₆₀ was used in the framework of the Convention, e.g., for the Gothenburg Protocol. The AOT₆₀ was based on the WHO Air Quality Guideline for ozone of 120 µg/m³ as eight-hour mean value. However, a recent review of the health effects of air pollution conducted by WHO suggests that severe effects of ozone may also occur at levels significantly lower than 60 ppb. Therefore, a new concept is currently being developed to account for effects of ozone on human health.

6.4 Concentrations of ozone in air

Surface ozone in Europe exhibits a varying pattern across the different regions. This is partly due to the large variations in climate from the warm Mediterranean in the south, the moist marine climate at the western border and polar climate in the far north. Furthermore, the dominant westerly wind flow causes a gradual build-up of continental emissions in clean, maritime air masses on their way across the continent. The topography of the Alps has a strong influence by inducing enhanced mixing between the boundary layer and the free troposphere above and has been shown to act as an effective means of transporting of man-made ozone from populated valleys into the free troposphere.

Figure 6.6 shows the observed 99-percentile of ozone based on hourly data in the period April-September for each of years 1999-2002, respectively (Hjellbrekke and Solberg, 2004, and

references therein). These data show a north-south gradient with highest peak values in south and central Europe and lowest in the far north. Due to the lack of monitoring sites in southeast it is, however, difficult to judge the spatial distribution in that area.

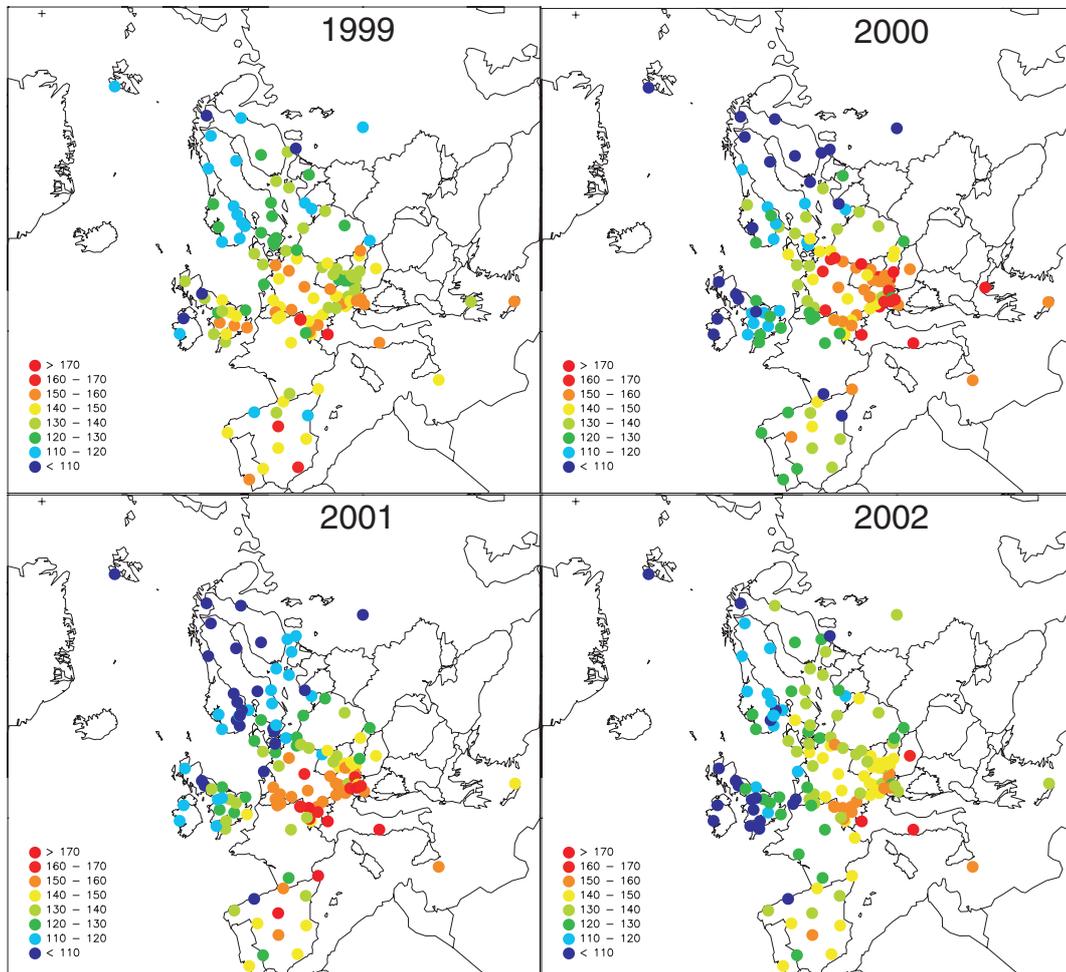


Figure 6.6 The observed 99-percentiles of ozone during April–September for the years 1999–2002 ($\mu\text{g}/\text{m}^3$).

Within the EUROTRAC project TOR-2 it was shown that the mean seasonal cycle of surface ozone shows a distinct spatial distribution over Europe (e.g. Monks et al., 2000). Sites at the northwest border of the continent mostly influenced by cleaner, Atlantic air masses show a smaller seasonal amplitude peaking in spring (May) while in the interior of Europe the monitoring sites display a broad summer maximum. The change from a more flat, springtime maximum cycle to the more pronounced summer-time peak cycle is due to the effect of continental emissions causing an ozone reduction in winter by titration with NO and ozone excess in summer due to photochemical formation. The mean seasonal cycles in ozone for two background sites as a function of the air masses' pollution level are shown in Figure 6.7 (Monks et al., 2003). The perturbation of the seasonal ozone cycle by anthropogenic emissions is important for the adverse effects on vegetation as the time of the ozone increase often coincide with the growing season in spring, the most vulnerable period of the plants' life.

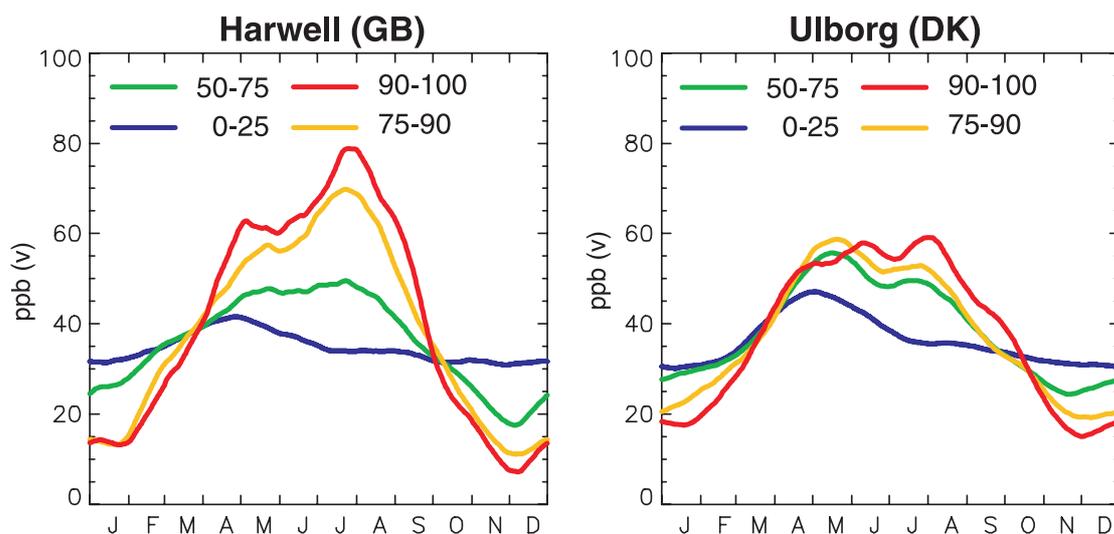


Figure 6.7 Seasonal cycles of ozone at the EMEP sites Harwell and Ulborg as a function of the NO_x emissions integrated along back trajectories from the time of measurement. The different curves represent seasonal cycles for the different quartiles of the trajectory integrated NO_x (Monks et al., 2003).

The regional ozone levels which are the focus of EMEP can be strongly modified by urban areas. A common modification is the local depression in ozone levels in the NO_x plume in and downwind of the city (section 6.1, Fig. 6.1). Emissions from city areas contribute to ozone formation further downwind, and such city-plume enhancements are expected to be most important in warm weather conditions, and especially in southern Europe. Local meteorological conditions can also play a strong role in determining the ozone concentration observed around cities. Sea-breezes have been studied extensively in this context (e.g. Kallos et al., 1993), but many types of mesoscale circulation are associated with elevated ozone levels (see e.g. Louka et al., 2003 for further details and many references).

Studies of ozone around urban areas have increased in recent years. Examples are the ESQUIF project around Paris (Vautard et al., 2003), the BERLIOZ project around Berlin (Volz-Thomas et al., 2003), BOCCALINO and PIPAPO around Milan and southern Switzerland (Prévôt et al., 1997; Neftel et al., 2002) and the ESCOMPTE project (Cros et al., 2004). Clear examples have been found in these studies of ozone plumes downwind of major cities, for example Dommen et al. (2002) observed ozone in the plume downwind of Milan was around 20-40 ppb higher than in adjacent areas.

However, even in regions where local ozone production may be expected to be strong, the regional ozone concentrations often dominate levels. This was seen in the Heilbronn experiment in Southern Germany, where strict emission reductions within the city had little effect on ozone concentrations, although reducing NO_2 level considerably (Bruckmann and Wichmann-Fiebig 1997; Moussiopoulos et al., 1997).

Moussiopoulos et al., 1998 investigated the relationship between regional scale emission controls, calculated with the EMEP (Lagrangian) ozone model, and local controls, calculated with the simple OFIS model, for two cities, Stuttgart in Germany and Athens in Greece. They concluded that urban VOC control is effective in reducing ozone primarily on the local or urban scale, whereas urban NO_x control may cause an increase of urban peak ozone while contributing to an effective reduction of regional ozone. More recently, the CITY_DELTA project has applied a number of mesoscale models in conjunction with the EMEP model, and the results from this

project will be used in developing future emission control strategies within the EU CAFÉ Programme.

6.4.1 Exceedance of the thresholds for vegetation

Figure 6.8 and 6.9 show the five-year averaged AOT40 values for crops and semi-natural vegetation (3-months growing season, May-July) for the EMEP stations with at least three years of monitoring data and at least 75% data capture each year in the two periods 1990-1994 and 1997-2001. Figures 6.10 and 6.11 show the similar figures for the AOT40 for forests (6-months growing season, April-September). The spatial variations are fairly similar over Europe for these two indicators, but with a larger area of exceedance for crops and semi-natural vegetation than for forests.

The average AOT40 value for crops and semi-natural vegetation during 1997-2001 shows that the 3000 ppb h threshold was exceeded in most areas of Europe except Ireland, north west UK, Scandinavia north of approx. 60°N and the Baltic states. There is a clear northwest-southeast gradient with a region of large exceedances in south Germany, Switzerland, Austria and Italy. The highest value was, however, found at Finokalia at Crete, with 19,200 ppb h followed by Krvavec in Slovenia (17,880 ppb h) and Viznar in Spain (17,837 ppb h).

The AOT40 map for crops and semi-natural vegetation for the period 1990-1994 indicate exceedances over a larger area than for the last five-years period. The average AOT40 levels for the 1990-94 period shows exceedances further north in Norway, Finland and the UK and generally higher AOT40 levels in many areas of Europe, particularly in the southern regions of the UK, although the poorer station coverage complicates the comparison.

The area of exceedance of the AOT40 threshold for forests for the period 1997-2001 is smaller and confined to the European mainland (Germany and further southeast), while the whole of UK, Scandinavia and the Baltic region is below the 10,000 ppb h limit. For the earlier five-years period, 1990-1994, the map indicates exceedance of the threshold for forests also in southern UK and southern Sweden. The stations with the largest exceedance in the 1997-2001 period were Sonnblick in Austria (32,241 ppb h), Krvavec in Slovenia (31,032 ppb h) and Giordan Lighthouse at Malta (30,879 ppb h). The data capture at Finokalia, Crete, was too low to calculate the AOT40 for forests.

These patterns are confirmed by the national EMEP assessments. Austria reports that both the critical level for forests and crops are exceeded at all background locations. The highest AOT40 values are observed at high alpine sites, with the maximum ever registered in Austria at Gerlitz in 1993 both for forests (47 300 ppb h) and crops (27 800 ppb h). In the Czech Republic the critical levels are exceeded for long periods not only in rural areas but also virtually over the whole Czech Republic. In France, measurements from 80 sites have been used to compute national maps which show clearly a large exceedance of the critical load of 10 000 ppbh. The areas with the greatest exceedances are the Ile-de-France, the Southeast and Northeast regions. In Spain the critical levels are exceeded at all stations (except at Niembro at the north coast). Values of the order of 10 000 ppb h for the 3-months AOT40 for crops and semi-natural vegetation, and 20 000 ppb h for the 6-months AOT40 for forests are typical. In Switzerland the 6-months AOT40 (April-September) has increased since 1990 and values of the order of 20 000 ppbh are typical.

A note of caution should be included, however, when interpreting these data. Whereas the air-sampling intake for the ozone monitors are normally at 2-3 meters above the ground, the critical levels refer to ozone concentrations measured close to the vegetation surfaces. The uptake by the vegetation and deposition to surfaces will lead to a significant concentration gradient towards the leaf surfaces and the stomata where the actual uptake in the plants take place. Thus, the monitoring

data are not directly comparable to the concentrations experienced by the plants, and the true AOT40 exposure will be smaller than given by the monitoring network.

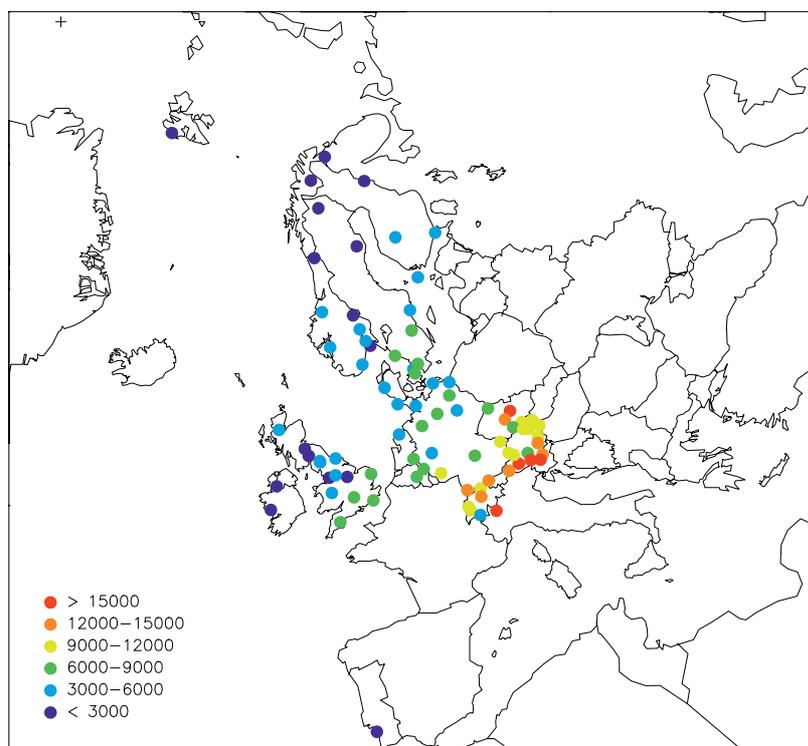


Figure 6.8 Five years' average AOT40 (ppb h) for crops and natural vegetation based on measured daylight ozone values May, June and July 1990-1994. Threshold value: 3.000 ppb h (dark blue is below the threshold).

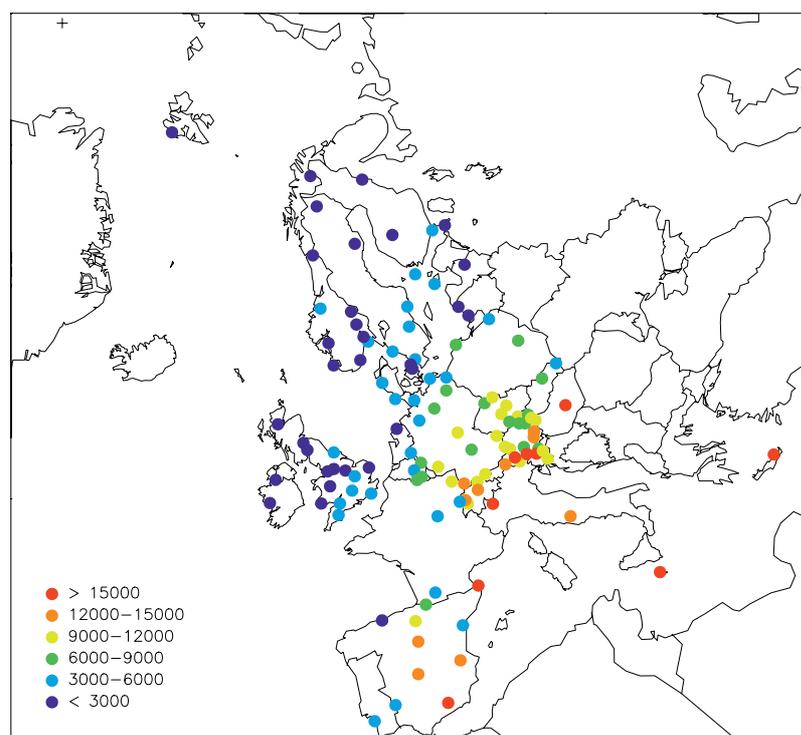


Figure 6.9 Same as for Figure 6.8 but for the period 1997-2001

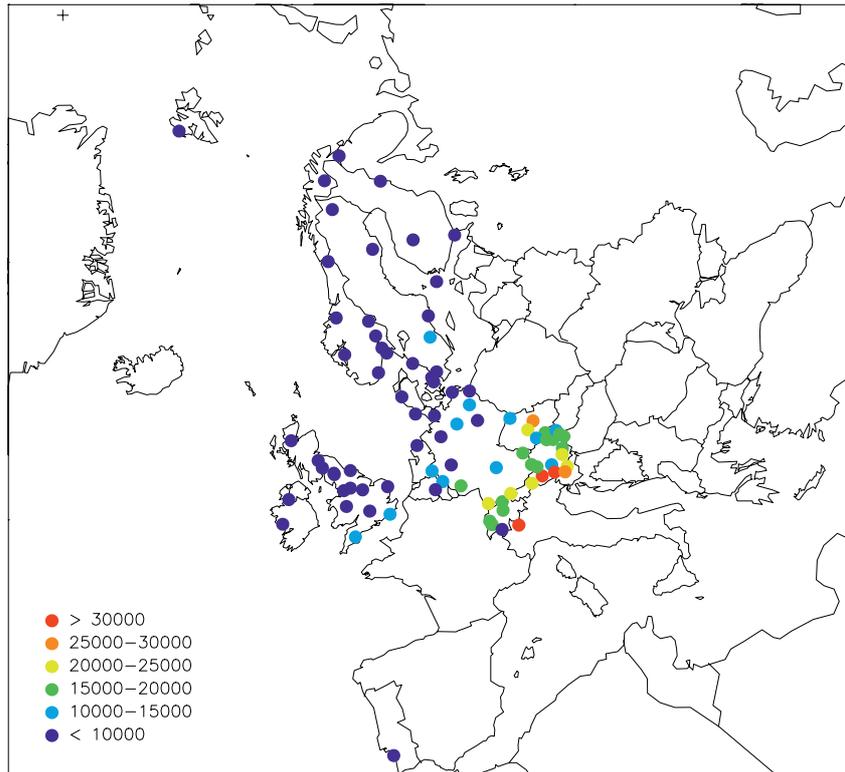


Figure 6.10 Five years' average AOT40 (ppb h) for forests based on measured daylight ozone values April-September 1990-1994. Threshold value: 10 000 ppb h (dark blue is below the threshold).

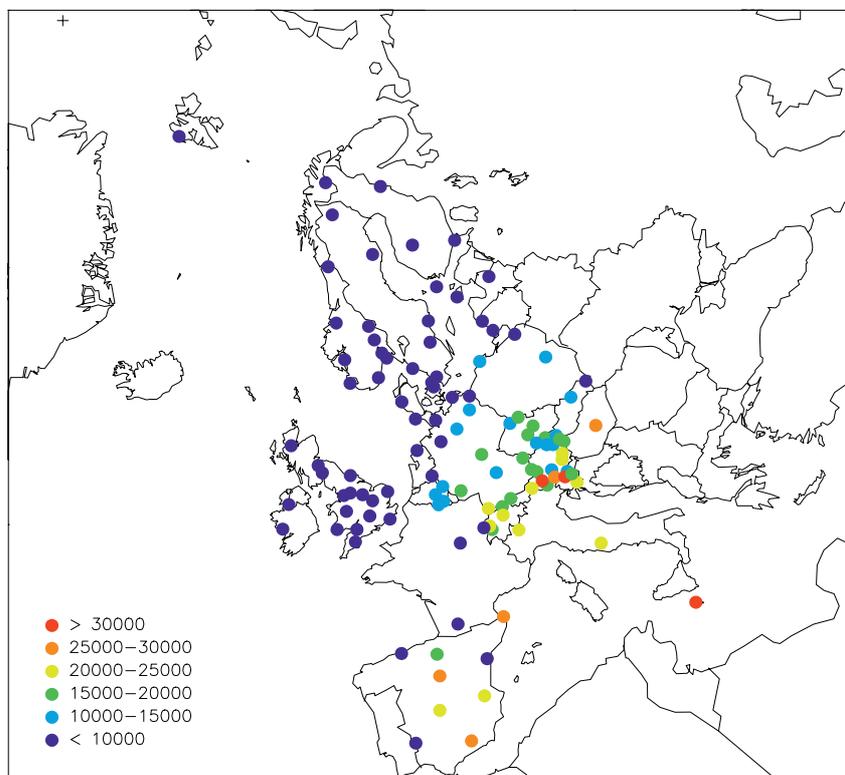


Figure 6.11 Same as for Figure 6.10 but for the period 1997-2001.

As shown above, the problems with exceedances are less in northern parts of Europe. For the UK a spatial interpolation technique has been used to prepare a fine resolved map of the AOT40 indexes (Figure 6.12). These maps indicate that the AOT40 threshold for crops and semi-natural vegetation was exceeded over 65% of the UK land area while the threshold for forests was exceeded over 4% of the land area (NEGTAP/2001). However, the authors comment that this difference in area of exceedance reflects that the AOT40 thresholds are based on a 5% reduction in the annual biomass increment for crops and semi-natural vegetation compared to a 10% reduction of trees. Thus, they conclude, it is misleading to compare the two maps, and, if anything, a more conservative approach should be used for trees to reflect the much longer life span of trees.

In Latvia, during the whole measurement period, the AOT40 for forests was not exceeded while the AOT40 for crops was exceeded once - in 1995.

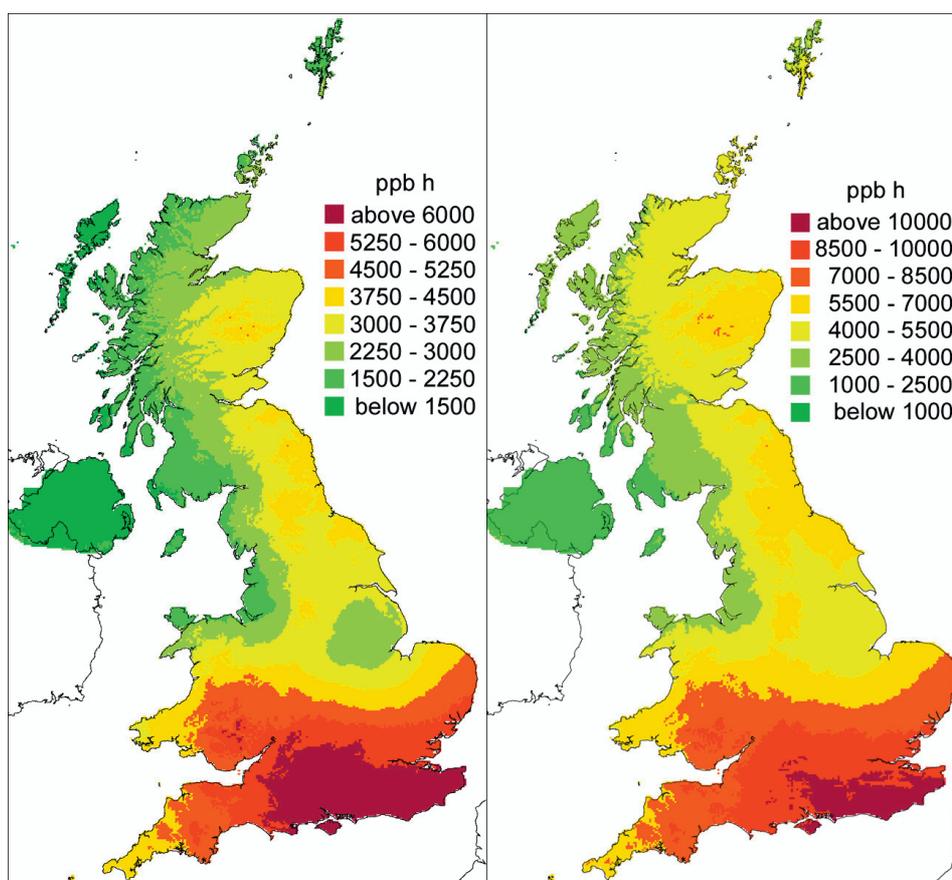


Figure 6.12 Left: Mean AOT40 for crops and semi-natural vegetation, calculated for May-July inclusive, for the five years 1994-1998. Critical level 3000 ppb h; Right: Mean AOT40 for forests, calculated for April-September inclusive, for the five years 1994-1998. Critical level 10,000 ppb h (adopted from NEGTA, 2001).

6.4.2 Results from other ozone assessments

Information on ozone levels is compiled by the European Environment Agency (2002). In its report on 2002, 1718 ozone monitoring sites were operational across Europe. In many countries, remote and rural monitoring stations report their results to both the EU AIRBASE database and to the EMEP monitoring network database. The highest peak hourly ozone concentrations reported throughout Europe during 2002 were 185, 196 and 192 ppb for three sites in Spain, 186 ppb at a

site in France and 189 ppb at a site in Italy. These levels are similar to the maximum levels reported during 2001.

The EU threshold for informing the public of 90 ppb maximum hourly concentration was exceeded in 17 out of the 27 countries reporting and was not exceeded in 9 countries during 2002. These latter countries were Denmark, Finland, Ireland, Sweden, Estonia, Lithuania, Latvia, Norway and Romania. One third of the stations (568 stations) reported one or more exceedances of the EU threshold for public information.

Peak ozone concentrations tend to be highest in central and southern Europe and lowest in Eastern and Northern Europe. So, for example, over the period 1997-2002, Finland has reported no exceedances of the 90 ppb information threshold and France, Spain and Italy regularly reported hourly peak concentrations in excess of 120 ppb.

Within EEA's third assessment of the state of the environment, it was found that most exceedances of the thresholds for human health are in central and southern European countries when based on many hundred ozone monitoring sites, mostly urban or suburban ones (EEA, 2003). EEA estimates that in 1995-1999, almost all the urban population were exposed to ozone concentrations above the threshold value for the protection of human health. For more than half that population, concentrations exceed the threshold for more than 15 days (EEA, 2002). EEA concludes that ground-level ozone is seen as one of the most prominent air pollution problems in Europe mainly because of its effects on human health, natural ecosystems and crops.

In the two phases of EUROTRAC, tropospheric ozone was a key research issue. It was found that the highest enhancement in European ozone from North American emissions occurs when the ozone concentrations are close to the critical values. 20% of the violations of the European air quality standards would not have happened without the North American emissions. Model calculations indicated that anthropogenic emissions in North America contribute 2-4 ppb to the average surface ozone concentration (occasionally up to 10 ppb).

In 2000 the North American Research Strategy for Tropospheric Ozone (NARSTO, 2000) delivered an assessment of tropospheric ozone. (NARSTO, 2000), including a number of recommendations and scientific findings. A main message is that ozone pollution occurs across all scales - from local air quality in cities through regional exceedances of thresholds for vegetation in rural areas to inter-continental transport. Furthermore, recent and anticipated changes to air quality policies have tended to move ozone standards and objectives closer to the background ozone concentration, and that this narrowing of the gap between background and air-quality standards requires more sophisticated air quality management practices.

6.5 Trends in ozone

Ozone is a secondary pollutant and its production is strongly influenced by the meteorological conditions from year to year in addition to the anthropogenic emissions. Thus, trends in surface ozone due to changes in emissions may be masked by the varying meteorology. Furthermore, only in certain areas of Europe are the measurement time series long enough to detect trends with any statistical significance. Nevertheless, reductions in peak ozone values are reported from several regions during the 1990s. A decrease in peak ozone values is also seen in the EMEP model calculations (see section 6.5.3 below). Model calculations also indicate that the reductions in the emissions of ozone precursors have resulted in reductions in average daily maximum ozone levels in summer. On the other hand, there is no clear trend in the measured exceedances of the threshold values for AOT40. Surface stations in the north and west regions in Europe report increasing background (hemispheric) concentrations. A declining trend of the extreme values may to some

extent be counterbalanced by a gradual rise in the background ozone and by an effect of climatic change causing higher risks of hot summers.

6.5.1 Global and hemispheric trends

Measurements from the early stages of industrialization indicate that ozone levels at that time may have been around 10 ppb (Volz and Kley, 1988; Marengo *et al.* 1994). Model calculations simulating the same time period typically gives ozone concentrations around 20 ppb (Berntsen *et al.*, 1997; Lelieveld and Dentener, 2000).

Studies of ozonesonde data in the free troposphere (Logan, 1999; Oltmans *et al.*, 1998; WMO, 2002) points to a general increase in free tropospheric ozone up to the mid 1980s and a mixed picture with many sites/regions showing no significant trend or even downward trends after that. However, analyses of the clean wind sector at several rural sites indicate an increase in the background ozone levels also after the mid 1980s (Roemer, 2001 and references within), particularly in the winter season. Contrary to the ozonesonde data, model calculations indicate that the increase in free tropospheric ozone has continued also after the mid 1980's. (Lelieveld and Dentener, 2000; Karlsdottir *et al.*, 2000).

For the US the NARSTO assessment (2000) found a decrease in the 1h daily max concentration of the order of 15% during 1986-1996. The most significant reductions in peak ozone values were seen in urban/suburban areas. The extent to which the downward ozone trend was caused by emission reductions could, however, not be tested by any reliable emission estimates or ambient measurements. The assessment concludes that population increase, growth in the number of vehicles and demand for energy have offset much of the ozone air quality benefits from emissions control. A completely different trend was found for Canada with a reduction in rural ozone concentrations and an increase in urban areas.

The link between climate change issues and surface ozone episodes is an emerging topic, as e.g. discussed at the Twenty-eighth meeting of the Task Force on Integrated Assessment Modelling, 2003, Haarlem, Netherlands. The feedback between extreme weather events that could be a result of future climate change and ozone exposure was exemplified in the summer 2003 in Central Europe. Exceptionally long-lasting and spatially extensive episodes of high ozone concentrations occurred, mainly in the first half of August. These episodes appeared to be associated with the extraordinarily hot temperatures over wide areas of Europe (Fiala *et al.*, 2003).

6.5.2 Trends in measured ozone concentrations in Europe

Surface ozone measurements have been a part of the EMEP extended (voluntary) measurement activities since the third phase (1 January 1984–31 December 1986). Due to the lack of funds, the systematic collection and checking of data within EMEP did not start before 1987. EMEP's ozone measurement program was a continuation of the OECD's oxidant data collection programme OXIDATE (Grennfelt *et al.*, 1989). In the first years the ozone monitoring stations were mostly located in the UK, central Europe (Germany) and Scandinavia.

The EMEP monitoring programme of VOC (volatile organic compounds) was initiated in 1989. Regular measurements of VOC started with the collection of grab samples of light hydrocarbons in the middle of 1992 and measurements of carbonyl compounds in 1993, both with a sampling frequency of two samples per week.

The monitoring network for ozone has gradually expanded to include more sites in south and east Europe. As shown in Figure 6.13 the ozone monitoring history in large parts of Europe is still very

short confining the possibility of making trend assessments to certain regions in the continent. Because of the major influence of meteorological variations even a 12-15 years' time series of ozone is short when the aim is to discover trends that are caused by trends in anthropogenic emissions. Simpson et al. (1997) estimated that if one attempts to identify emission trends by the wait-and-see approach from the monitoring data alone we would need of the order of 30 years of data. Obviously it is crucial to improve the data evaluation and to link the monitoring data to model calculations.

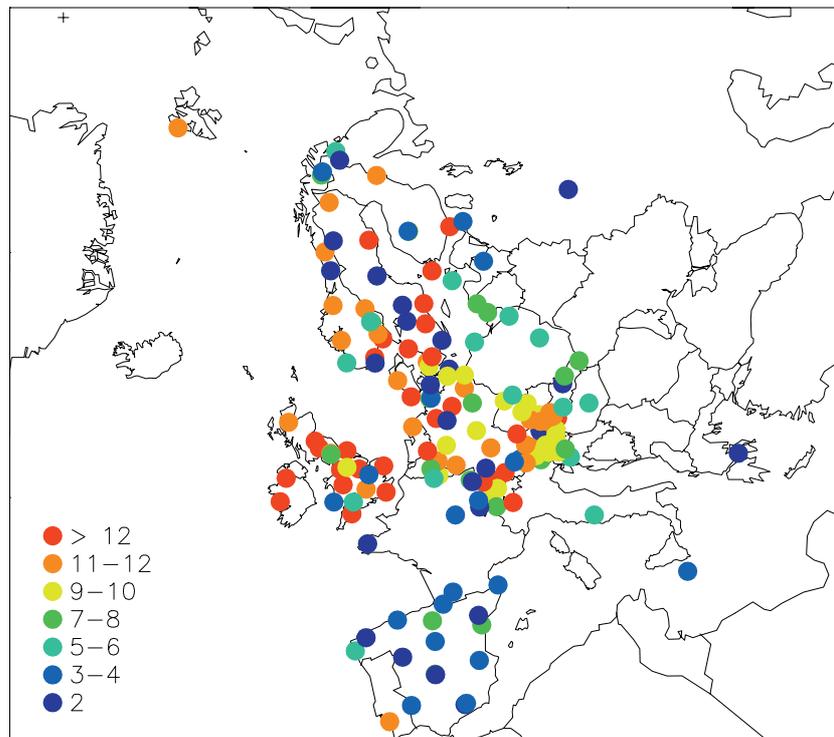


Figure 6.13 The number of years with monitoring of surface ozone within EMEP (1988-2001 assuming 75% data capture).

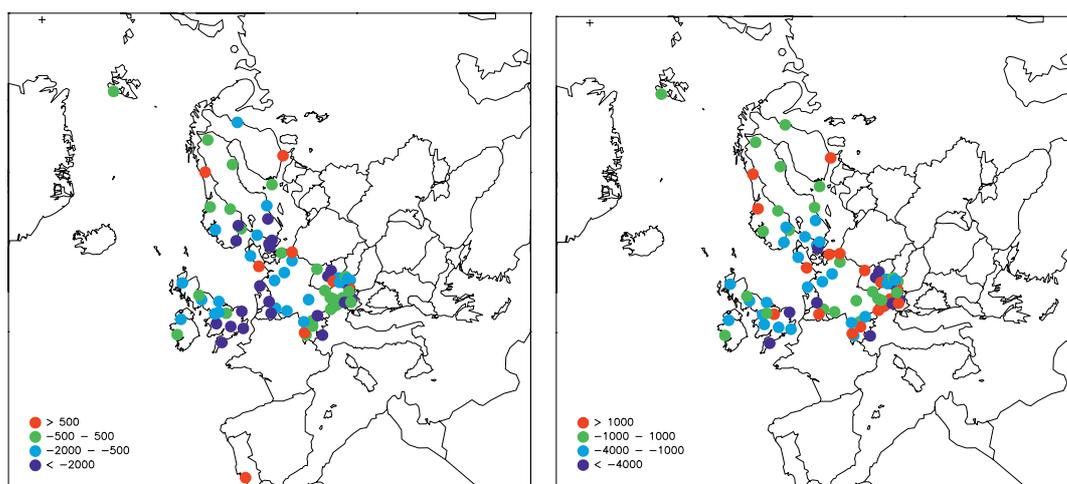


Figure 6.14 The change in AOT40 from the five-year period 1990-1994 to the period 1997-2001 for three months (May-July) left, and for six months (April-September), right. Red colour marks increases of more than 500 ppb h and 1000 ppb h, respectively, while blue colours mark decreases.

The reported trends in measured ozone from different regions in Europe vary. Stations in northwest Europe report an increase in the background ozone concentration, and the growth rates estimated independently by different authors from various locations in Scandinavia, UK and Ireland are all in the range 0.35-0.50 ppb per year. Ozone trend estimates for central Europe indicate either no significant trend in the data or a reduction in the peak values of ozone. However, the trend calculations have been performed on different statistics (annual mean, high percentiles etc) in different countries complicating the comparison.

Overall, the reported exceedances of thresholds for protection of vegetation, measured by the AOT40 index, don't show clear trends during the 1990s and is apparently too dependent on the meteorological variability to reflect any effect of reduced European emissions. Furthermore, the increase in background ozone may counteract this effect particularly for a quantity as AOT40. Nevertheless, a reduction in the 3-months' and 6-months' AOT40 values is found over large regions in Europe when comparing the period 1990-1994 with the period 1997-2001 (Figure 6.14). Whether this reflects reduced European emissions of precursors or different weather climatology within these two 5-years periods is difficult to say based on the observational data alone. Additionally, an *increase* in the 6-months' AOT40 value for forests is seen at several sites, e.g. in North Norway and in central Europe possibly reflecting an increase in the background ozone concentration.

In Ireland, at Mace Head on the west coast, background ozone concentrations (selected on the basis of air mass trajectories) show a significant positive trend of 0.49 ± 0.19 ppb per year (Figure 6.15) during the period 1987- 2003 (Simmonds et al., 2004). Furthermore, a major anomaly is evident in these data in 1998-1999, likely caused by large-scale biomass burning events in tropical and boreal regions coupled with an intense El Nino event.

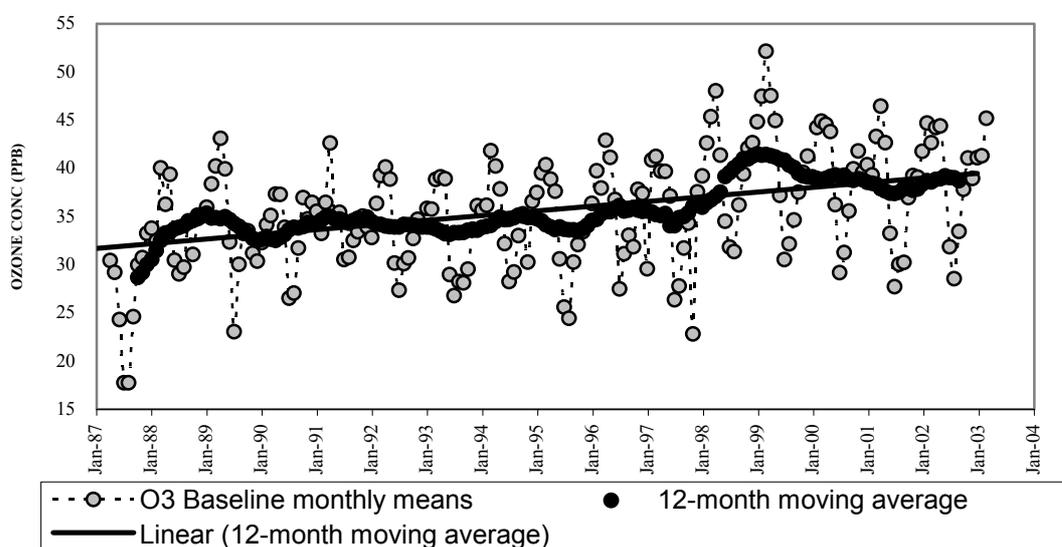


Figure 6.15 Mace Head Ozone baseline monthly means and 12-month moving average (Simmonds et al., 2004).

In the UK it has been estimated that peak ozone concentrations at the EMEP stations have declined about 30% in the period 1986-1999 (NEGTA, 2001). At the same time a slight increase in the annual average concentration is seen. Based on model calculations using the IPCC scenarios, NEGTA (2001) finds it likely that the mean ozone concentrations will be substantially larger by the middle of the 21st century. Thus, harmful effects from surface ozone are likely to remain

significant beyond 2010. Statistically significant downward trends in the annual maximum concentrations of the order of 3 ppb per year are found for 8 monitoring sites. Downward trends are also found for the 8 h running mean concentration (exceeding 50 ppb) and AOT40 but these trends are not statistically significant.

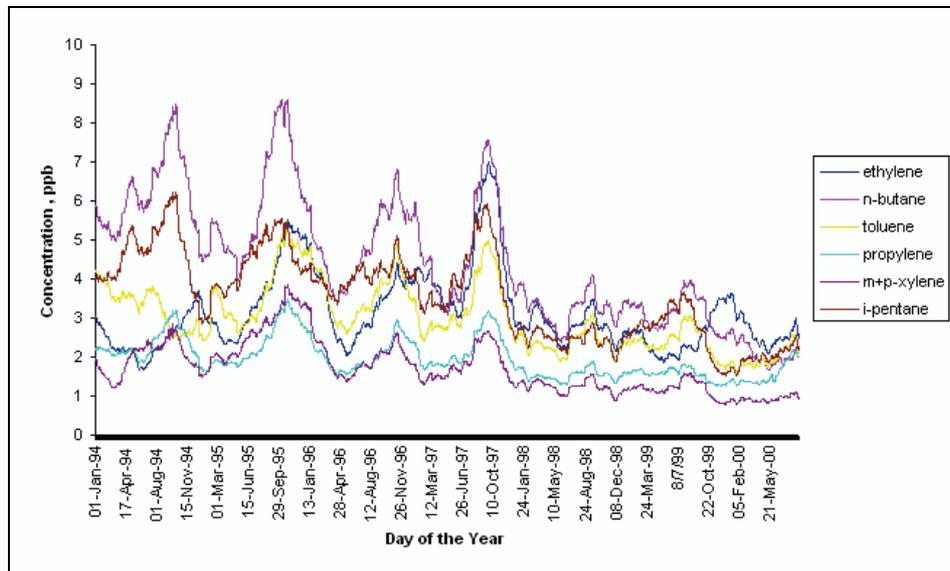


Figure 6.16 Observed 90-day running mean concentrations in 6 selected organic compounds for an urban background site in central London.

Based on observed trends in individual VOC concentrations, see Figure 6.16, together with detailed model calculations of the potential for ozone formation for the individual VOCs, Derwent et al. (2003) concluded that downwards trend in episodic peak ozone concentrations in north west Europe is to be expected during the 1990s of about -2.17 to -2.67 ppb yr^{-1} , to which a further -0.7 ppb yr^{-1} should be added from the non-monitored VOC species. When trends in other anthropogenic emissions (NO_x , SO_2 , CO) were added together a net trend of -3.4 ppb yr^{-1} was estimated which compares closely with the observed ozone trends of -1.9 to -2.9 ppb yr^{-1} across the British Isles. It is clear that the impact of the motor vehicle emission controls have brought about a substantial reduction in episodic peak ozone concentrations in northwest Europe during the 1990s, see Figure 6.17. Not only has there been a steady decline in the magnitude of the episodic peak ozone concentrations but here has also been a reduction in the number of days when the maximum 8-hour mean ozone concentration exceeded 50 ppb.

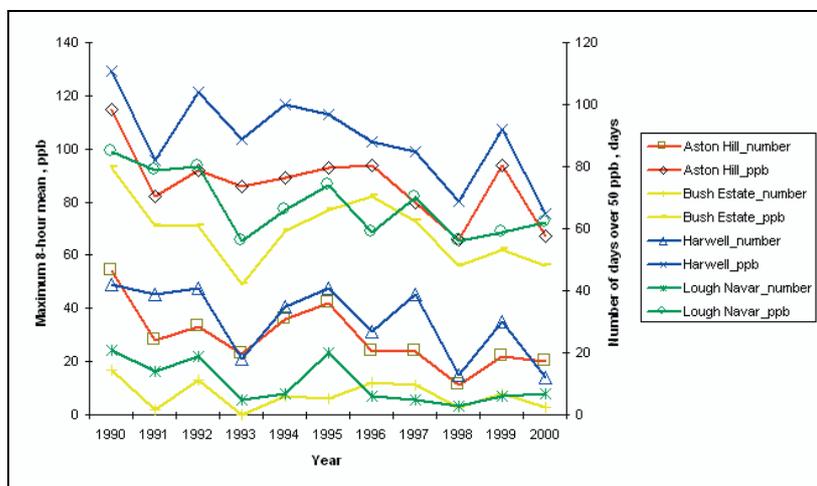


Figure 6.17 Time series of the maximum 8-hour mean ozone concentration and the number of 50 ppb 8-hour mean ozone concentration exceedance days at four United Kingdom EMEP sites between 1990 and 2000.

Within the EUROTRAC project TOR-2 downward trends in the ozone maxima (annual peaks, 98- or 95-percentiles) over the last 10-13 years were reported for various areas (Roemer, 2001). A consistent picture with increasing ozone minima during the 1990s was found in the polluted areas in the Netherlands, Germany and Switzerland by the reduced titration with NO. The increasing ozone background concentrations found are not entirely undisputed since downward trends was reported from vertical soundings made over the last 13 years at Uccle, Belgium and from surface measurements made at a Caucasian mountain site (Kislovodsk).

In Germany there is no clear trend at the EMEP ozone sites, but the data indicates a weak upward trend of the medium concentrations. However, results from more than 300 national ozone sites between 1990 and 2000 including urban locations show a pronounced downward trend of the higher percentiles while upward trend for low and medium percentiles (Beilke and Wallasch, 2000). During 1990-1997 a drop in the 99 percentile of $3.3 \mu\text{g m}^{-3}$ per year was found. In the same study no trend in AOT40 during 1990-1999 was found, reflecting that for medium percentile ozone concentrations, the various trends may cancel each other.

In Austria only 3 of 16 background ozone monitoring stations with time series starting 1992 or earlier, have an increasing trend significant at 99% confidence level of the annual mean value. Both the critical levels for forests, pasture and natural vegetation (10,000 ppb h) and for crops (3000 ppb h) are exceeded at all background locations in Austria. The inter-annual variation is large at all sites, with high values at most sites in 1994 and 2000. Most sites show an upward trend of both AOT40 values, but with low statistical significance (Figure 6.18).

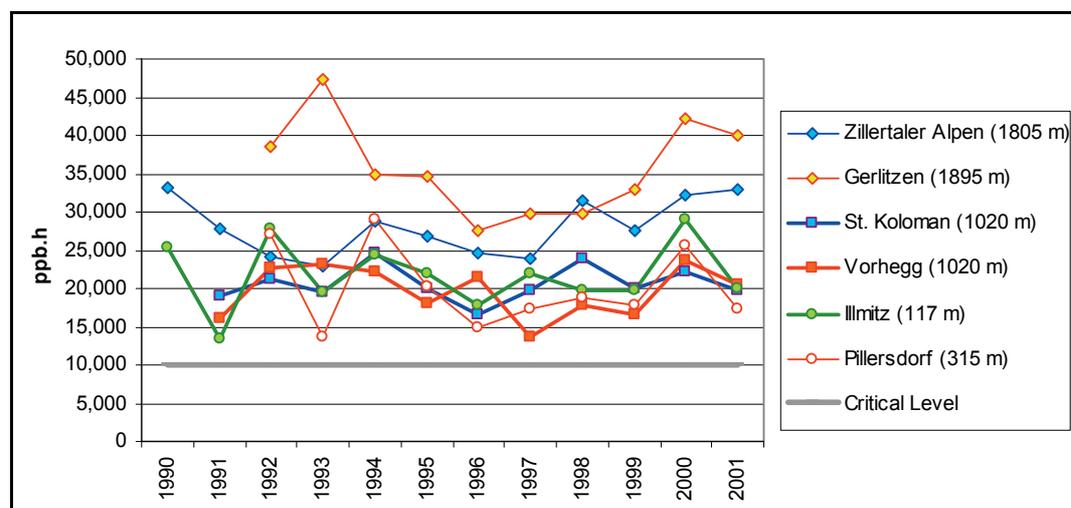


Figure 6.18. AOT40 values for forests in Austria (April – September, daylight hours)

In France no significant trends in exceedances of threshold levels were observed at the rural sites from the beginning of the measurements. The inter-annual variability in observed ozone concentrations is explained by the annual variability of photochemical activity.

In Italy no decrease in the number of days of exceedance of $65 \mu\text{g/m}^3$ (24h daily average) could be found from the measurements at Ispra since 1990. Since 1996 an apparent increase is indicated at both Ispra and Montelibretti. The number of days of exceedance of the $180 \mu\text{g m}^{-3}$ (1h) limit clearly decreased at Ispra from 1991 to 1997 but this trend is not apparent thereafter. The AOT40 values also decreased at Ispra over the 1991-1996 period but have levelled afterwards (Figure 6.19).

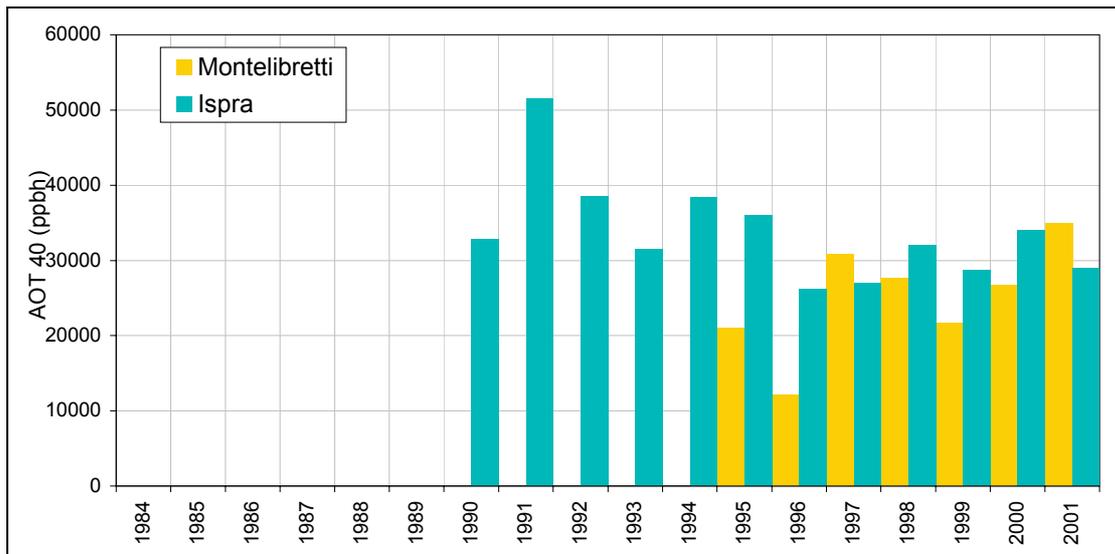


Figure 6.19 AOT40 for forest (April-September) for the Italian stations in 1990-2001.

In Switzerland the monitoring data since 1990 indicate not only an increase of the annual mean concentration at all sites but also in the AOT40 (April-September).

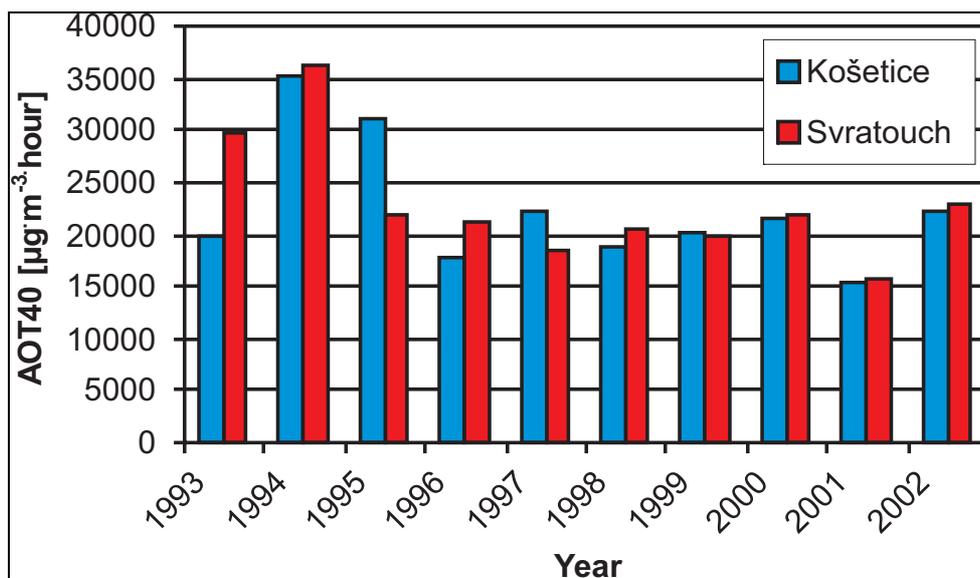


Figure 6.20. AOT40 for forests in the Czech Republic

In the Czech Republic a slight decline in average annual concentrations of ozone and a more distinct drop of average daily maxima have been observed since 1996. The number of episodes of high surface ozone concentrations dropped markedly in the second half of the 1990s. A slightly decreasing tendency of AOT40 at the Czech EMEP stations was observed in 1994-1996 (Figure 6.20), while in the subsequent years no trend in AOT40 has been observed.

In Slovakia an annual average increase of ground level ozone concentration has been estimated at about $1 \mu\text{g m}^{-3}$ per year for the period 1969-1992. During the 1990s, however, no significant trend was observed at the Slovak stations.

In Norway a reduction in the 99-percentile of the daily (daytime) ozone data in the southern part of the country in the summer half year of the order of 1 ppb/year was found during the 1990s for some sites. For sites further north a statistically significant increase in the mean ozone concentration of 0.3-0.5 ppb/year was found for the winter half year. An increasing trend in the mean ozone concentration was found also during the summer but is less clear.

In Sweden increasing trends over the years 1991-2002 are found in the northern part. The annual increase is about 0.34 ppb per year and also the higher percentile concentrations are increasing. It is likely that the increase is the result of a general enhancement in the northern hemispheric background. At Rörvik, in southwestern Sweden, model calculations indicate that a decrease should have occurred in the ozone summer maxima, but this is not supported by the monitoring data. The winter average of daytime ozone has increased as well as the daily winter maximum concentrations. Reduced NO_x emissions could partly explain the increased ozone concentrations. However, since also the sum of NO₂+O₃ is increasing, part of the observed change in ozone must be attributed to a genuine increase in ozone, supporting the assumption that the northern hemispheric ozone background concentrations are increasing.

An evaluation for the Nordic countries (Solberg et al., 2004) indicated that the frequency of high ozone values has decreased in the 1990s. Several results taken together indicate that it is likely that there has been an improvement in ozone episodes, that is to say peak values have been reduced, in southern Norway and southern Sweden due to European emission reductions during the 1990s. The model results indicate a reduction of the order of 30 ug/m³ (15 ppb) for the highest ozone peak values and less for the less pronounced episodes over the decade. The 99-percentiles of summer six-months hourly data have probably been reduced by the order of 10-20 ug/m³ (5-10 ppb) in the same region. For Finland and for the northern part of the region, the conclusions are more difficult to assess and become more uncertain. Although the model indicates similar results for southern Finland as for southern Sweden and Norway the agreement with the measurements are poorer, possibly reflecting that ozone episodes in Finland in general are more linked to transport from the east rather than from Sweden and Norway and that emission data for Russia and for eastern Europe, in general, is less well-established.

6.5.3 Calculated trends of ozone in Europe

Ozone has been calculated by the EMEP Eulerian photochemistry model for the years 1980, 1985, 1990, 1995 – 2000. In the calculations ozone climatology from Logan (1999) are used as lateral boundary concentrations. However, in order to accommodate interannual variability in background ozone and a general upward trend in background surface ozone at sites close to the Atlantic Ocean, the lateral boundary concentrations are modified based on the measurements at Mace Head, Ireland (the Mace Head correction). With this method we account for the year-to-year variations in background ozone. The adjustment (in ppb ozone) in lateral boundary concentration is the same at all levels. As ozone generally increases with altitude, the relative correction is largest near the surface and small in the upper troposphere. The method is described in Simpson et al., 2003.

In Figure 6.21 the measured and model calculated frequency distribution of daily maximum ozone at 18 sites measuring ozone in 1990, 1995 and 2000 are shown. The sites are confined to northern and western parts of Europe. The annual mean ozone is well reproduced by the model. However, the model underestimates the high ozone events and overestimates low ozone episodes. A likely cause for this is that the model resolution is too coarse to capture the very high and the very low events. Without the Mace Head correction of the lateral boundary concentrations of ozone mentioned above the model will underestimate the mean values and the model calculated frequency distribution curve would be increasingly displaced to the left for the latter years.

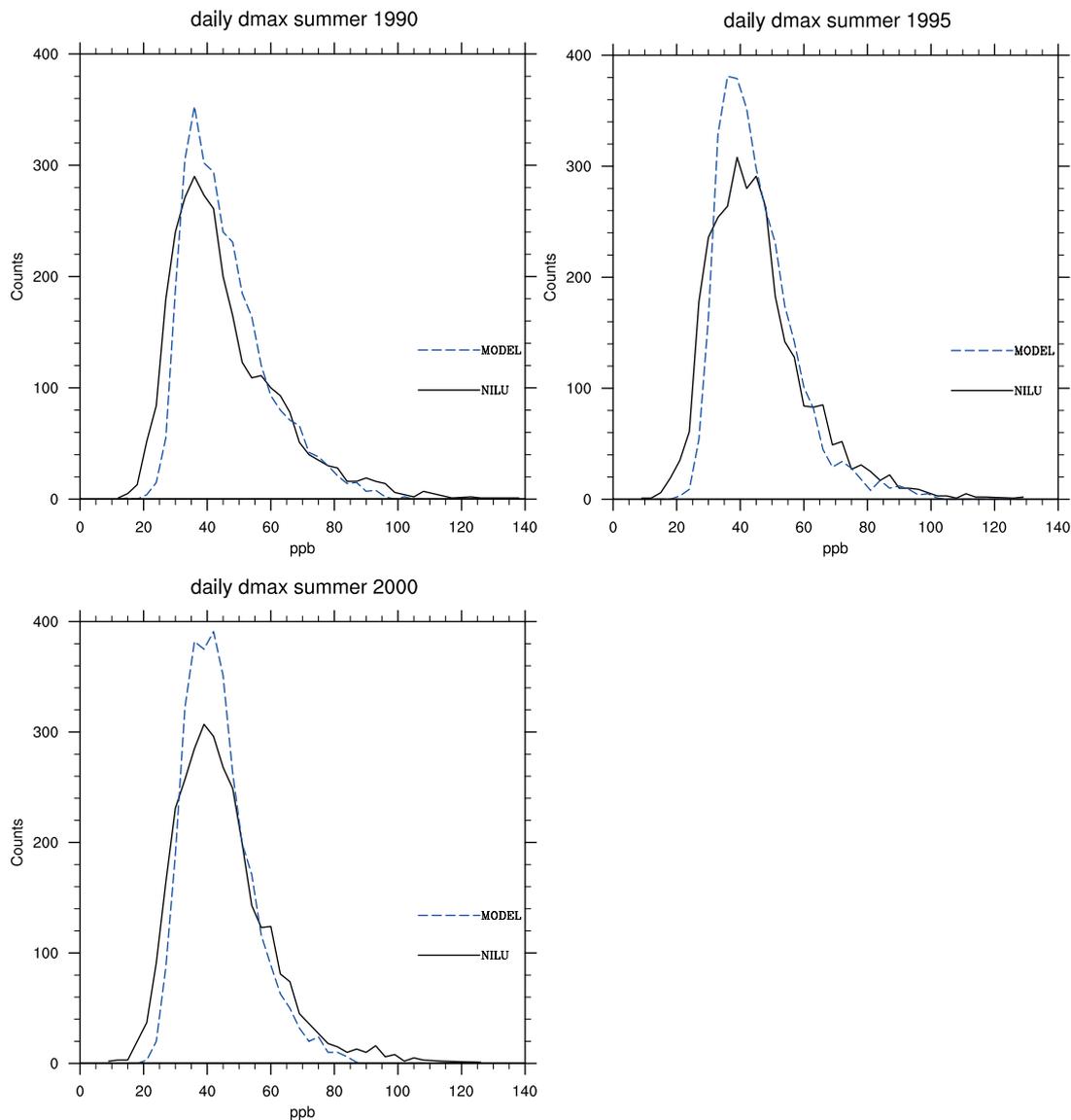


Figure 6.21 Model calculated and measured frequency distribution of ozone for 18 sites in north and western parts of Europe.

Figure 6.22 (left panel) depicts the average daily maximum modelled ozone levels for the summer 1990. Levels are in general high over central Europe and the Mediterranean with levels exceeding 55 ppb. Figure 6.22 (right panel) depicts the average daily maximum modelled ozone for the highest 7 days in 1990. The highest levels are in general located further north than the summer average with mean peak levels exceeding 85 ppb.

In Figure 6.23 measured and calculated time series of monthly averaged ozone are depicted for 1990 and 1995 to 2000. The measured ozone levels are well reproduced by the model for the ensemble of 57 sites with measurements for the abovementioned years. Trends in calculated (and measured) ozone are to a large extent masked by the large inter-annual variability in ozone levels. The data indicate increased winter concentrations the last years of this period.

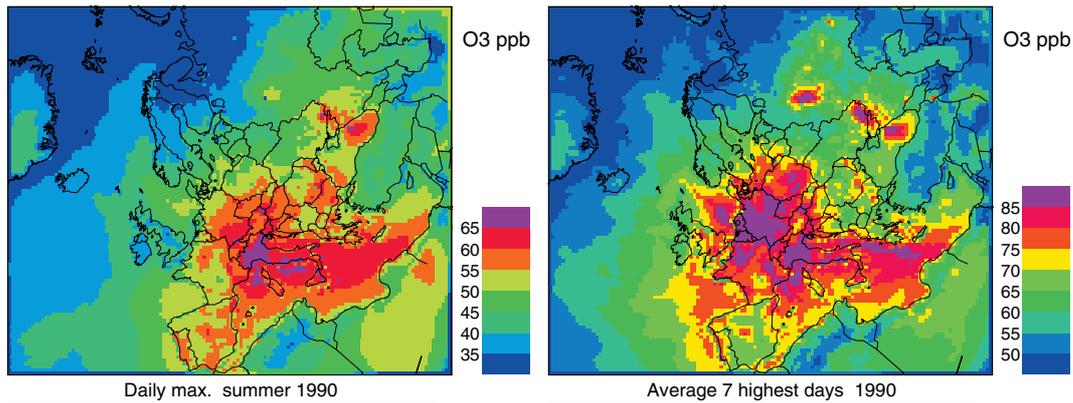


Figure 6.22 Left panel: Model calculated daily maximum ozone concentration in summer 1990 (June, July, August); Right panel: Average concentration for the 7 days with the highest ozone concentration in 1990.

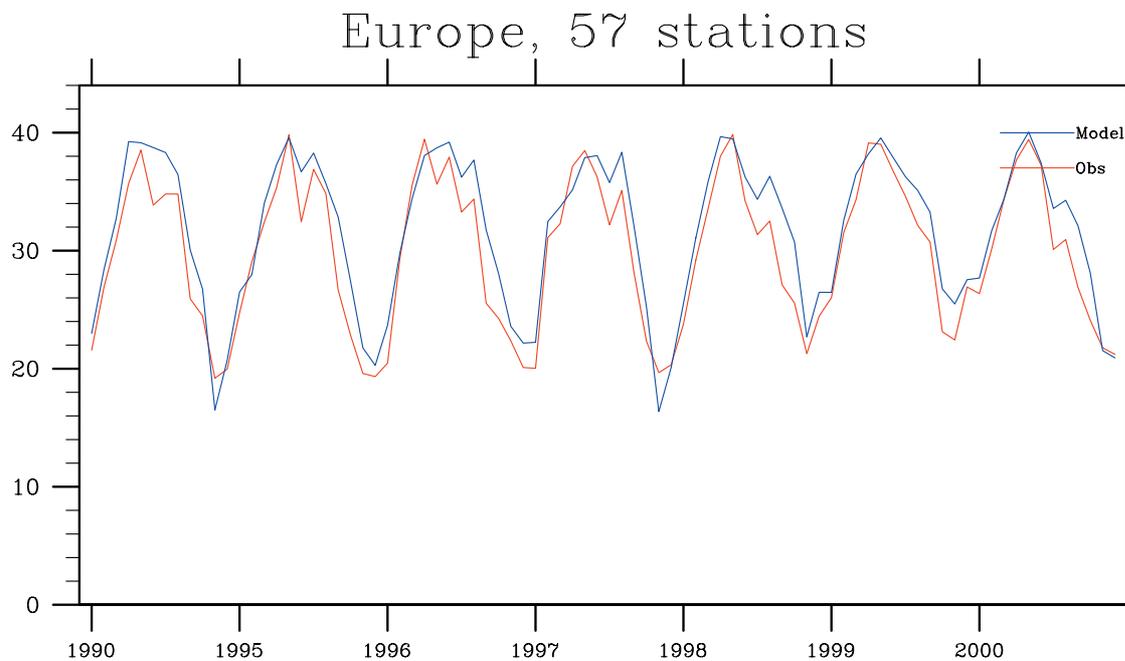


Figure 6.23 Model calculated and measured monthly mean ozone (ppbv) for surface ozone at sites with continuous measurements for the years 1990 to 2000.

In order to study the effect of European emission changes alone (disregarding the fact that European emissions to some extent will affect hemispheric free tropospheric ozone used as lateral boundary concentrations) a model run has been made with 1990 meteorology and lateral boundary concentrations and year 2000 emissions. In Figure 6.24 this model run is compared to the standard model run for 1990. In Figure 6.24 we also compare the standard model runs for 1999 and 1990. Although emissions of ozone precursors have changed over this decade with reductions of the order of 30% for NO_x in many countries, these changes are, as noted above, often masked by meteorological factors. The reduction in calculated peak ozone levels from 1990 is clear for both the 1999 calculation and 1990 model calculation with year 2000 emissions. The reductions in peak ozone as seen in the bottom two panels in Figure 6.24 are of the order of 10 – 15 ppb throughout

large parts of central Europe. Over the Iberian Peninsula and Turkey, peak ozone levels have increased following an increase in emissions in ozone precursors. The marked reductions in peak ozone levels are comparable to what is observed (see discussion above).

Although less pronounced, there is also a marked decrease in the average summer daily maximum ozone levels as a result of changing emissions from 1990 to 2000 (Figure 6.24, upper left). Comparing 1999 and 1990 (Figure 6.24, upper right) this reduction is broadly speaking confined to the latitudinal band between 50° and 55° N over Europe, with no change or a small increase outside this band. In the Atlantic there is an increase, reflecting the increase in lateral boundary concentrations. On the other hand calculated annual mean ozone levels (not shown) increase almost throughout the entire model domain from 1990 to 1999. This is caused by a combined effect of increased lateral boundary concentrations and less titration in winter as a result of reductions in NO_x emissions in most of Europe. The increase in winter ozone in the last decade can be seen for both modelled and measured ozone in Figure 6.23.

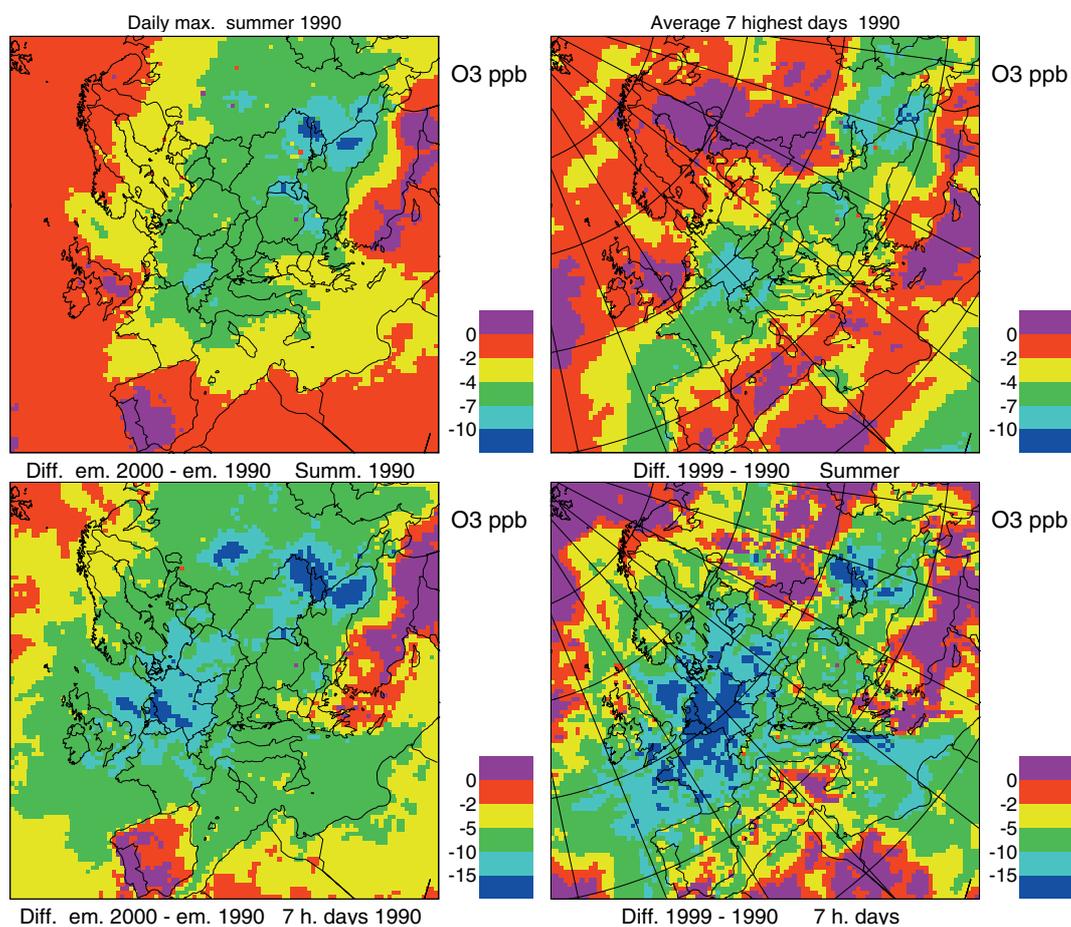


Figure 6.24 Differences in model calculated daily ozone in ppb. Upper left: difference in summer (June, July, August) ozone with 1990 meteorology and 2000 versus 1990 emissions. Upper right: 1999 - 1990 summer ozone. Bottom left: Difference for the 7 highest days with 1990 meteorology and 2000 versus 1990 emissions. Bottom right: difference for the 7 highest days 1999 – 1990.

6.6 Implications of increased background concentrations

The European anthropogenic and biogenic influence is added on top of the hemispherical background ozone. Above the atmospheric boundary layer tropospheric ozone has a chemical residence time of several weeks allowing inter-continental transport and hemispheric mixing to take place. This hemispheric background reflects the combined effect of the emissions from all northern hemispheric continents added to the naturally occurring ozone. Naturally occurring ozone is due to stratospheric-tropospheric exchange and production by lightning. Measurements from the 19th century, such as the Montsouris data from Paris (Volz and Kley, 1988) indicate a natural concentration level of 10-20 ppb.

As anthropogenic emissions in many areas in Europe have decreased while environmental problems due to ozone still are widespread, the importance of regional and hemispherical scale ozone has gained increased importance. Inter-continental transport of ozone has an important influence for European abatement strategies and has been the topic at several EMEP workshops. Furthermore, the rural ozone concentration is controlling the human exposures in urban areas of both ozone itself in a direct way, and of NO₂ through the indirect link by the NO + O₃ → NO₂ reaction. Thus, any policies to abate human health effects from air pollution have to consider the changes in the surrounding large-scale ozone concentration which in turn depend (to some extent) on the trends in hemispheric background ozone.

The contribution to annual mean surface ozone from stratosphere-troposphere exchange (Figure 6.25), the major natural source of ozone, shows a maximum that peaks over Ireland and falls off into central Europe, in global model calculations (Derwent et al. 2004). Intercontinental transport from North America appears to contribute significantly more than stratosphere-troposphere exchange and shows the same fall-off across Europe. A contribution from intercontinental transport from Asia can be discerned but the largest single contribution comes from internal production within Europe itself. Because the NO_x emissions from North America, Asia and Europe have exhibited different trends over the 1970s-1990s (Naja et al. 2003), it may be possible to explain why there have been different observed trends in surface ozone in different parts of Europe during the 1970s-1990s.

A long-term trend in the hemispheric background ozone concentration may have a substantial impact on environmental effects that are related to medium-range ozone concentrations. As pointed out by Coyle et al. (2003) increasing tropospheric background ozone concentrations have considerable significance for future assessments of the risks of ozone impacts on vegetation in Europe. This change is also accompanied by an increase in the early season exposure of vegetation to harmful ozone concentrations.

The sensitivity of the AOT40 parameter to the background level of ozone is well known and is a problem for modelling studies. In the simplest way, the effect of an increased background concentration of 5 ppb could be illustrated by the AOT35 value which is identical to the AOT40 when all ozone concentrations are increased by 5 ppb.

Figure 6.26 and 6.27 show the AOT35 fields (equal to the AOT40 fields assuming a 5 ppb uniform increase) for the period 1997-2001, and could be directly compared to Figure 6.9 and 6.11. With this rather minor offset representative of a 0.5 ppb increase per year (presently reported from background sites) during a decade a dramatic increase in the area of exceedance of the threshold for crops and semi-natural vegetation is seen. Compared to the observed data (Figure 6.9) an offset of 5 ppb lifts nearly all of UK, Ireland, the Nordic and Baltic countries above the threshold value of 3000 ppb h for crops and semi-natural vegetation.

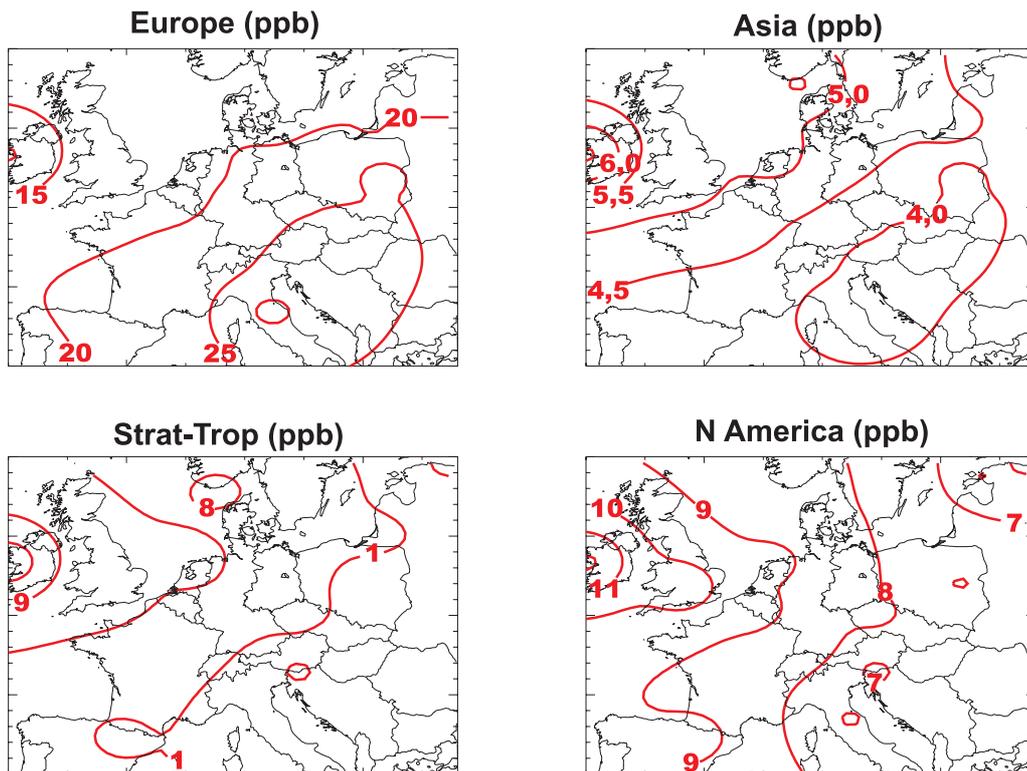


Figure 6.25 Spatial patterns of the annual average contributions in ppb to surface ozone from internal production within Europe, intercontinental transport from Asia and North America and from stratosphere-troposphere exchange calculated with a global Lagrangian transport model (Derwent et al. 2004).

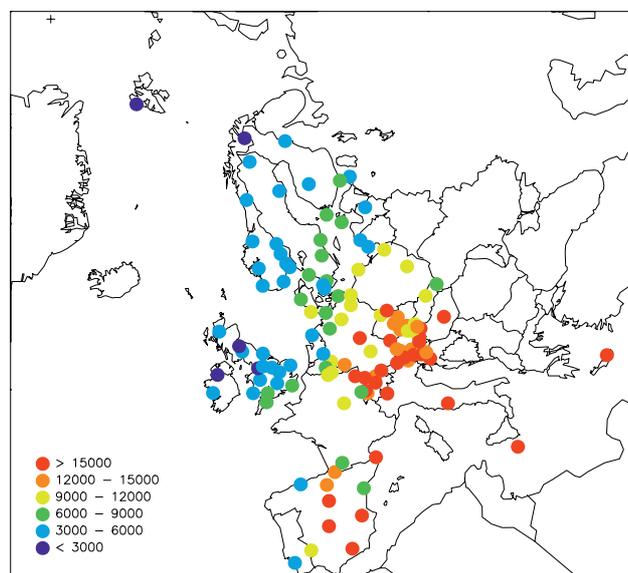


Figure 6.26 Same as figure 6.9 but for AOT35 (i.e. 3-months average AOT35 1997-2001), corresponding to AOT40 with a background increase of 5 ppb. Threshold value: 3000 ppb h (dark blue is below the threshold).

The influence on the exceedance of the threshold value for forests is smaller, but marked increases are seen in central Europe although the area of exceedances is not increased as much as for crops and semi-natural vegetation.

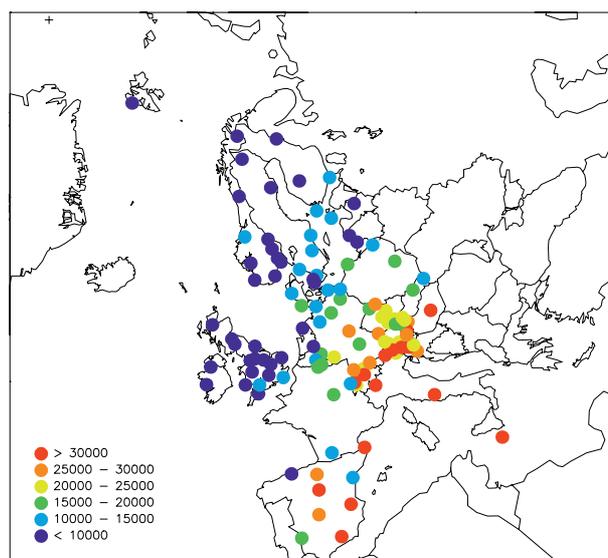


Figure 6.27 Same as Figure 6.11 but for AOT35 (i.e. 6-months average AOT35 1997-2001), corresponding to AOT40 with a background increase of 5 ppb. Threshold value: 10,000 ppb h (dark blue is below the threshold).

6.7 Conclusions and implications

Even though the emissions of ozone precursors have decreased over large parts of Europe since the late 1980s, ozone threshold values are frequently exceeded particularly in South and Central Europe. A reduction in peak ozone values during the 1990s is seen in several regions in Europe, while there is no coherent trend in AOT40. Ozone trends are strongly influenced by inter-annual variations in weather conditions and trends in the hemispheric background concentrations. Only in certain areas of Europe are the monitoring time series long enough to detect long-term trends with sufficient significance.

Several mechanisms will contribute to the future development of the world wide surface ozone concentration distribution. One mechanism is the effect of regional and global changes in anthropogenic precursor emissions. Another is the contribution due to changes in the cultivation and use of terrestrial ecosystems. A third mechanism is the contribution to ozone variability from climate variability and the underlying “global warming”.

Stations in the north and west of Europe report increasing hemispheric background ozone concentrations with increasing trends of 0.3-0.5 ppb yr⁻¹. Background ozone levels are presently close to what is considered harmful for vegetation and with respect to health. Even small percentage changes in the background concentrations will affect the exceedance of critical levels. In order to meet the standards further reductions in ozone precursors than already planned may be needed. Even a small future increase in background ozone is going to make it increasingly difficult to meet the standards.

Gradually, the effect from increasing global emissions of ozone precursors (in developing countries) and the effects of climate change could jeopardize the effect of reduced emissions of ozone precursors in Europe. This implies that a regional (European) air quality strategy is not longer sufficient and calls for a hemispheric or global perspective in the abatement of surface ozone in Europe.

Acknowledgement

Dr Mhairi Coyle at CEH, Edinburgh is acknowledged for the Figure on mapped AOT40 in the UK. Dr Peter Simmonds, University of Bristol, is acknowledged for the Figure on ozone trends at Mace Head. Finally, our thanks are due to all those responsible for drafting the national contributions in part 2 from which this chapter has been compiled.

References

- Ashmore, M.R. and R.B. Wilson, (eds), 1994. *Critical Levels for Air Pollutants in Europe*. Department of Environment, London, UK.
- Beilke, S. and Wallasch, M. 2000. The Ozone concentration in Germany since 1990 and prognoses for the future development. (In German) *Immissionsschutz* 5, 149-155.
- Berntsen, T.K., I.S.A. Isaksen, G. Myhre, J.S. Fuglestad, F. Stordal, T. Alsvik, Larsen, R.S. Freckleton and K.P. Shine, 1997. Effects of anthropogenic emissions on tropospheric ozone and its radiative forcing. *J. Geophys. Res.* 102, 28,101-28,126.
- Bruckmann, P. and M. Wichmann-Fiebig, 1997. Conclusions for summer smog regulations drawn from field studies and model calculations in Germany.
- Coyle, M., Fowler, D. and Ashmore, M. 2003. New Directions: Implications of increasing tropospheric background ozone concentrations for vegetation. *Atmos. Environ.* 37, 153-154.
- Cros, B., P. Durand, E. Frejafon, C. Kottmeier, P.E. Perros, V.-H. Peuch, J.L. Ponche, D. Robin, F. Said, G. Toupance, and H. Wortham, 2004. The ESCOMPTE program: an overview. *Atmos. Res.* 69, 241–279.
- Derwent, R.G., Jenkin, M.E., Saunders, S.M., Pilling, M.J., Simmonds, P.G., Passant, N.R., Dollard, G.J., Dumitrean, P., Kent, A. 2003. Photochemical ozone formation in north west Europe and its control, *Atmos. Environ.* 37, 1983-1991.
- Derwent, R.G., Stevenson, D.S., Collins, W.J., and Johnson, C.E., 2004. Intercontinental transport and the origins of the ozone observed at surface sites in Europe. *Atmos. Environ.* 38, 1891-1901.
- Dommen, J., A.S.H. Prévôt, B. Neining, and Bäumle, 2002. Characterisation of the photooxidant formation in the metropolitan areas of Milan from aircraft measurements. *J. Geophys. Res.* 102 (D22), art.-nr.: 8197, 10.1029/2000JD000283.
- EEA, 2002. Environmental signals 2002. Benchmarking the millennium, Environmental assessment report No. 9, *European Environment Agency*, Kongens Nytorv 6, DK-1050 Copenhagen K.
- EEA, 2003. Europe's environment: the third assessment, Environmental assessment report No. 10, *European Environment Agency*, Kongens Nytorv 6, DK-1050 Copenhagen K.
- Emberson L.D., Ashmore M.R., Cambridge H.M., Simpson D. and Tuovinen J.P., 2000, Modelling stomatal ozone flux across Europe, *Env. Poll.* 109, 403-413.
- European Environment Agency. 2002. Air pollution by ozone in Europe in summer 2002. EEA Topic Report No. 6/2002, Luxembourg: Office for Official Publications of the European Communities.

- Fiala, J., Cernikovskiy, L., de Leeuw, F. and Kurfuerst, P. 2003. Air pollution by ozone in Europe in summer 2003. Overview of exceedances of EC ozone threshold values during the summer season April-August 2003 and comparisons with previous years. *European Environment Agency Topic Report 3/2003*, EEA, Kongens Nytorv 6, DK-1050 Copenhagen K.
- Fuhrer, J. and B. Achermann, (eds.), 1994. *UN-ECE Workshop on critical levels for ozone, 1-4 November 1993*. Swiss Federal Research Station for Agricultural Chemistry.
- Grennfelt, P., Hoem, K., Saltbones, J. and Schjoldager, J., 1989. Oxidant data collection in OECD-Europe 1985-87 (OXIDATE). Report on ozone, nitrogen dioxide and peroxyacetyl nitrate. October 1986-March 1987, April-September 1987 and October-December 1987. Lillestrøm (NILU OR 63/89). Norwegian Institute for Air Research P.O. Box 100, NO-2027 Kjeller, Norway.
- Guenther, A., C.N. Hewitt, D. Erickson, R. Fall, C. Geron, T. Graedel, P. Harley, L. Klinger, M. Lerdau, W.A. McKay, T. Pierce, R. Scholes, R. Steinbrecher, R. Tallamraju, J. Taylor, and P. Zimmerman. A global model of natural volatile organic compound emissions. *J. Geophys. Res.* 100 (D5): 8873–8892, 1995.
- Guenther, A.B., C. Geron, T. Pierce, B. Lamb, P. Harley, and R. Fall, 2003. Natural emissions of non-methane volatile organic compounds, carbon monoxide, and oxides of nitrogen from North America. *Atmosph. Environ.* 34, 2205–2230.
- Hjellbrekke, A. and S. Solberg, 2004. Ozone measurements 2002. EMEP/CCC-Report 2/2004. Norwegian Institute for Air Research P.O. Box 100, NO-2027 Kjeller, Norway.
- Kallos, G., P. Kassomenos, and R. Pielke, 1993. Synoptic and mesoscale weather conditions during air pollution episodes in Athens, Greece. *Boundary Layer Meteorology*, 62, 163–184.
- Kärenlampi, L. and L. Skärby, (eds), 1996. *Critical Levels for Ozone in Europe: Testing and Finalising the Concepts*. University of Kuopio, Department of Ecology and Environmental Science. 15-17 April 1996, Kuopio, Finland.
- Karlsdottir S., I.S.A. Isaksen, G. Myhre and T.K. Berntsen, 2000. Trend analysis of O₃ and CO in the period 1980-1996; A 3-D model study, *J. Geophys. Res.* 105, 28.907-28.934.
- Karlsson, P.E., G. Selldén, and H. Pleijel, (eds.), 2003. *Establishing Ozone Critical Levels II, UNECE Workshop Report*. Swedish Environmental Research Institute. IVL Report B1523.
- Lelieveld, J. and F. Dentener, 2000. What controls tropospheric ozone? *J. Geophys. Res.* 105, 3531-3551.
- Logan, J.A., A.J. Megretskaia, A.J. Miller, G.C. Tiao, D. Choi, L. Zhang, R.S. Stolarski G.J. Labow, S.M. Hollandsworth, G.E. Bodeker, H. Claude, D. DeMuer, J.B. Kerr, D.W. Tarasik, S.J. Oltmans, B. Johnson, F. Schmidlin, J. Staehelin, P. Viatte, O. Uchino, 1999. Trends in the vertical distribution of ozone: An analysis of ozonesonde data, *J. Geophys. Res.*, 104, 26373-26399.
- Louka, P., G. Finzi, M. Volta, and I. Colbeck, 2003. Photochemical smog in South European cities. In N. Moussiopoulos, editor, *SATURN. Studying Atmospheric Pollution in Urban Areas*, pages 185–222. EUROTRAC, Garmisch-Partenkirchen.

- Marenco, A., H. Gouget, P. Nedelec, J.-P. Pages and F. Karcher, 1994. Evidence of long-term increase in tropospheric ozone from Pic du Midi data series: Consequences: Positive radiative radiative forcing. *J. Geophys. Res.* 99, 16617-16632.
- Monks P.S.M., 2000. A review of the observations and origins of the spring ozone maximum, *Atmos. Environ.* 34, 3545-3561.
- Monks P.S., Rickard, A.R., Dentener, F., Jonson, J.E., Lindskog, A., Roemer, M., Schuepbach, E., Friedli, T.K. and Solberg, S. 2003. *TROTREP Synthesis and Integration Report*, EU contract EVK2-CT-1999-00043. URL: <http://atmos.chem.le.ac.uk/trotrep/>
- Moussiopoulos, N., Sahm, P., Turlou, P.M., Friedrich, R., Simpson, D. and Lutz, M., 2000. Assessing ozone abatement strategies in terms of their effectiveness on the regional and urban scales, *Atmos. Environ.* 34, 4691-4699.
- Moussiopoulos, N., P. Sahm, R. Kunz, T. Vögele, Ch. Scheider, and Ch. Kessler, 1997. High resolution simulations of the wind flow and the ozone formation during the Heilbronn ozone experiment. *Atmospheric Environment*, 34, 4691–4699.
- Moussiopoulos, N., P. Sahm, P.M. Turlou, R. Friedrich, B. Wickert, S. Reis, and D. Simpson, 1998. Technical expertise in the context of the Commission's Communication on an Ozone Strategy. Final report to European Commission DGXI. Contract B4-3040/98/000052/MAR/D3.
- Naja, M., Akimoto, H. and Staehelin, J. 2003. Ozone in background and photochemically aged air over central Europe: Analysis of long-term ozonesonde data from Hohenpeißenberg and Payerne. *J. Geophys. Res.* 108, 4063, doi: 10.1029/2002JD002477.
- NARSTO, 2000. An assessment of tropospheric ozone pollution: A North American perspective. URL: www.cgenv.com/Narsto
- Neftel and Spirig, (eds), 2003. LOOP. Limitation of Oxidant Production. Final report, EUROTRAC.
- Neftel, A., C. Spirig, A.S.H. Prévôt, M. Furger, J. Stutz, B. Vogel, and J. Hjorth, 2002. Sensitivity of photooxidant production in the Milan basin: An overview of results from a EUROTRAC-2 Limitation of Oxidant Production field experiment. *J. Geophys. Res.*, 107:8188 doi:10.1029/2001JD001263.
- NEGTA (National Expert Group on Transboundary Air Pollution), 2001. *Transboundary air pollution: acidification, eutrophication and ground-level ozone in the UK*. Edinburgh, National Expert Group on Transboundary Air Pollution. URL: <http://www.nbu.ac.uk/negtap/>
- Oltmans, S.J., A.S. Lefohn, H.E. Scheel, J.M. Harris, H. Levy, I.E Galbally, E.-G. Brunke, C.P. Meyer, J.A. Lathrop, B.J. Johnson, D.S. Shadwick, E. Cuevas, F.J. Schmidlin, D.W. Tarasick, H. Claude, J.B. Kerr, O. Uchino, and V. Mohnen, 1998. Trends in ozone in the troposphere. *Geophys. Res. Lett.*, 25:139–142.
- Prévôt, A.S.H, J. Staehelin, G.L. Kok, R.D. Schillawski, B. Neininger, T. Staffelbach, A. Neftel, H. Wernli, and J. Dommen, 1997. The Milan photo-oxidant plume. *J. Geophys. Res.*, 102:22375–22388.
- Roemer, M., 2001. Trends of ozone and precursors in Europe. Status report TOR-2, TNO report R 2001/244.

- Simmonds, P.G., Derwent, R.G., Manning, A.L., Spain, G. 2004. Significant growth in surface ozone at Mace Head, Ireland, 1987-2003. *Atmos. Environ.* 38, 4769-4778.
- D. Simpson, 1995. Biogenic emissions in Europe 2: Implications for ozone control strategies. *J. Geophys. Res.*, 100(D11):22891–22906.
- D. Simpson, A. Guenther, C.N. Hewitt, and R. Steinbrecher, 1995. Biogenic emissions in Europe 1. Estimates and uncertainties. *J. Geophys. Res.*, 100(D11):22875–22890.
- Simpson, D., K. Olendrzynski, A. Semb, E. Støren and S. Unger, 1997. Photochemical oxidant modelling in Europe: multi-annual modelling and source-receptor relationships. EMEP/MSC-W Report 3/97. The Norwegian Meteorological Institute, O.O. Box 43-Blindern, NO-0313 Oslo, Norway.
- D. Simpson, W. Winiwarter, G. Börjesson, S. Cinderby, A. Ferreira, A. Guenther, C. N. Hewitt, R. Janson, M. A. K. Khalil, S. Owen, T. E. Pierce, H. Puxbaum, M. Shearer, U. Skiba, R. Steinbrecher, L. Tarrasón, and M. G. Öquist, 1999. Inventorying emissions from nature in Europe. *J. Geophys. Res.*, 104(D7):8113–8152.
- Solberg S., R. Bergström, J. Langner, T. Laurila and A. Lindskog, 2004. Changes in Nordic surface ozone episodes due to European emission reductions in the 1990s, *Atmos. Environ.* (in press).
- H. E. Stewart, C. N. Hewitt, R. G. H. Bunce, R. Steinbrecher, G. Smiatek, and T. Schoenemeyer, 2003. A highly spatially and temporally resolved inventory for biogenic isoprene and monoterpene emissions: Model description and application to Great Britain. *J. Geophys. Res.*, 108(D20, 4644): doi:10.1029/2002JD002694.
- Vautard, R., L. Menut, M. Beekmann, P. Chazette, P. H. Flamant, D. Gombert, D. Guédalia, D. Kley, M.-P. Lefebvre, D. Martin, G. Mégie, P. Perros, and G. Toupance, 2003. A synthesis of the Air Pollution Over the Paris Region (ESQUIF) field campaign. *J. Geophys. Res.* 108(D17).
- B. Vogel, F. Fiedler, and H. Vogel, 1995. Influence of topography and biogenic volatile organic compounds emission in the state of Baden-Württemberg on ozone concentrations during episodes of high air temperatures. *J. Geophys. Res.*, 100:22907–22928.
- Volz A. and Kley, D. 1988. Evaluation of the Montsouris series of ozone measurements made in the 19th-century. *Nature* 332, 240-242.
- Volz-Thomas, A., H. Geiss, A. Hofzumahaus, and K.-H. Becker, 2003. Introduction to Special Section: Photochemistry Experiment in BERLIOZ. *J. Geophys. Res.*, 108 (D4).
- WMO, Scientific assessment of ozone depletion, 2002. World Meteorological Organization. Global ozone research and monitoring project, report No. 47, 2002.