

WHAT CONSTITUTES THE OZONE (*) BACKGROUND OVER EUROPE?

(*) we mean ozone between 0 and 10-12 km altitude, hence tropospheric ozone

If all continental European man-made emissions of gases leading to the production of ozone (O_3) were switched off, there would still be ozone over Europe. That ozone is referred to as *background ozone*. It is derived from natural sources of ozone precursors in Europe, intrusions of ozone from the stratosphere, and from long-range inter-continental transport of ozone and its precursors formed from natural and anthropogenic sources in various regions of the world. European anthropogenic emissions generally lead to an increase of the ozone levels compared to the background levels. However, close to sources of nitrogen oxide (NO), ozone is reduced, largely due to reaction of NO with O_3 .

It is important to notice that ozone is the third most important anthropogenic greenhouse gas after carbon dioxide (CO_2) and methane (CH_4).

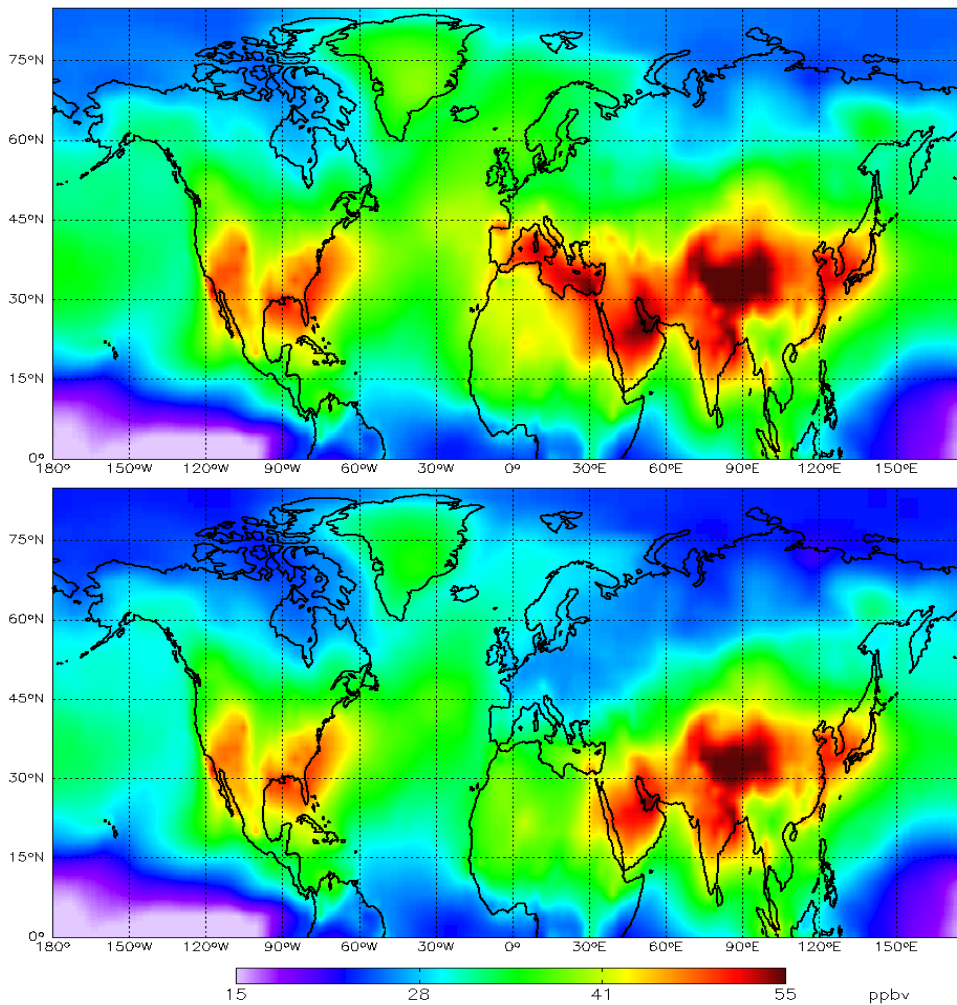


Figure 1: Annual mean ozone at the Earth's surface, for 1997, simulated by the GEOS-CHEM model. The top panel shows ozone from all sources; in the lower panel anthropogenic emissions on the European continent have been switched off, to reveal background ozone levels over Europe.

(source: Isabelle Bey, EPFL Lausanne)

1 BACKGROUND OZONE OVER EUROPE

1.1. How much and for what reasons have background ozone levels in Europe changed during the last decades?

1. Background ozone has increased by up to 5 ppbv/decade over the last 20 to 30 years, according to measurements at sea level and on mountain tops that are less influenced by European sources. This has been attributed to the worldwide increase in anthropogenic activities, including growth in ozone precursor emissions from industry, road, air and ship transport, households and agriculture. In addition to an upward trend, background ozone also shows considerable year-to-year variability, partly due to varying precursor emissions, such as from forest fires, but also due to meteorological variability, which can alter the efficiency of long-range transport from particular sources.

Supporting material

Long term growth

Ozone hemispheric background includes ozone derived from stratospheric input, tropospheric formation from precursors (NO_x and VOC) from biogenic sources, biomass burning emissions, methane oxidation and anthropogenic sources from various regions of the world. Ozone produced by local European sources builds upon this background. European ozone background levels (e.g. as measured at Mace Head, Ireland, Izana, Tenerife, and Zugspitze, Germany) have increased by up to 5 ppb/decade over the last 20 to 30 years (Oltmans, 2006).

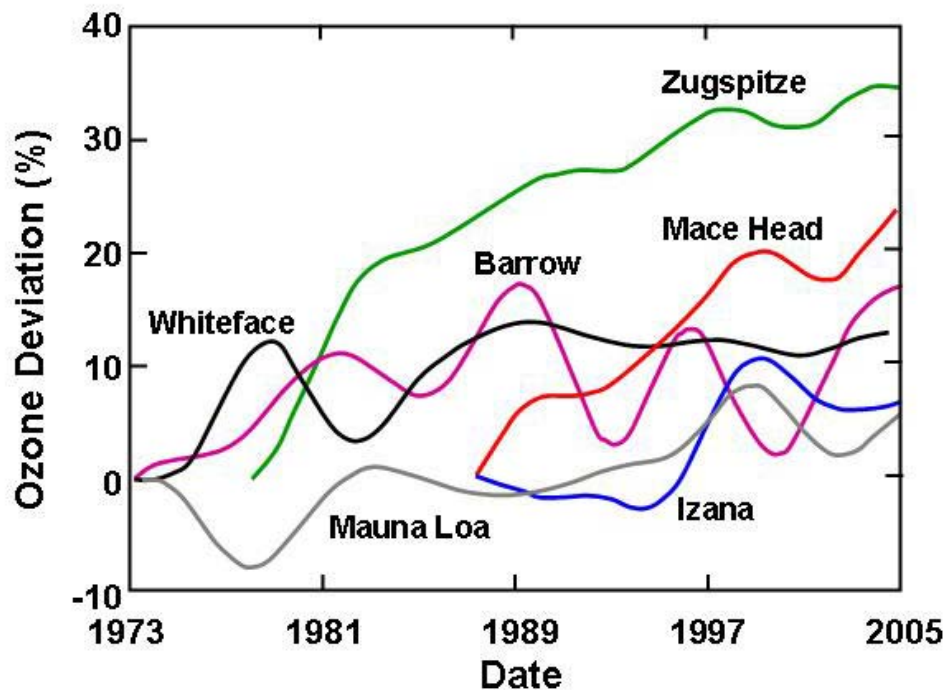


Figure 1.1: Recent ozone trends from a range of northern hemisphere ground-based stations. Analysis of historical ozone records has indicated that tropospheric ozone levels in both hemispheres have increased by a factor of 3-4 over the last century (Volz and Kley, 1988, Anfossi *et al.*, 1991, Sandroni *et al.*, 1992). This has been attributed to the worldwide increase in

anthropogenic activities, including growth in ozone precursor emissions from industry, road, air, and ship transport, domestic sources, and agriculture.

Recent trends

In recent years, thanks to improvements in technology, and to emission controls, ozone precursor emissions in Europe have diminished, despite the continuing increase in traffic and industrial emissions. However, the ozone picture is not so simple due to the non-linear behaviour of ozone production related to the complexity of the atmospheric chemical processes involved (TROTREP, 2002, Li *et al.*, 2003).

Rural Ozone

In general, rural ozone declined during the last 15 years (TROTREP, 2002 and Derwent *et al.*, 2006), the detailed trend at a number of UK sites being shown in Figure 1.2. In Europe, the picture at the EMEP sites is more mixed, but when the nature of the site is taken into account the discrepancies can be explained. The increases found are at sites close to conurbations; the starting values were very low due to ozone depletion by excess NO. The more background sites, which are less affected by ozone depletion, show a decrease.

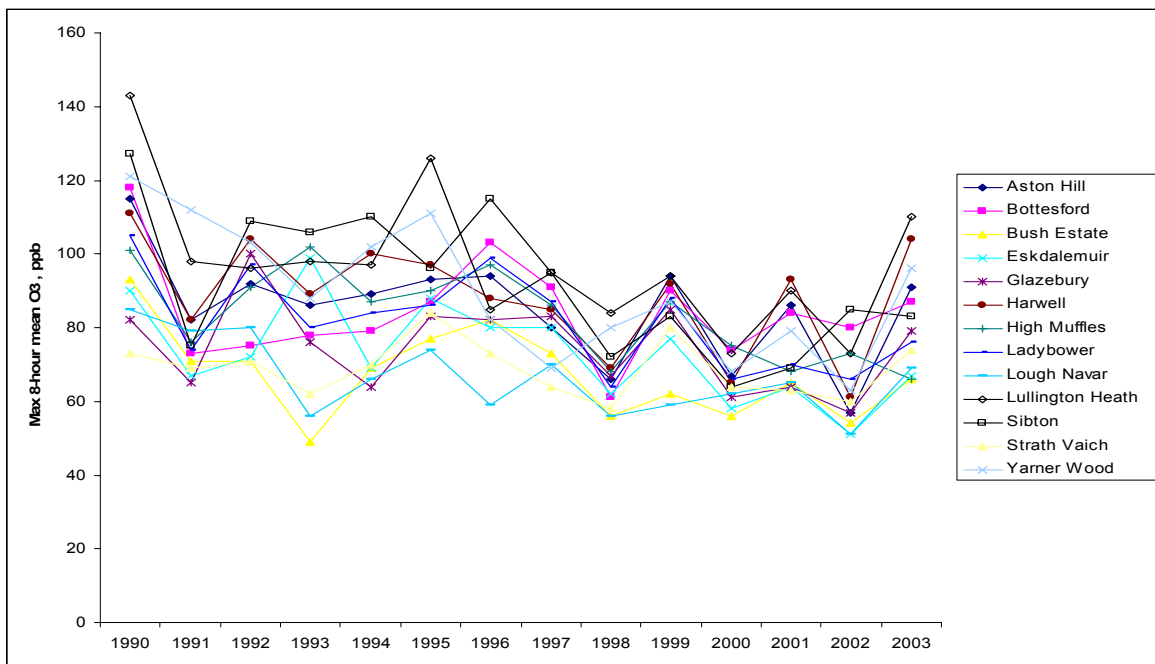


Figure 1.2. Time series of the maximum 8-hourly mean ozone concentrations monitored at a selection of long-running rural EMEP background sites in the United Kingdom between 1990 and 2003. (Source: Derwent, 2006)

Ozone at rural sites is affected by three factors (Figure 1.3):

- the decreasing intensity of the regional ozone pollution episodes, tending to reduce the ozone metric;
- the decreasing depletion of ozone by traffic NO_x emissions, which increases the metric;
- the growth in hemispheric or global baseline ozone.

Thus rural concentrations reflect a combination of background ozone and that produced by more local activities (probably up to the regional scale). When precursor emissions (NO_x , VOC) are diminished, there is a decrease in rural ozone, though not necessarily in proportion to the decrease in precursors.

Urban ozone

In cities and conurbations, ozone concentrations are generally lower than in the countryside, due the depletion of much of the ozone formed by reaction with NO , one of the precursors which occurs at high levels within the city (the depletion effect). Thus, a reduction in precursor emissions will initially bring about an *increase* in ozone. Only when precursor concentrations are drastically reduced can one expect ozone concentrations begin to diminish.

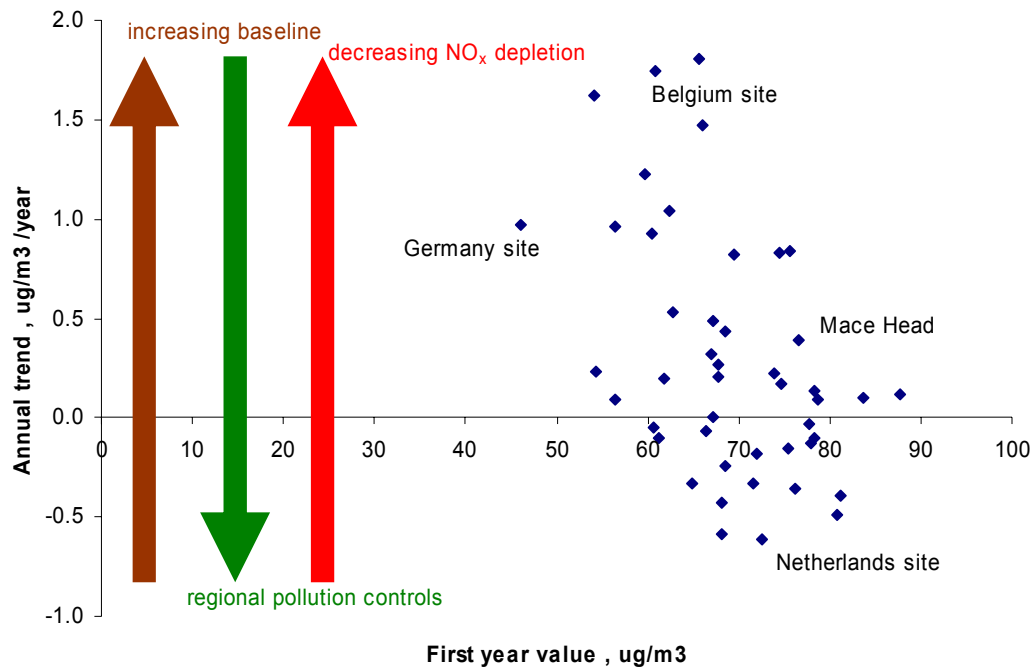


Fig. 1.3. A scatter plot of the trends in the annual average daily maximum 8-hour mean ozone concentrations observed at 46 EMEP rural sites over the period 1990-2002 plotted against the initial 1990 value of the ozone metric. (Derwent, 2006).

Ozone exposure

The effect on exposure of the population to ozone will be complex. Although one may initially be reducing the overall concentration field of ozone in rural areas by reducing precursor emissions, the increases within cities may actually increase the exposure to ozone of more of the population.

Imported ozone

Part of the rural background ozone can be attributed to ozone imported into Europe at higher levels in the troposphere from the North Atlantic. Trends at Mace Head (Derwent *et al.*, 2006), on the extreme west coast of Ireland, indicate that, under appropriate meteorological conditions, the ozone arriving in Europe from the West is increasing also at ground level.

Background ozone from the North Atlantic can be attributed in part to export from North America but is probably a reflection of the general situation at mid-latitudes around the northern hemisphere. The major producers of tropospheric ozone on the hemispheric scale are North America, Europe, China and Japan, and the amount from China is likely to increase as the economy grows. Curbing European emissions will certainly help slow the growth in background ozone, but global agreement is actually required.

1.2 Is there a latitude dependence in background ozone levels over Europe?

1. Yes. Models and observations suggest a strong latitudinal gradient in background ozone levels over Europe (see Fig. 1). Typically, surface annual averaged background ozone over the Mediterranean basin is about 30 to 35 ppbv while it ranges from 20 to 25 ppbv over Northern Europe. The latitudinal variation reflects gradients in ozone photochemistry, in transport patterns of ozone and some of its precursors into Europe, and also the higher removal by dry deposition on land than on sea (in this case the Mediterranean Sea).

1.3 Which changes can be anticipated for the coming 20 to 30 years? How certain are we about these changes?

1. Changes in surface background ozone over Europe will be controlled by emission changes throughout the northern hemisphere due to economic growth combined with air pollution and climate change policies. Changes in natural sources in Europe or changes in the input from the stratosphere will be less influential.

2. The following statements are based on the ensemble average of 26 global models which calculated ozone concentrations averaged over Europe for the years 2000 and 2030. When considering presently planned emission controls in the world, the models project an average ozone *increase* over Europe of 0.6 ppbv/decade. For a more optimistic scenario in which all possible technical control options are implemented, an ozone *reduction* in Europe of - 0.9 ppbv/decade is possible. However, under a more pessimistic high growth scenario of the Intergovernmental Panel on Climate Change, ozone *increases* by 1.3 ppbv/decade over Europe.

3. In specific areas that better represent background conditions, such as over the Atlantic Ocean off the coast of the European continent, the changes can be up to 1.3, -1 and 2 ppbv/decade for the three scenarios used above.

4. The model uncertainty associated with these results is about 0.7 ppbv/decade. Additional uncertainty arises when from climate change effects are included in the analysis.

Supporting material

Analyses using all the global models available in ACCENT (Stevenson *et al.* (2006), Dentener *et al.* (2006), suggest that by 2030 (following the 'CLE' scenario, where the current legislation has been implemented), the annual average mixing ratio of ozone in the OECD European countries will have increased by 1.8 ppbv, but with decreases of up to 3 ppbv in central/southern Europe. The uncertainties in the mixing ratios, found by comparing results from different models, are appreciable, being 1 to 2 ppbv.

See also Derwent *et al.* (2006) for an analysis of changes in transport of ozone to Europe from the Atlantic Ocean.

Uncertainties

Under the CLE scenario, the mean change across Europe is more like 2 ppbv per decade; but as mentioned above, some places experience decreases, so there are significant inter-regional differences. The uncertainties (inter-model differences) are of the order of 20-30%, but the European average uncertainties are smaller; uncertainties for individual grid squares are larger.

However, when other emission scenarios are considered, the uncertainties are large - much larger than the inter-model uncertainties so the main source of uncertainty in the future predictions is in the future emissions, rather than the models.

It is also clear that the trends are different in different seasons - winter O₃ will increase if we reduce emissions, whereas summer O₃ will decrease, and vice-versa.

1.4 Is the increase of 1.2 ppbv per decade in Europe, assumed in the analysis leading to the Strategy, reasonable?

1. Yes. Based on the model results presented in Question 1.3, trends for the period 2000 to 2030 ranging from - 0.9 ppbv/decade to + 1.3 ppbv/decade are forecast. On the other hand, observations of ozone over the last 2-3 decades indicate a trend of up to + 5 ppbv/decade. Given the uncertainties in calculated and measured trends, and the lack of firm knowledge concerning climate change effects, the assumption of a future + 1.2 ppbv/decade rate of increase is not unreasonable. However the consideration of an upper limit trend of + 5 ppbv/decade would be advisable in future analyses.

1.5 How much would such changes in background levels influence (long-term) health- and vegetation-relevant metrics of surface ozone?

1. We focus here on that part of the background ozone that is transported into Europe, most often from the west, and whose future trend will be controlled by changes in emissions throughout the northern hemisphere. This part of the European background ozone is referred to as “*hemispheric ozone*”.
2. The largest impact of hemispheric ozone on ozone levels over Europe is obviously expected during meteorological conditions when such transport into Europe occurs.
3. High (peak) ozone levels (e.g. >80 ppbv) over Europe are typically found during stagnant conditions during which transport into Europe is less important and emissions in Europe are the major contributor to the ozone formation.
4. Over the last decade, observations have shown that high (peak) ozone concentrations have significantly decreased because of the reduction in European emissions of ozone precursors.
5. Often used health- and vegetation-relevant metrics are SOMO35 and AOT40, which are integrals in time of surface ozone concentrations *greater than* 35 or 40 ppbv respectively.
6. The decrease in SOMO35 and AOT40 due to the decrease in high (peak) ozone levels will be off-set by the increase of background ozone. This will particularly be true in the Mediterranean area where the present background ozone values are already 30 - 35 ppbv.
7. In conclusion: the increase of hemispheric ozone is *not* expected to have an important effect on high (peak) ozone levels, but it will increase the long-term exposure metrics such as AOT40 and SOMO35.

Supporting material

The changes to be expected in Europe will differ for rural sites and for conurbations.

Vegetation exposure

For rural sites, the levels of exposure are determined by a combination of imported ozone and those from local ozone precursors. They are roughly constant at the present time. The reduction due to reduced precursor emissions will at least be balanced and probably increased by the increasing ozone imported into Europe from the hemispheric background.

The EMEP model suggests that the increase of imported ozone from the hemispheric background is likely to be larger in the inflow areas (mainly western/Atlantic) of Europe (Jonson *et al.*, 2006). However plots of the likely change in AOT40 levels show that in regions where ozone levels are small (Scandinavia), or are reduced by the depletion effect (London and North Western Europe) the changes in exposure are likely to be small. On the contrary, although the differences are small in Central and Southern Europe, levels are often above the threshold and AOT40 increases.

The background levels appear to be approaching the thresholds identified as harmful to plant growth, and so may have considerable consequences for agricultural productivity and the health of European ecosystems.

Population exposure

In cities, the reductions in precursor emissions are unlikely to move outside the titration regime (depletion zone, due to the reaction of ozone with NO) and so ozone levels are likely to increase. Increases in the background will add to these.

The effect on population exposure may be complex. Reductions in precursors may actually increase ozone levels in populated conurbations. So, although one may be reducing the overall regional concentration field of ozone, the increases within city may increase the total exposure of the population.

1.6 What are the important precursors for background ozone, and how will they change in the next 20 to 30 years?

1. The most important precursors of background ozone are methane (CH₄) and carbon monoxide (CO), which are long-lived gases, and nitrogen oxides (NO_x) and non-methane volatile organic compounds (NMVOC), relatively short-lived species. The mix of these short- and long-lived gases will be a critical factor in future trends.
2. Model calculations indicate that half of the increase of tropospheric ozone since pre-industrial times is due to the summed increase of CH₄, CO and NMVOC emissions (ca. 25 % for CH₄, and 25 % for CO + NMVOC). The other half is due to changes in the chemistry of the atmosphere induced by the increase in NO_x.

Background:

CH₄ concentrations influence the “background” CH₄-CO-NO_x-O₃ chemistry. E.g. Dentener *et al.*, 2005 estimate that an increase of CH₄ from the current 1750 ppbV to 2050 ppbV in 2030 may induce a hemispheric O₃ increase of 1-2 ppbV, confirming earlier studies by Fiore *et al.* and Prather *et al.*.

CO plays a role similar to that of CH₄. An assessment by Wang and Jacobs (1998), comes to the conclusion that the increase since preindustrial times in CH₄ alone would cause an increase in the ozone burden of about 20%, the increase of CO and NMVOC during this period would have approximately the same effect; only the remaining 60% are explained by the impact of increasing NO_x-emissions, although the relative increase in NO_x-emissions is much larger than those of CH₄, CO and NMVOC.

1.7 Are these findings robust enough to justify additional emission control requirements in Europe?

1. Yes. Reductions of NO_x and VOC emissions in Europe will further reduce high (peak) ozone levels over Europe and will also reduce Europe's contribution to hemispheric ozone. Clearly, an effective control of hemispheric ozone, and its contribution to background ozone, will require the reduction of the emissions of NO_x, NMVOC, CH₄ and CO also in other regions in the northern hemisphere.
2. Much attention has been paid to the effectiveness of methane emission reductions on future ozone and global warming. Methane emission reductions are relatively cheap. Because of the 8-9 years lifetime of CH₄ in the atmosphere, emission reductions would show effects on its global concentration and hence on ozone concentrations already within the period up till 2030, with benefits for both air quality and climate.
3. Less attention is paid to carbon monoxide (CO) emission reduction, to how it is linked to carbon dioxide emissions, and to its potential to influence background ozone levels and global warming. Emissions of CO in the industrial regions of the northern hemisphere are substantially underestimated and, when used in models of atmospheric transport and chemistry, do not account for the observed CO concentrations.

Supporting material

Concerning CO:

A comparison of present-day carbon monoxide emissions in 26 state-of-the-art atmospheric chemistry models with satellite observations from the MOPITT instrument and surface observations showed large underestimates on Northern Hemisphere extratropical CO in the simulations (Shindell et al., 2006).

1.8 Is there a link to be expected between climate change and the change in the emissions and concentrations of ozone precursors?

1. Yes. Clear links have been identified, and some quantitative modelling studies have been performed. These include effects related to changes in chemistry (via changes in temperature or water vapour), emissions (e.g., biogenic VOC, lightning and soil NO_x, wetland methane, and wildfires), and dynamics (e.g., convective mixing, precipitation, stratosphere-troposphere exchange, and boundary layer ventilation). It is difficult to assign a single universal trend in background ozone due to climate change, and it is as yet not clear if the overall impact of climate change will be an increase or decrease of background ozone.

Supporting material

See Isakson *et al.*, 2003, for the identification of the links and Stevenson *et al.*, 2005, for a quantitative modeling study.

A number of studies (AQEQ,2006, EEA, 2004, ACCENT, 2005) have looked at the effect of climate and emissions, the major changes will include a change in biogenic emissions with changing climate.

With respect to biogenic emission (see also Chapter 3), this will vary across Europe with respect to the individual biome and how this responds to change. For example, in northern Europe during the summer heatwave of 2003, there was a marked non-linear increase in biogenic compounds. This effect may not be seen for example in the Mediterranean where the plants are better adapted for water/stress.

Another further possible climate-related factor is the loss of ozone by dry deposition; this is dependant upon soil moisture. Under dry conditions the stomata openings are almost completely closed because the plants are conserving water, resulting in nearly zero uptake of ozone. If the climate (in the Mediterranean say) becomes drier, the loss of ozone by dry deposition will diminish, and increase ozone levels, possibly with deleterious health effects.

For a discussion of the role of biogenics see Fiore *et al.*, 2005.

1.9 Are there biases (i.e. systematic under- or overestimations) introduced in the analysis leading to the Strategy, due to the lack in scientific understanding discussed above?

1. The assumption of a 1.2 ppbv/decade increase in background ozone over Europe, made in the current analysis, is in the range of the recent projections/scenarios up to 2030, which range from – 1 to + 2 ppbv/decade. It is therefore not unreasonable and does not introduce a major bias in the prediction of future ozone levels. Nonetheless, it would be prudent to include an upper limit trend of + 5 ppbv/decade in future analyses, to reflect the observed trends of the past decades.

1.10 Which research within the next 3-4 years could improve future analyses?

1. There is room for multi-model ensemble calculations of hemispheric and global ozone, dedicated to the issue of what constitutes and influences the ozone background over Europe (and other world regions). It is possible to systematically validate models with monitoring data, in particular with remote sensing data that are increasingly becoming available.

2. It is possible and desirable to better link global socio/economic scenario modeling with global emissions and air pollution modeling. Future trends in hemispheric ozone depend primarily on future economic development and the implementation of air pollution, climate and other policies throughout the world.

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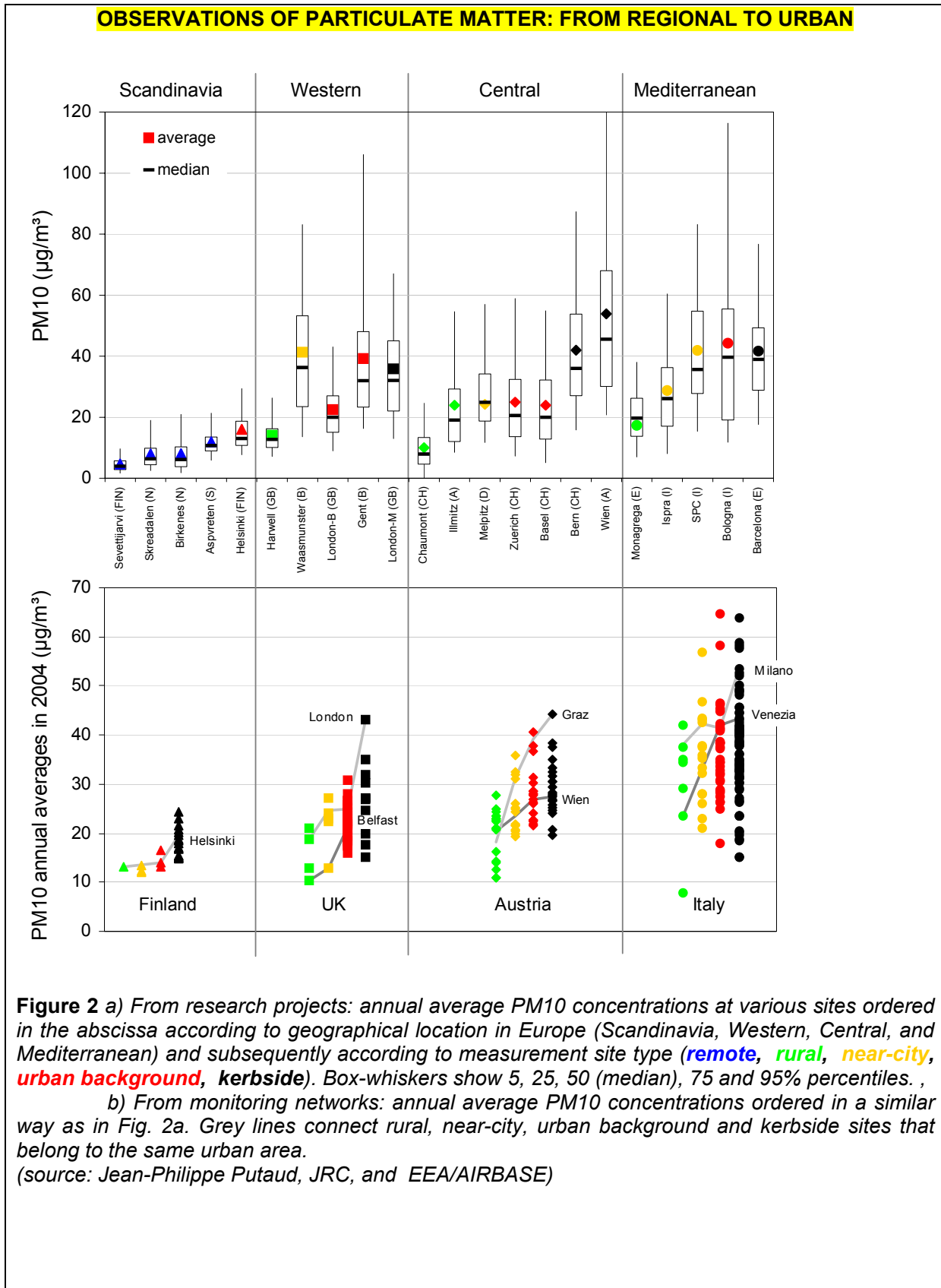
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2 LINKING REGIONAL AND URBAN SCALES

2.1 What is the observed change of air pollution levels between rural and urban areas?

1. The observations presented in Fig. 2 show that yearly averaged PM10 concentrations generally increase when moving from rural areas to open areas (i.e out of street canyons) within a city, with increments ranging from a few $\mu\text{g m}^{-3}$ to nearly $20 \mu\text{g m}^{-3}$. These *urban increments* appear to be relatively low in highly polluted areas such as Belgium/Holland and the Po Valley. This seems to indicate that in these areas emissions in urban centres largely influence the regional background.
2. When moving from open areas within cities to hotspots (e.g. at kerbsides or in street canyons) yearly averaged PM10 concentrations increase once again, with increments of 5 to $20 \mu\text{g m}^{-3}$. There seems to be no obvious relationship between these *street increments* and the level of regional or urban background PM10 pollution.
3. The few data available for yearly averaged PM2.5 concentrations show smaller absolute increments. The data further show that the relative contribution of PM2.5 to PM10 *decreases* when moving towards urban hotspots.
4. The observed decrease of surface O_3 within urban areas is largely (but not solely) explained by the reaction of O_3 with NO emitted from traffic ($\text{O}_3 + \text{NO} \rightarrow \text{NO}_2 + \text{O}_2$). Consistently, the gradients in $\text{O}_x = \text{NO}_2 + \text{O}_3$ are much smaller than of either O_3 or NO_2 .

Supporting material

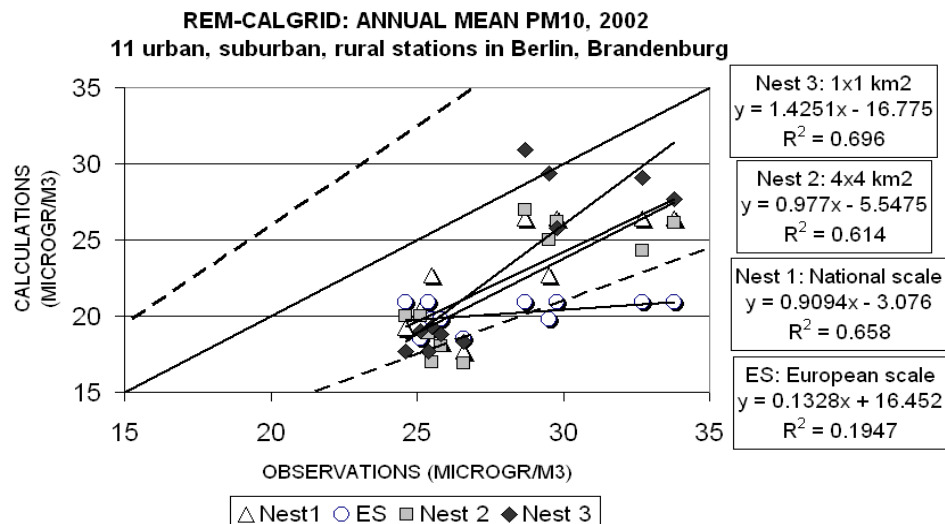
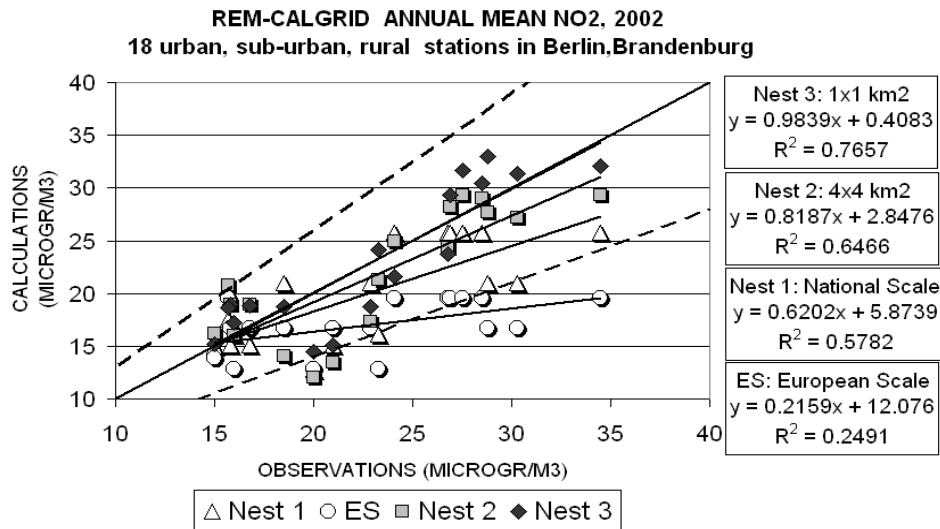


Figure 2.1: Scatter diagram of observed and calculated NO₂ and PM₁₀ annual means in the greater Berlin area at four scales, including regression lines and correlation coefficients. Dashed lines indicate the range of +/- 50% of the observations. (Based on “ Analyzing the response of a chemical transport model to emissions reductions utilizing various grid resolutions *Rainer Stern et al., 2006.*)

The figures clearly show that increasing the grid resolution in the 3-D Eulerian grid model REMCALGRID-RCG, from 0.5 x 0.25 latlong, about 25 x 25 km² on a European scale, down to 4 x 4 km², and further down to 1 x 1 km² leads to a better model performance both for PM₁₀ and NO₂. These results indicate that, provided that the meteorological data on fine scales are available as well as the emission data, fine scale modelling is needed to obtain a detailed and correct picture of PM₁₀ and NO₂ concentration levels in urban areas.

2.2 How well can we model the observed change in air pollutant levels between rural and urban areas?

1. If we talk about the *relative* changes, the answer is: rather well if the model has the right horizontal resolution. Models of transport and chemistry of air pollutants over Europe, used in policy development, typically use a horizontal grid-resolution of 50x50 km². Some of these models can zoom down to a resolution of 1x1 km². When reducing the grid from 50x50 km² to 1x1 km² over a specific urban area, such models calculate higher concentrations of PM₁₀ more in agreement with the observations in that urban area.
2. In urban areas the calculated PM₁₀ concentrations still increase substantially when going from 5x5 km² to 1x1 km² *provided that* urban specific meteorological fields are used, and not simply interpolated fields from the larger grid.
3. In order to understand pollutant fields at the hot-spot scale, i.e. below 1x1 km², different modeling approaches must be used. They do exist, but are not further discussed in this report.
4. The confidence in modeling *absolute* concentrations of O₃ is high, except for low ozone conditions, e.g during nights and during winter.
5. The confidence in modeling *absolute* concentrations of NO₂ and especially PM is limited. Models generally have an incomplete description of PM chemistry and dynamics. Natural sources (see Question 3), resuspension of dust, abrasion products of vehicles and secondary organic aerosol formation (see Question 4) are usually not considered. This leads to a general underestimation of PM levels both in rural and urban environments, but most likely for different reasons.

2.3 What is the current understanding of apportioning air pollution in urban areas to sources inside and outside these areas?

1. There is a solid qualitative understanding, based on observations and model calculations, that the concentrations of urban O₃ and PM are indeed determined by sources inside *and* outside the urban area (see Fig. 3 for some definitions).
2. PM₁₀ sampled at a kerbside consists of mineral particles, primary organic particles and secondary inorganic particles that can qualitatively be attributed to respectively local resuspension of road dust, combustion throughout the urban area, and sources like traffic, power plants and agriculture tens to hundreds of kilometers away from the sampling point.
3. Secondary aerosols (*see Figure 5 for a definition of primary and secondary aerosols*) such as sulfates, nitrates and secondary organic aerosols accumulate in the PM_{2.5} fraction, which is more subject to long range transport. Hence secondary aerosols tend to dominate the regional PM_{2.5} background which invades urban areas. There is however no observational evidence that secondary PM_{2.5} produced from local urban sources adds in a significant way to the PM_{2.5} mass concentration in that very same urban area.

3. The observed wide ranges in urban increments (see Question 2.1) show that the share between inside and outside sources to urban particulate matter differs greatly between cities.

2.4 What is the confidence in the current methods for modelling the contribution of sources inside urban areas in a Europe-wide assessment?

1. Models of transport and chemistry of air pollutants over Europe that zoom down to a resolution of $1 \times 1 \text{ km}^2$ over a city *in principle* allow for source apportionment of PM₁₀, PM_{2.5}, NO₂ and O₃, not only with respect to sectors, but also with respect to locations in- and outside the city. For example, such analyses have been especially useful for showing the major impact of local heavy duty traffic to urban PM.

2. *In practice*, such a source apportionment is hampered by poor regional and urban emission inventories, and in the case of PM also by the inadequate measuring and modeling of PM (see Question 2.2).

2.5 Are there biases introduced in the analysis leading to the Strategy due to the lack in scientific understanding?

1. The current analysis is based on a model with a $50 \times 50 \text{ km}^2$ grid resolution. As such, PM concentrations calculated for a grid in which there is a city, will be lower than what is expected within that city (unless the city covers the whole $50 \times 50 \text{ km}^2$ grid).

2. To overcome this problem, the current analysis adds an urban increment (see Fig. 3) to the $50 \times 50 \text{ km}^2$ grid concentrations, which is derived from an off-line analysis with $5 \times 5 \text{ km}^2$ grid urban models, according to the so called City-Delta approach.

3. This approach of calculating urban increments is only applied to primary PM_{2.5}, as there is no observational evidence of a significant production of secondary PM_{2.5} mass from local sources. The approach relies on $5 \times 5 \text{ km}^2$ grid models, which are believed to represent mean population exposure to PM. However, such models do not capture the true complexity of the urban background and local/hotspot atmosphere occurring at the finer scale (see Question 2.1), which might explain why the modeled concentrations of PM_{2.5} within the current analysis are lower than the observed data, in the few cases where such data are available.

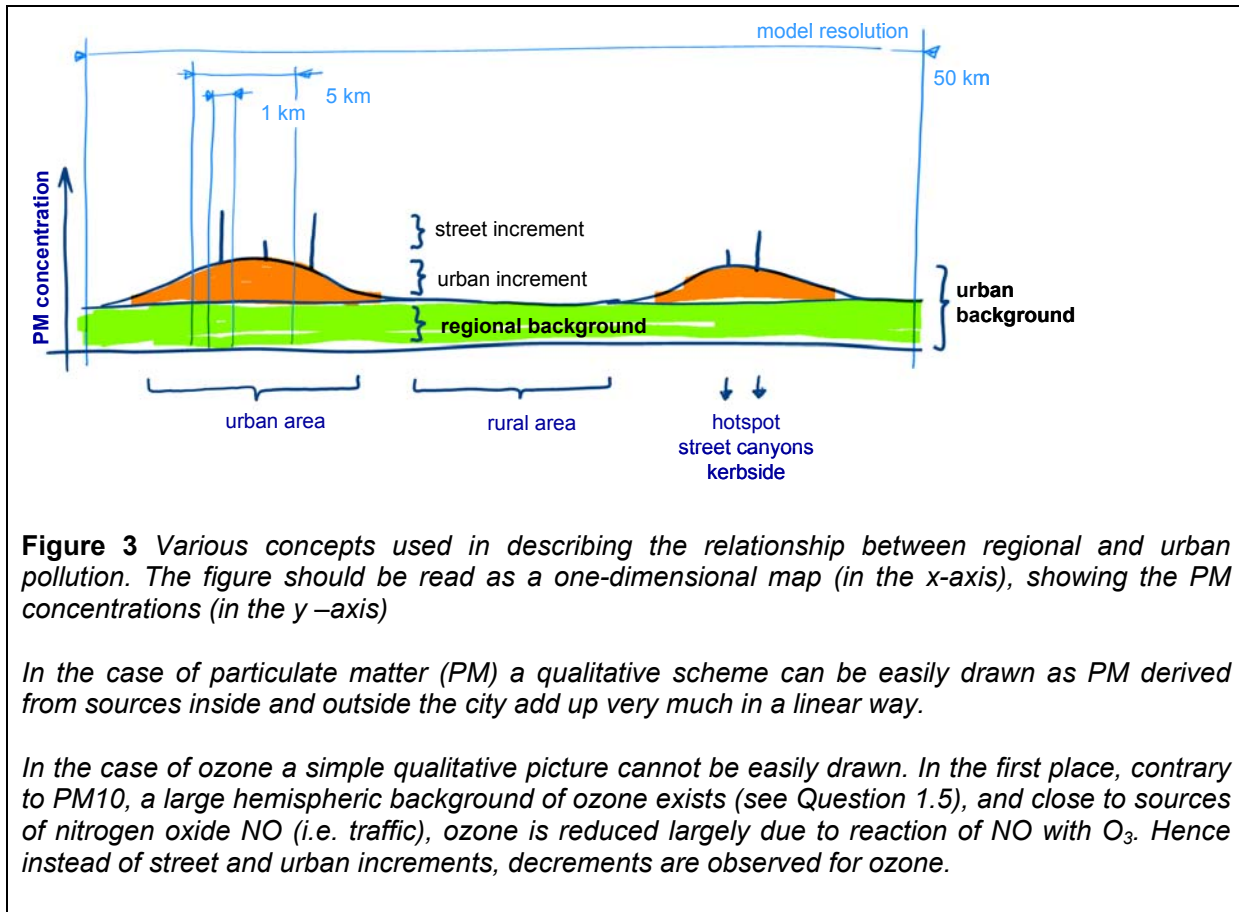
2.6 Which research within the next 3-4 years could improve future analyses?

1. Further analysis and possible improvement of the City Delta approach for PM_{2.5} must be performed. Further research into a City-Delta type approach for ozone is required.

2. The observations of PM, NO₂ and ozone must continuously be improved, documenting in a consistent way the transition from rural to urban environments. An analysis of the representativeness of observations, including meteorological observations within the urban environment, can be performed.

3. There is room for further model intercomparison studies and multi-model ensemble calculations to determine model uncertainties.

4. The reduction of uncertainties in the assessment of concentration fields of air pollutants can be attempted by assimilation of observations in model calculations.



References

Rainer Stern *et al.*, Analyzing the response of a chemical transport model to emissions reductions utilizing various grid resolutions, Proc. 2 th ITM on Air Pollution Modelling and its Application, Leipzig, Germany, May 2006

ON THE MEANING OF 'ANTHROPOGENIC' AND 'NATURAL' IN THIS REPORT

The major biogeochemical cycles on Earth, those of carbon, sulfur and nitrogen, have been extensively influenced by human activity. Hence, there is a contribution from human activity to most of the chemical species involved in the issues considered here, and in the processes creating them.

For the purposes of this report, which is focused on policy development to improve air quality in Europe through to 2020, *anthropogenic emissions* refers to those emissions that are provoked by man himself and that are amenable to practical and direct control. *Natural emissions* are those directly caused by natural processes (e.g. lightning, wind, biological processes such as plant respiration, etc.) which are not amenable to control. Natural emissions caused by biological processes are also called *biogenic emissions*.

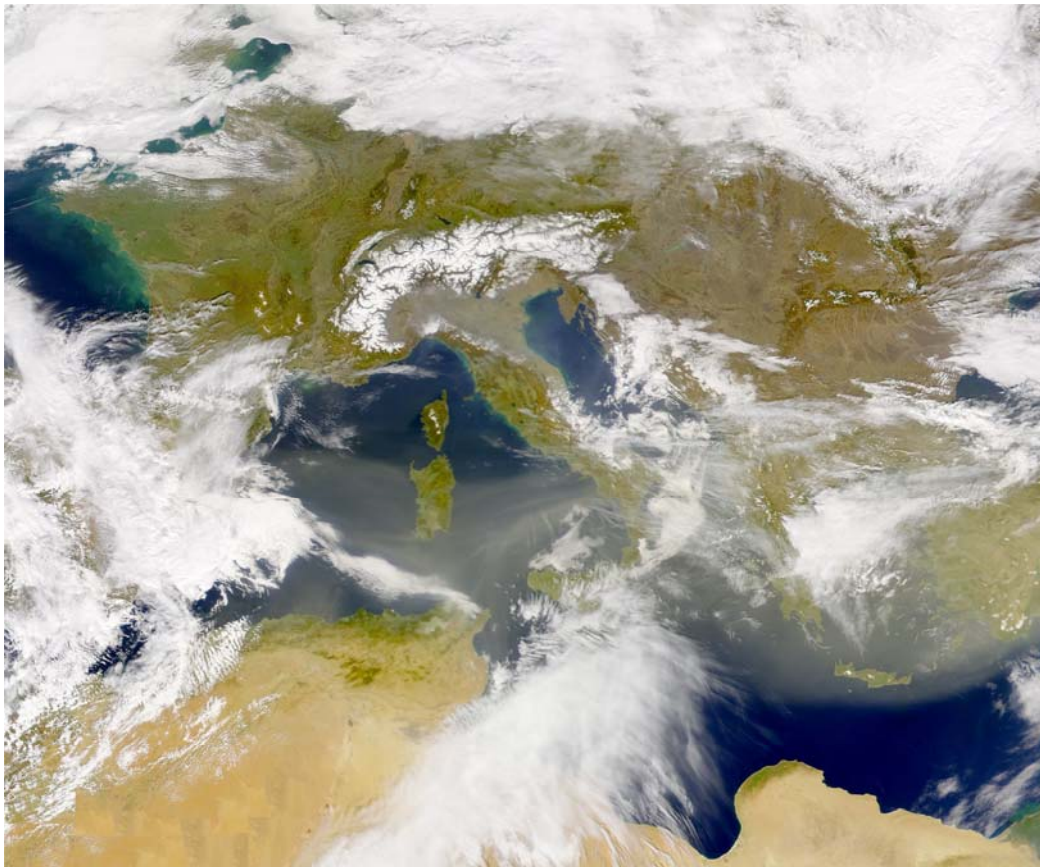


Figure 4: A Saharan dust plume on 2 March 2002 covering the Mediterranean basin from Spain to Turkey. Also visible is the high pollution over Northern Italy. Desert dust plumes have mostly a natural origin. They are lifted to an altitude of several thousand meters where they can travel long distances. Saharan dust is known to contribute to PM10 mass concentrations; e.g. in Barcelona by up to 25-35 %, in the Po Valley by up to 5-10% on an annual average.

(source: SeaWIFS project NASA / GSFC ORBIMAGE, through Joseph Prospero, and Jean-Philippe Putaud)

3 NATURAL EMISSIONS AND AIR POLLUTION

3.1 What are the contributions of natural aerosol and gaseous species to levels of particulate matter, ozone and other pollutants over Europe?

Aerosols

1. The natural contributions to annual average PM₁₀ concentrations in Europe can range from 5 % to 50%. The largest values are found in southern Europe because of Saharan dust transport (see Fig. 4), and in coastal regions of western Europe and northern Europe where large concentrations of sea salt aerosols do occur. In both cases these natural aerosols lead to high levels (above 50 µg/m³ during a number of days per year) and contribute to exceedances of EU limit values.
2. The oxidation of biogenic volatile organic compounds, emissions from vegetation wild fires, pollen and biological debris (pieces of insects and leaves), produce particulate matter of biogenic nature. Recent work has quantified relationships between *number and mass* concentration of fine particles on the one hand, and accumulated up-wind emissions of terpenes on the other, in clean air masses over the boreal forests.
3. Some recent specialised short-term studies in clean and polluted European cities, have reported the unexpected result that biogenic particles can contribute 41% to 60% of the total organic fraction of PM₁₀. In rural areas the contribution rises to 45-75 %. These values refer to measurements during summer time.

Gases

4. Soil emissions of nitrogen oxide (NO) are estimated to represent only 7% of the total NO source strength in Europe.
5. Current scientific understanding suggests that natural emissions of ammonia (NH₃) contribute approximately 4% of the total European NH₃ source strength. Uncertainties in natural source strength estimates and especially missing sources may in the next decade result in the natural source term being revised upwards significantly.
6. A significant fraction, 20 – 60 %, of European volatile organic compounds emissions is of biogenic origin. The wide range reflects the large uncertainties in measuring these emissions. Over the coming few decades the effects of climate change will most likely lead to an increase in these emissions due to increasing temperatures.

Supporting material

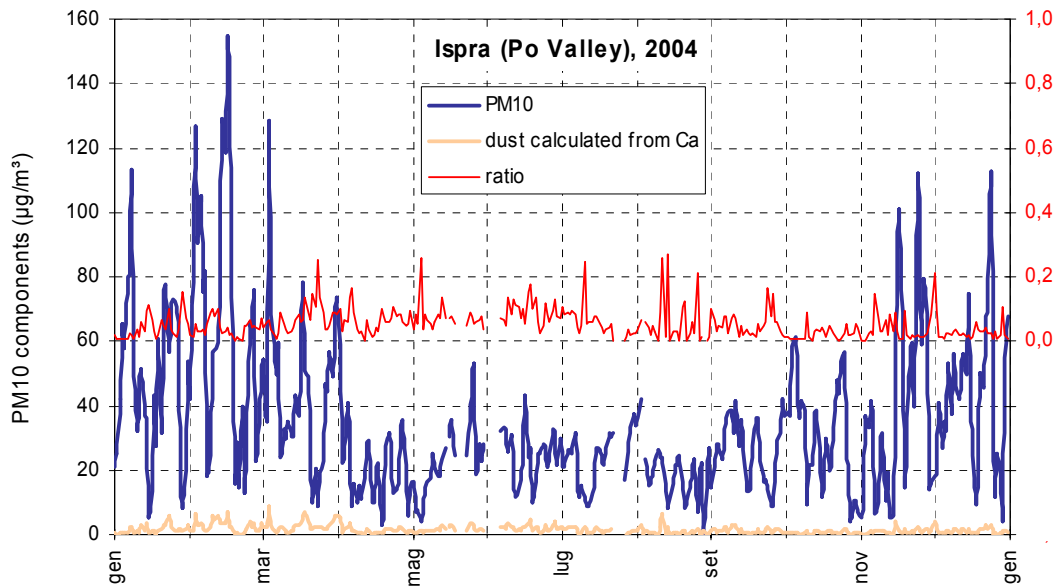
Natural Aerosols

Main aerosol components from natural sources are: dust, sea-salt, secondary organic aerosol and primary organic biological particles as well as ash from volcanoes.

Natural aerosol types can be classified as follows: dust, sea-salt/sea-spray, marine non-sea-salt (nss)-sulphate, biogenic secondary organic aerosol and primary biological aerosol particles, primary organic particles. These sources vary regionally, and consequently their contributions and importance to total PM levels will also vary regionally. Of these natural aerosol types, three can be identified as potentially contributing significantly to total PM mass: sea-salt, dust and secondary organic aerosol. For each source, an example region is selected to quantify current and future contributions of these natural sources to (a) present EU exceedance levels for PM and (b) future exceedance levels based on the proposed new Directive on Ambient Air Quality and Cleaner Air for Europe.

The direct emission of surface derived particles from terrestrial surfaces resulting from the mechanical action of wind is the main process leading to injection of surface derived particles into the atmosphere. This material is generally referred to as dust. Ambient aerosol measurements show the importance of these sources, especially in southern Europe where the contribution to PM₁₀ concentrations are typically 10 to 40 %. (Querol et al. 2004) and exceedances of air quality standards occur as a consequence of episodes, especially of Saharan dust. In addition to mineral dust emission to the atmosphere by the wind, mechanical action by vehicles and other anthropogenic activity injects additional particulate material into the atmosphere, especially in cities. In some urban areas this source may be the dominant contributor to the mass within the ambient PM₁₀ on windy days. The analysis of urban aerosols may indicate soil derived particles, and be interpreted as 'natural' in origin. However, if the process leading to the injection of this material into the atmosphere is vehicle related, the source is of course anthropogenic. In the case of wind derived particles, this is a natural process although the material injected into the atmosphere may be either natural or anthropogenic in origin.

The Mediterranean region is likely to be significantly influenced by dust emissions. Current PM levels show a clear seasonal trend, with markedly higher values in summer. The present annual mean values of PM_{2.5} at southern European (Spain) regional background sites, attributed to dust 1-3 $\mu\text{g m}^{-3}$ [8-20%] of the total PM_{2.5} mass [12-16 $\mu\text{g m}^{-3}$]. While these levels could be considered small in terms of current threshold levels, such dust concentrations will contribute significantly to the proposed new PM_{2.5} threshold of 16 $\mu\text{g m}^{-3}$.



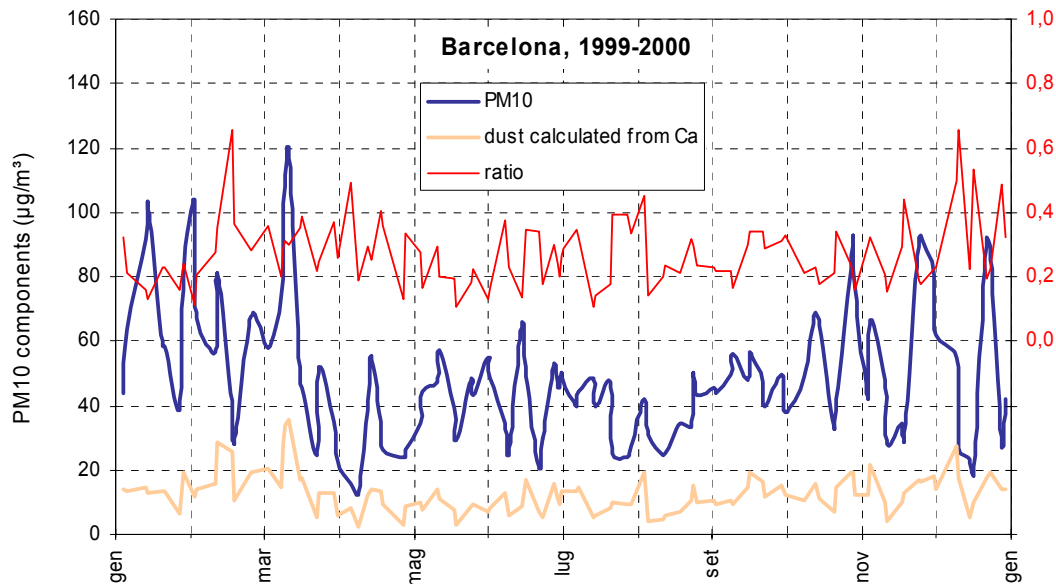


Fig. 3.1. Measured ratios of dust/PM10 in Ispra (Northern Italy) vs. Barcelona, showing the elevated dust levels at the Spanish site (courtesy J.-P. Putaud).

Measured natural contributions (as a percentage of particulate mass [PM] for PM₁₀ and PM_{2.5}) of aerosol dust are outlined below for a range of different type sites, [regional background, urban] for Southern Europe, Central Europe and for Northern Europe:

Regional background

Southern Europe (Spain):

- PM₁₀ ~ 12 - 40% (Querol et al, 2003; CAFÉ Report, 2003)
- PM₁₀ ~ 13% for Atlantic region of Iberian Peninsula (CAFÉ Report, 2003)
- PM_{2.5} ~ 8 - 20 % (Querol et al, 2003 ; CAFÉ Report, 2003)

Northern Europe: (Sweden, Norway)

- PM₁₀ ~ 5 - 10% (Putaud et al, 2004)
- PM₁₀ ~ 10 - 15 % (CAFÉ Report, 2003)
- PM_{2.5} ~ 2 - 5% (Putaud et al, 2004)

Central Europe: (Austria, Germany, Italy, Netherlands, Switzerland, and UK)

- PM₁₀ ~ 5 - 10% (CAFÉ Report, 2003)
- PM_{2.5} ~ 2 - 8%, (CAFÉ Report, 2003)

Modelling work shows that modelling alone is a good tool to detect the occurrence of, for example, Saharan dust transport episodes, but models alone are not able to quantify the natural dust load of PM₁₀ or of PM_{2.5} levels. That is why measurements, which complement modelling tools, are needed to: a) validate modelling, and b) determine the natural dust load in a given region and for a given episode.

The current model used in support of policy development in Europe does not include emissions of soil dust.

Coastal regions in Europe are likely to be significantly influenced by **sea-salt aerosol**. Annual mean values of PM₁₀ at coastal sites (e.g. Mace Head, Ireland) are within the present standards. Present annual coastal mean values of PM_{2.5} attributed to sea-salt of 2-3 µg m⁻³ [> 25%] of the total PM_{2.5}

mass [8-12 $\mu\text{g m}^{-3}$] will impact on the proposed new PM_{2.5} Directive. The percentage contribution of sea-salt to PM_{2.5} approaches ~95% under high wind conditions, which are prevalent in the winter, early spring seasons, which has a critical impact on the proposed new Directive values.

Biogenic organic aerosol in urban background sites in Europe constitutes the third area of potential impact on PM levels. Current PM₁₀ levels at urban background sites in Europe (CAFÉ Report, 2004) are within present EU standards. Present annual mean values of PM_{2.5} at central European urban background sites, attribute 5-8 $\mu\text{g m}^{-3}$ (25 - 35%) of the total PM_{2.5} mass (16-30 $\mu\text{g m}^{-3}$) to organic aerosol. A summer natural biogenic contribution of ~ 60% (Szidat et al, 2006) of total organic aerosol mass results in a natural contribution of 15-20% of PM_{2.5} mass (2.5 – 6 $\mu\text{g m}^{-3}$), which will clearly impact on the proposed new PM_{2.5} Directive.

Work by Tunved et al., (2006) show that in the Northern European boreal region, there is a very good correlation between aerosol mass (for particle diameter < 0.45 μm) and accumulation mode number concentration with estimated terpene emission loadings, due to substantial gas to particle formation over the boreal forests.

¹⁴C analysis suggest that OC from non-fossil fuel sources is by far the biggest contributor to total carbonaceous aerosol (TC) for several European cities in summertime : Zurich (Szidat et al., 2006); Milan, Marseille, Geneva and Odense (Glasius et al., 2000; Hansen et al., 2004), with typically about 40-60% of TC. This fraction is increased to about 70% at rural sites in Europe. Characterization of aerosol fractions suggested that the OC found in Zuerich (Szidat et al., 2006) during summer was mainly from biogenic, with the largest contribution from biogenic SOA. Biogenic SOA appeared still to make significant contributions to TC in winter. Wood combustion was found to account for about 40% of OC in winter in Zurich and fossil fuels represented ~ 30% of OC throughout the year.

Using a combination of ¹⁴C analyses and chemical characterisation, the CARBOSOL Project (2006) showed that summer SOA from non-fossil fuel sources becomes dominant (average of ~ 55% of TC) based on 2 years (July 2002 – October 2004) of observations at 6 European sites representing maritime (Aveiro, Portugal; Azores), continental rural background (K-Puszt, Hungary), and elevated sites (Puy de Dôme, 1450 m asl; Schauinsland, 1205 m asl; Sonnblick, 3106 m asl). There was a surprisingly high contribution of SOA from non-fossil fuels in winter, ranging from 21 to 44% of total carbon.

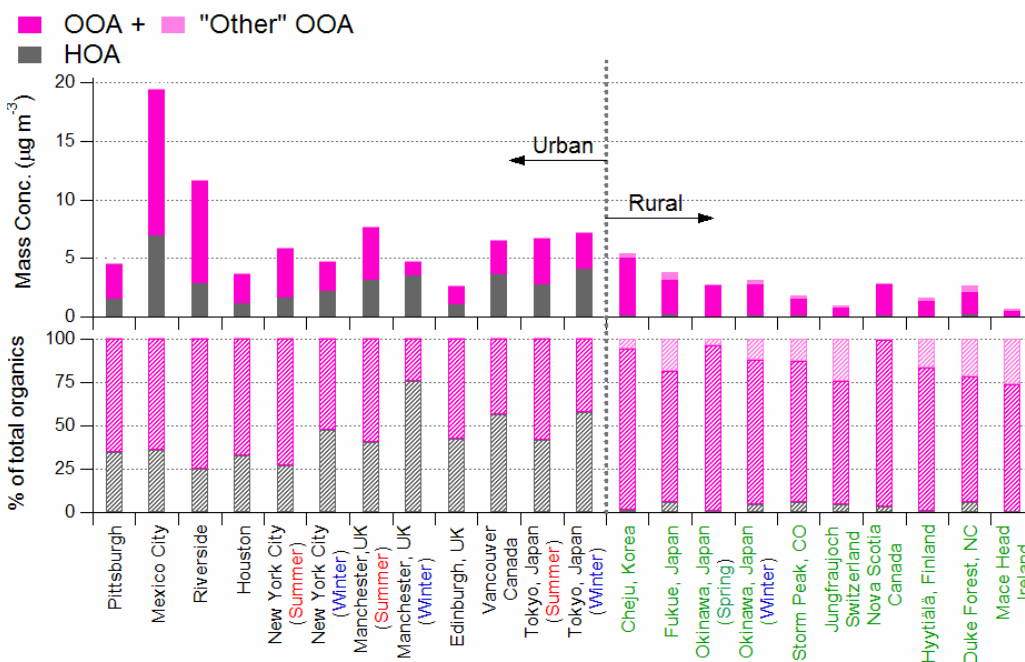
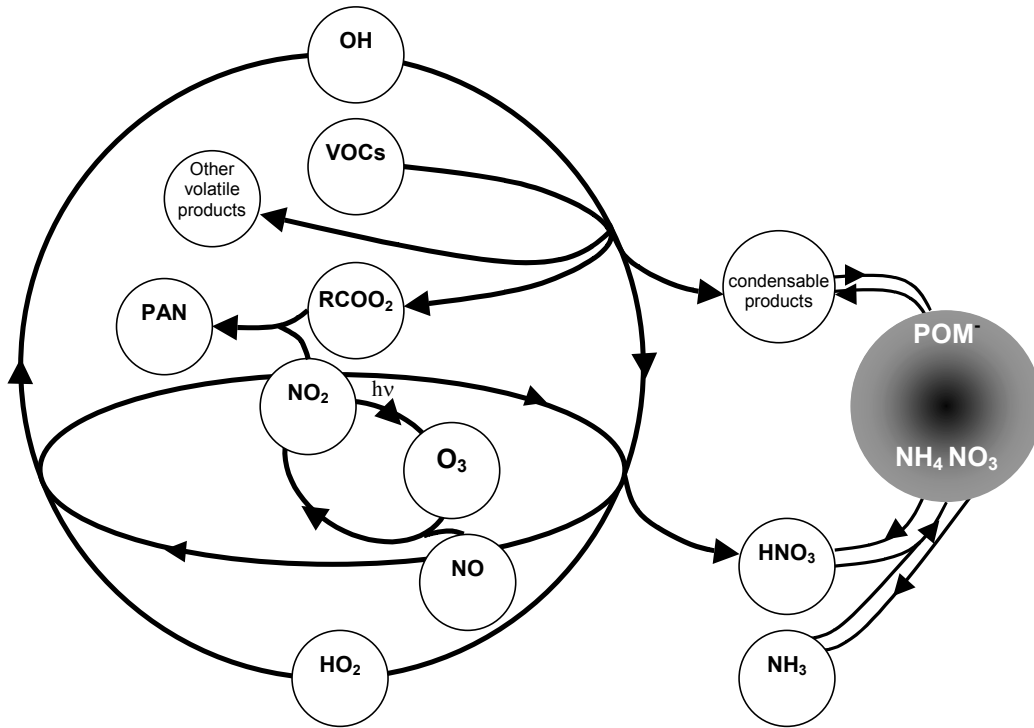


Figure 3.2. Summary of the deconvolution of OM measured by the AMS (non-refractory aerosol within $\text{PM}_{1.0}$ only) into freshly emitted hydrocarbon like aerosol (HOA) and oxygenated aerosol (OOA); Secondary Organic Aerosol will be OOA. In the rural environment a second distinct class of OOA could be identified, which may be linked to biogenic SOA (Zhang, et al., in preparation).

Aerosol Mass Spectrometer measurements (see Figure 3.2) in various regions around Europe differentiate between two classifications of detected organic aerosol, namely oxygenated and hydrocarbon-like (i.e. compounds containing only carbon and hydrogen atoms) carbonaceous aerosol. Results from various regions around Europe indicate that in non-urban regions, oxygenated organic aerosols dominate the major fraction of the organic aerosol and in the urban environment, the degree of oxygenated or hydrocarbon-like aerosol vary with city and location within a city. Few measurements have reported such fractions of generic speciation.

Overall, the number of observational studies is relatively low.

The extent to which heterogeneous aerosol chemistry is important in SOA formation is currently unknown (Kanakidou et al., 2005). The most rigorous approach to gas phase modeling of SOA is to represent the gas phase chemistry with a fully explicit mechanism – such as the University of Leeds Master Chemical Mechanism (<http://www.chem.leeds.uk/Atmospheric/MCM/mcmproj.html>). However, this approach requires knowledge of rate constants – many of which are unknown in the case of SOA forming chemical mechanisms according to Kanakidou et al. (2005), who conclude that targeted chamber and field observations are needed to allow evaluation and provide confidence to chemical mechanisms used in regional (and global) models that treat SOA formation. Consequently, there are large uncertainties in evaluating SOA modeling.



In the future, the biogenic secondary aerosol organic component will become relatively more important as emissions from anthropogenic primary and precursor aerosol sources [inorganic + organic] reduce.

Gases SO_2 , NO , NH_3 , VOC

Sulphur

The main source of biogenic source of sulphur is oceanic dimethylsulphide (DMS), which originates from phytoplankton. DMS emissions exhibit a seasonal trend, with higher emissions during the summer months due to increased productivity. Leck and Rohde (1991) estimate that on an annual basis DMS emissions make up max. 0.7 % of the total Northern Europe S emissions, while during July, i.e. a summer month, this fraction rises to 3.5%. Considering the budget of Scandinavia only, between 20 - 70% of sulphur emissions are of biogenic origin (DMS) during the summer (July). Similarly, Kouvarakis et al. (2002) found that during summer, biogenic sulphur emissions can make up to 26% of the total S budget in the Eastern Mediterranean (Greece).

Total oceanic DMS emissions from the North Atlantic Ocean and the North Sea were estimated at $1600 \text{ kt S yr}^{-1}$ (Tarrason et al., 1995) for 1988. Gondwe et al (2003) estimated that the DMS contribution to the overall atmospheric burden of non-sea salt sulphate amounts to only 9% in the Northern Hemisphere due to very large anthropogenic source. (In contrast the burden in the Southern Hemisphere makes up 43 %.)

The changes of DMS emissions due to global warming have been investigated by Bopp et al., 2004: It was found that, using a scenario with doubling of CO_2 , the global annual DMS flux would only increase by 3%, but for the 40 - 60° latitude band, an almost 20 % increase in annual DMS flux would be observed. This was explained by the shift of species which produce more DMS to these latitudes.

Based on a scenario of increasing biogenic S (DMS) emissions with global warming, and decreasing (land-based) anthropogenic S emissions in Europe, it seems likely that biogenic marine emissions will become a larger fraction of the total European Sulphur budget, although anthropogenic emissions dominate total emission throughout the period.

Terrestrial soils emit a range of sulphur compounds. However, emissions from soil appear to be very small relative to current or projected anthropogenic emissions.

Impact on acidity /acidification: Very large reductions in sulphur emission have been made in Europe in the last three decades. The benefits of the control measures in ambient concentration and deposition reductions and reduced environmental damage are now clear and for some ecosystems recovery is evident. There is substantial evidence of non-linearity in the emission-deposition relationship which has reduced the benefits of emission reductions in some areas, for example along the west coast of Europe (Fowler et al 2001).

Volcanic emissions remain an important source in small areas of southern Europe and notably in Southern Italy.

In conclusion, natural sulphur emissions from marine and terrestrial biogenic sources represent a small (< 5%) contribution to the European sulphur budget, but with continued declines in anthropogenic sulphur emissions and an increase in marine biogenic emissions with climate change, the natural sources will become more important with time. The contribution of marine sources of sulphur to aerosol concentrations entering Europe from the Atlantic is less than $1 \mu\text{g m}^{-3}$, and is therefore negligible in the context of the thresholds for air quality assessment.

Nitrogen

Contributions to the gaseous and aerosol phase nitrogen compounds over Europe from natural sources are best separated between oxidized and reduced compounds as they have very different sources and spatial distributions.

Oxidized Nitrogen

Natural emissions of oxidized nitrogen occur as NO and N₂O, although the latter makes no significant contribution to pollution over Europe in the troposphere. This section therefore considers only NO emissions which derive from microbial transformations of nitrogen compounds in soil through nitrification and denitrification. The main source of NO is through nitrification and is very sensitive to nitrogen supply, soil temperature, soil water status and the water filled pore space, which influences the effective diffusion path length to the atmosphere.

The emissions of NO from soil in Europe amount to approx 540 kTonnes N annually (Stohl et al., 1996), which is equivalent to about 7% of European total emissions. While considered natural, a substantial fraction of the emitted NO is from agricultural soils, and due to the fertilizer input to the land, and even in the case of the semi natural and natural landscapes of Europe, some of the NO emission is due to the nitrogen deposition from anthropogenic sources onto the soils and vegetation and recycled to the atmosphere. It is important to note that;

1. Soil emissions are increasing in relative terms in Europe, as combustion sources decline
2. That the response to temperature is positive, and increases by about 10% per deg C, all other conditions remaining constant.

3. The importance of soil NO emissions in tropospheric ozone production throughout Europe is larger than its contribution to the emission total because the emission occurs in areas remote from industrial and traffic sources, including substantial areas of Europe remote from major industrial or traffic sources, clean air environments in which ozone production tends to be limited by the availability of NO_x.

In conclusion soil emissions of nitric oxide represents only 7% of the total source strength in Europe and while the response to climate change is expected to be positive, this natural source is unlikely to exceed 10% of European emissions in the period to 2030.

Reduced Nitrogen

Reduced nitrogen, largely as NH₃, is predominantly an agricultural pollutant, and is emitted mainly from animal excretions. There are of course emissions from natural fauna, although these do not contribute much to the total emission throughout Europe, and has been estimated at 127 kT N annually (Handley et al, 2001). However, it is clear that not all natural sources have been included in the emission estimates, and for some parts of Europe the missing sources may be very important, especially for aerosol production in remote regions. One of the missing sources, from natural vegetation occurs whenever ambient concentrations are less than the compensation point of NH₃ for the vegetation (Sutton et al., 2001). The NH₄⁺ is found in apoplast fluids, and coupled to the atmosphere through stomata. In remote regions ambient NH₃ concentrations are small, typically <0.1 ug NH₃ m⁻³, because the transit time of air to these regions is much longer than the atmospheric lifetime of NH₃. In these circumstances, the vegetation present provides the regional source, and substantial evidence for the process has been obtained by measurements in parts of remote western Scotland (Sutton et al 2001).

The emissions from these sources are very sensitive to temperature, through the gas/ liquid phase partitioning, as has been demonstrated by Flechard et al. (1996).

The magnitude of these sources throughout Europe has not been estimated and any extrapolation from the available evidence would be very speculative. However, given the very large source area it is likely to exceed other natural sources.

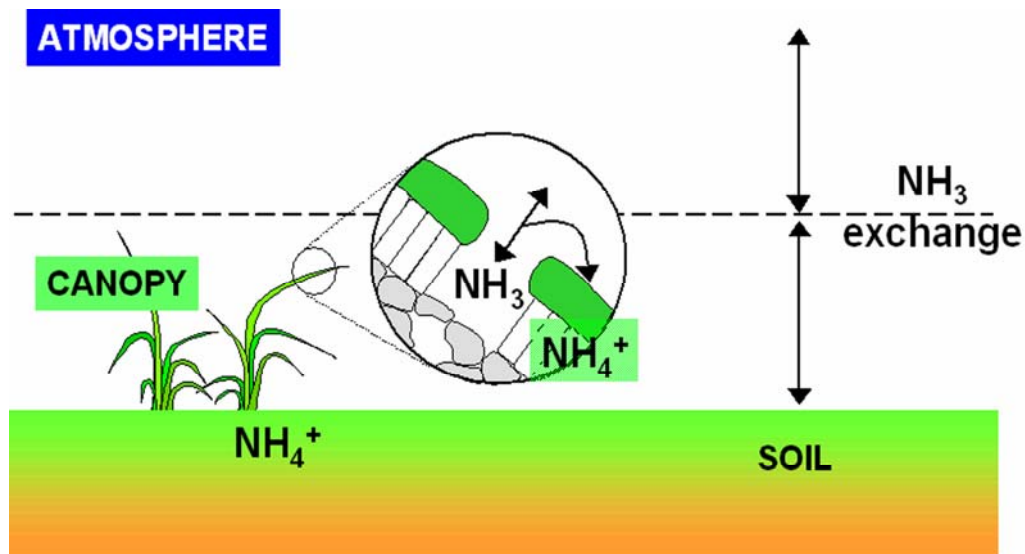


Figure 3.3. A diagrammatic representation of the exchange of ammonia between vegetation and the atmosphere, showing that ammonia is released from vegetation to the atmosphere whenever the ambient concentration is below the equilibrium ammonium concentration in the plant fluids linked to the atmosphere through stomata, and vice versa.

In conclusion, natural emissions of NH_3 contribute approximately ~4% of the total European source strength. Uncertainties in natural sources and especially missing sources may in the next decade result in the natural source term being revised upwards significantly and positive responses to temperature are likely to further increase this natural source.

VOC

The emission of volatile organic compounds from vegetation is recognised as a major contributor to VOC emission in Europe, and especially in the warmer parts of Europe. The total non methane VOC emission in Europe has been estimated at approximately 13 Tg annually, and this represents about 40% of the total emission (Simpson et al., 1999). The uncertainty in this value is very large, as the fraction of the vegetation characterised for the different VOC species is limited and the sensitivities to the full range of environmental variables which influence emissions restricts the list even further. Increased temperatures lead to increased emissions of biogenic VOCs such as isoprene and is considered in more detail in section 2.3. Biogenic VOC emissions rates increase rapidly with leaf temperature. It is likely that during photochemical pollution episodes at high ambient temperatures, biogenic VOC emissions will be at a maximum and may dominate total VOC emissions.

A more detailed method has been developed to quantify natural biogenic VOC emissions from vegetation for country scale emission estimates (Stewart et al., 2003); in this study, spatial distributions of a range of species were used with radiation, temperature and emission potentials to map emissions at a spatial scale of 12 x 12 km for Great Britain. The dominant sources were conifer and broad leaf forests. Even in this detailed approach the uncertainty in the emission estimates was substantial and for some components of the inventory approached a factor of 4.

At the global scale, the total emissions of VOC have been constrained by column measurements of formaldehyde (Guenther et al., 2006) and this work suggests that globally the uncertainty in emissions is closer to a factor of two. However, the uncertainty increases at regional scale and for shorter time scales, and especially when considering episodes of photochemical pollution. Many very reactive biogenic VOC have not been characterised (such as sesquiterpenes) but the very rapid reaction of some of these species reduces their wider scale impact on atmospheric composition as many of the reaction products are removed within plant canopies. However, the limited knowledge of these emissions and their fate further increases the uncertainty in biogenic VOC emissions. The largest uncertainty in biogenic VOC emissions is due to uncertainties in the spatially disaggregated species composition of Europe and the spectrum of VOC emissions associated with each. The uncertainty in natural VOC emissions from vegetation in Europe must therefore be considered substantial and an important constraint on the accuracy of the effects of emission control strategies for anthropogenic VOC and NO_x emissions.

3.2 How well can we separate the natural aerosol and gaseous species from the anthropogenic ones?

1. Only in a few cases can this separation be done on the basis of routine measurements that could be used in regulatory monitoring networks.

2. It is possible for sea salt aerosols, for instance. However, distinguishing between desert dust and resuspended road dust already requires measurements of elements (like Ca, Al, Si, Fe, ...) that are not common in routine monitoring programs. Analysis of the origin of the air mass (e.g. by back-trajectories) can help in the analysis
3. Specialised techniques such as functional grouping, C¹⁴ analysis and molecular speciation are developing to separate biogenic from anthropogenic organic aerosols. They will *not* be available for routine monitoring in the foreseeable future.
4. Comparing pre-industrial with present day concentrations gives an estimate of the anthropogenic contribution. For example, the O₃ concentration in the northern hemisphere was at most 15 ppbv in pre-industrial times as compared to 20 – 35 ppbv today.
5. Models of atmospheric transport and chemistry can in principle be used to separate the contribution of anthropogenic and natural emissions (see e.g. Fig. 1), however, in the case of aerosols in particular, such analyses are hampered by poor emission inventories, the incompleteness of the PM description in such models (see *Question 2.2*) and the lack of measuring data for validation.

Supporting material

Nowadays it is not possible to distinguish the anthropogenic fraction of Secondary Organic Aerosol from the natural fraction by using standard analytical methodologies. C¹⁴-analysis (which is not suitable for routine measurements) allows to determine the fraction of ‘contemporary’, non-fossil, carbon, but in order to do further source identification (e.g. to distinguish between primary and secondary biogenic organic aerosol), chemical information is needed. In spite of the impressive efforts by the scientific community, organic aerosol composition and its relation to the different sources is still poorly understood: today information on the complete molecular composition of organic particles cannot be obtained with existing techniques and is unlikely to be achievable in the foreseeable future. The awareness of this limitation has guided the scientific community in trying alternative routes: current strategies include, in addition to C¹⁴ analysis (Szidat et al., 2004), both improvements to existing instrumentation, to pursue single component analysis as well as new methodologies that do not rely on full chemical speciation, such as functional group characterisation and analysis of molecular fragments (Decesari et al., 2000; Russel et al., 2002; Zhang et al., 2005). Recently, these complementary analytical strategies have been used in “near source measurements field campaigns” as well as in laboratory experiments for characterisation of anthropogenic and biogenic SOA and many advances have been made in understanding their composition and their relation to main formation processes (Cavalli et al., 2005 ; Zhang et al., 2005). In a recent publication, an attempt to use a source classification within which aerosol properties, defined as “distinguishing characteristics”, can be determined, has been pursued (Fuzzi et al., 2006). Even if the process of distinguishing anthropogenic and biogenic SOA by chemical analysis is still under development, this is considered a priority issue not only for air quality problems but also for climate.

3.3 To what extent do natural emissions interact with emissions from anthropogenic sources?

1. There are indeed a number of *direct* interactions between natural emissions and anthropogenic emissions.
2. The most important interactions are those linked to VOC- NO_x- O₃ chemistry: e.g. biogenic and anthropogenic VOCs both interact with NO_x to produce O₃. Ozone, in turn, transforms biogenic VOC into secondary organic aerosol (SOA, see *Question 4*).

3. Also, the more SOA mass is present, the more organic condensable material can dissolve from the gas into the aerosol phase (*see Question 4, Fig. 6*). Hence an increase in anthropogenic (or biogenic) SOA will be “*amplified*” by the dissolution of more biogenic (or anthropogenic) compounds.
4. Another potentially important *indirect* interaction is the anthropogenic emission of CO₂, leading to global warming, which in turn might affect natural emissions (*see Question 3.4*)

Supporting material:

All natural aerosols interact with anthropogenic emissions by providing surfaces on which condensation and chemical reactions can take place. Further, by scattering or absorbing sunlight, they influence atmospheric photochemistry.

Laboratory chamber experiments suggest that the oxidation of terpenes may represent the most important biogenic source of secondary organic aerosol and that the reaction with ozone gives higher yields of SOA than the competing oxidation reactions with OH or NO₃ radicals. Increasing levels of particles from any source promotes the partitioning of VOC oxidation products into the particle phase (Kanakidou *et al.*, 2005). According to model studies, consistent with ice-core studies (CARBOSOL) the formation of SOA from biogenic precursors has increased considerably since pre-industrial times because of higher ozone levels and higher levels of pre-existing aerosol (Tsigarides *et al.* 2006). (See also Question 4.1).

In the case of ozone, elevated concentrations of NO_x in plumes of urban air interact directly with biogenic VOC sources as the air is advected over rural areas. Such interactions, especially with the more reactive VOC such as isoprene, can dominate ozone production during events.

The chemical processing related to ozone formation is quite well understood and satisfactory models to quantify the rates of ozone production exist. The most important limitation in quantifying the importance of biogenic VOC sources in the production of ozone and secondary organic aerosols is a lack of knowledge of the full spectrum of VOC emissions from European plant species, the influence of environmental variables on emission rates and land use information to quantify the spatially and temporally disaggregated species cover of the landscape.

The interaction of mineral dust and sea salt aerosol with nitric acid has been well demonstrated in laboratory studies and impacts have been found in modelling studies [Bauer *et al.*, 2003]. Several field campaigns have shown an anticorrelation between ozone and dust loadings, which may be caused by the removal of nitric acid, but also by the direct uptake of ozone as well as of species involved in the processes that lead to the photochemical formation of ozone in the troposphere (HO₂ radicals and H₂O₂) (de Reus *et al.*, 2005). Also, sea-salt, through aqueous phase chemical processes and halogen recycling leads to ozone reductions.

3.4 How well can we quantify expected changes in the contribution of natural emissions during the next 20 to 30 years, e.g., due to climate change?

1. It is expected that global warming and the resulting changes in local temperature, precipitation, winds, suitability for growth of species, etc ...will have an effect on natural emissions. The effects observed in the biosphere-atmosphere system during the summer of 2003 have been an indication of this. The magnitude and sign of such climate effects depend on the specific emission. In general, predictions of such climate effects are afflicted by large uncertainties.

2. Evidence suggests that present-day desert dust emissions and the subsequent long-range transport are largely driven by natural meteorological processes coupled with climate conditions in the source areas. The currently observed inter-annual variability of dust transport is largely due to the variability in these conditions. There is however no scientific consensus on the effect of climate change on future emissions of dust and the consequent transport.

3. Increases in temperature will enhance NH_3 emissions from soils by approx 20% per deg C, the soil NO emissions are enhanced by approx. 10% per deg C. It seems likely that these emissions, as well as those of biogenic VOCs, will increase over the coming decades. The expected response to climate of natural marine sources of volatile sulfur compounds is small, less than 5% up to 2100.

4. Land-use change is also expected to have an effect on natural emissions due to changes in vegetation. Soil disturbance (e.g., through agriculture, grazing, etc) coupled with increased aridity could lead to increased dust mobilization, with substantial local and regional impacts.

Supporting material

Most of the natural terrestrial emissions of gases are sensitive to temperature and water supply, either in soils or vegetation, these emissions would therefore be expected to change with climate. Marine emissions of trace gases and aerosol emissions from terrestrial and marine surfaces are also sensitive to aspects of the physical climate, especially wind speed. Most, but by no means all of the responses to the current and expected changes in climate suggest positive feedback, i.e. increasing emissions over the coming decades.

Aerosols

Biogenic Marine aerosol: increase in sea surface temperature (SST) will lead to increased stratification of ocean surface layers, reducing biological activity and possibly reducing the organic fraction of marine aerosol. On the other hand increases in winds will lead to increased production of primary marine aerosol. There is however no consensus on increasing wind speeds with increasing temperatures associated with global warming.

Mineral Dust: No consensus on effect of climate induced dust loadings. Some models predict an increase in mineral dust loadings, others predict a decrease.

VOC

Currently approx 40% of European VOC is natural, temperature responses are positive and range from 5% to 20% per deg C, thus from the expected temperature changes alone, we would expect natural VOC sources, including SOA precursors, to increase in absolute terms. In relative terms, the increase will be larger as anthropogenic emissions decline. However, there are important caveats, because in prolonged hot and dry weather, such as in the summer of 2003, reduced soil water can suppress the VOC production by vegetation. Direct effects of the increasing concentrations of CO_2 on VOC emissions are complex. There are several contributions to the overall effect, first increasing biomass leads to an increase in VOC emission, but increases in CO_2 have been shown to decrease isoprene emission. Overall therefore the net effect depends on the magnitude of the individual processes.

Land use changes and the consequent change in species composition will also modify the range and source of VOC compounds emitted. It is also important to note that to date the natural emissions in the European inventory do not include the many of the very reactive compounds. The magnitude of these changes and their spatial distribution in Europe are highly uncertain. Even the current spatial

distribution of VOC emission in Europe is at present uncertain due to the relatively small number of species for which VOC emissions have been fully characterised.

NH₃ and NO

Increases in temperature will also increase 'natural' NH₃ emission by approx 20% per deg C. The NO soil source increases at approx 10% per deg C. Thus emissions of both NH₃ and NO are expected to increase in a warmer climate. Given that the expected changes in temperature (and other changes in meteorology) over the next 20 years are modest, it is reasonable to expect emissions of these gases to increase, but the overall change is unlikely to be large over this period.

For biogenic marine aerosols: increase in sea surface temperature (SST) will lead to increased stratification of ocean surface layers, reducing biological activity and possibly reducing the organic fraction of marine aerosol. On the other hand increases in winds will lead to increased production of primary marine aerosol. There is however no consensus on the effect of increasing temperatures on wind speeds. Overall therefore the effect of climate change on marine aerosols are too uncertain to conclude even the direction of the net effect. There is no consensus on effect of climate induced dust loadings. Some models predict an increase in mineral dust loadings, others predict a decrease.

Increases in temperature will increase 'natural' NH₃ by approx 20% per deg C, the soil NO source increases at approx 10% per deg C. It seems likely that these emissions will increase over the coming decades. Lastly, the response to climate of natural marine source of sulphur is small, less than 5% over the current century.

3.5 Are there biases introduced in the analysis leading to the Strategy due to the lack in scientific understanding?

1. For estimating health impacts from PM, the current analysis does not consider the emissions of natural aerosols such as dust and sea salt, nor those derived from the oxidation of biogenic VOCs, biomass burning and biological debris. Hence the absolute PM_{2.5} concentrations and the risk to human health in the baseline scenario might be underestimated.
2. Whether the exclusion of biogenic VOC emissions in the current analysis leads to a significant bias in ozone levels, is less clear. Here the VOC/NO_x/O₃ system is much more non-linear and natural and anthropogenic emissions of VOCs much more inter-twined.

3.6 Which research within the next 3-4 years could improve future analyses?

1. A better quantification of the contribution of biogenic VOCs to the overall VOC emissions in Europe is both highly desirable and feasible.
2. It is time to develop strategies to account for anthropogenic *and* natural PM in epidemiological studies so as to reduce the uncertainties in such studies. In fact a large uncertainty in the assessment of the health effects of PM relates to the question whether different types of natural and anthropogenic particles are equally harmful.
3. One can perform a first analysis of the effects of reductions of anthropogenic emissions on ozone and PM concentrations, using models that either include or exclude natural emissions. Such

an analysis would shed light on the importance of considering natural emissions in the development of air pollution abatement strategies

4. Operational forecast models can be further developed to include desert dust and forest fires events and their impact on air pollution. These forecasts should be systematically tested against measurements.

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Primary aerosol particles such as sea salt and dust are emitted directly into the atmosphere. Secondary aerosol particles consist of condensable material produced by chemical transformation of gases emitted in the atmosphere. Sulfates and nitrates in PM derive from sulfur dioxide and nitrogen dioxide respectively. Secondary organic aerosols (SOA) derive from volatile organic compounds (VOCs) that can either be natural or anthropogenic.

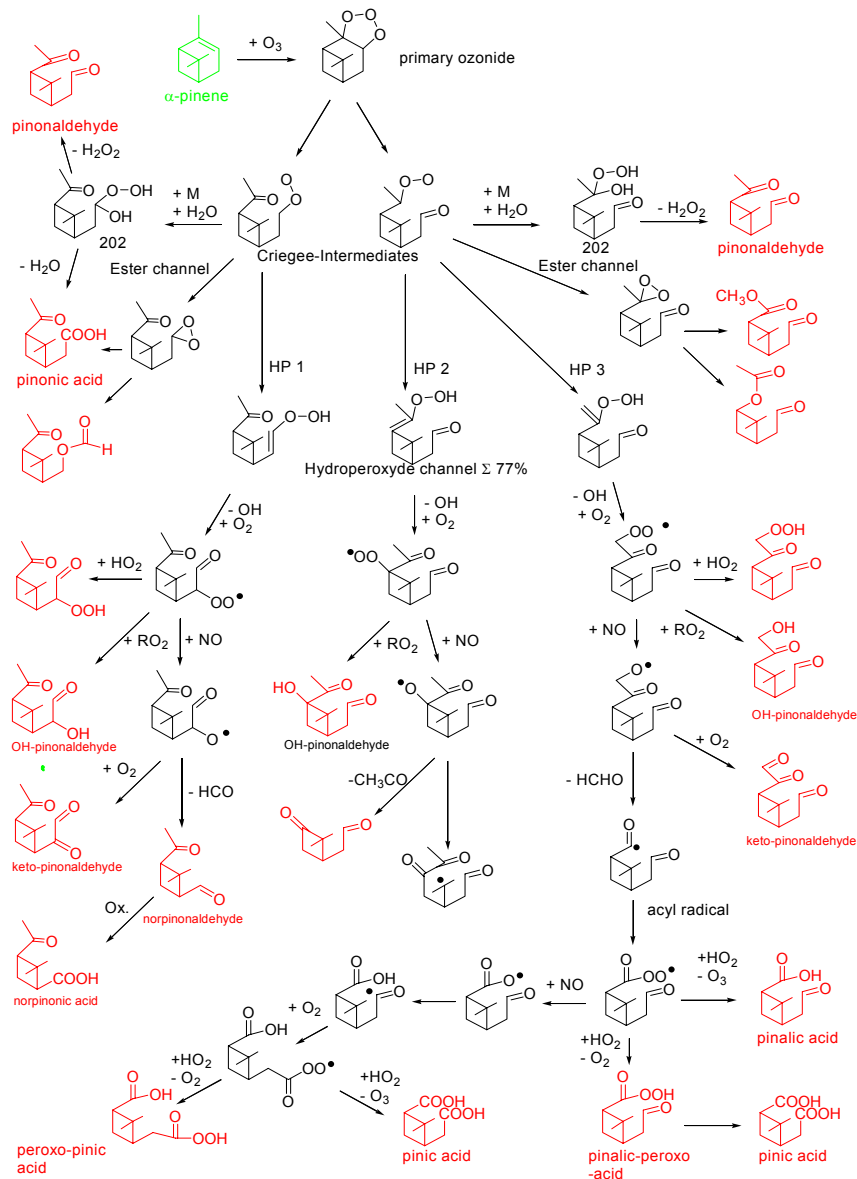


Figure 5. An illustration on how complex the formation of secondary organic aerosols can be. Shown is the chemical mechanism proposed in the scientific literature to describe the transformation of α -pinene (in green) into a wide range of condensable compounds (in red). (source: Winterhalther et al., 2003)

4 SECONDARY ORGANIC AEROSOLS

4.1 Which anthropogenic and natural sources contribute to the formation of secondary organic aerosols (SOA)?

1. Anthropogenic sources of SOA relate to transportation, fossil fuel and biomass combustion processes. From these processes, the dominant SOA precursors are volatile organic compounds (VOC) in the form of aromatics (toluene, xylenes, trimethylbenzenes, etc).
2. Natural sources are biogenic and relate to terrestrial vegetation and marine biota. From terrestrial biota, predominantly forests, the important SOA precursors are VOCs such as isoprene, terpenes, sesquiterpenes as well as some partially oxygenated compounds. From marine biota, evidence exists about precursor emissions; however, understanding and quantification of the processes and resulting SOA formation is largely unknown.
3. In general, biogenic VOCs are more reactive and are transformed more efficiently into condensable compounds than anthropogenic VOCs.

Supporting material

Terrestrial Vegetation

With regard to the naturally emitted VOC from vegetation the main precursors of secondary organic aerosol are isoprene, terpenes, sesquiterpenes and terpenoid alcohols. Due to the chemical complexity of the VOC precursors, there is no breakdown of this source to individual compounds. The most studied of these species is isoprene (Griffin et al., 1999; Lindfors, 2000); however, a large uncertainty exists in the quantification of secondary organic aerosol produced from isoprene oxidation. Terpenes and sesquiterpenes are more reactive than isoprene and have a greater aerosol formation potential, but formation of secondary organic aerosol from these species has proven even more difficult to quantify compared to isoprene. Sesquiterpenes, although emitted in significantly lower amounts than other secondary organic aerosol precursors, produce a significantly higher yield of organic aerosol. In summary, little information is available on the biogenic emission of chemical species of interest for SOA formation other than isoprene.

Several chamber studies have addressed the formation of SOA from monoterpenes and isoprene. Most recently, the photooxidation a reasonably extensive range of monoterpenes, oxygenated monoterpenes, and sesquiterpenes were conducted individually at the Caltech Indoor Chamber Facility under atmospherically relevant HC/NO_x ratios in order to evaluate the time evolution of the transformation processes and to determine the yields of secondary organic aerosol and gas-phase oxidation products (Lee, et al., 2006). Aerosol yields from different terpenes ranged from 1% to 68% and numerous unidentified products were found; however, some of the characteristic product ions were also seen above forest canopies indicating that these unidentified species can still be measured using specialized techniques in the atmosphere.

Marine biota:

Recent studies by O'Dowd et al., 2004, and Yoon et al., 2006 pointed to a significant and sometimes dominant organic fraction associated with sub-micron marine aerosol. While these studies supported the majority of this organic fraction being primary organic aerosol produced by the bubble bursting process, they also suggested that a notable fraction was also likely to result from secondary formation processes. The organic fraction also possessed a seasonality with peak concentrations occurring in both the early and late summer periods. Additional studies, utilizing aerosol growth factors in near-saturation organic vapour fields also confirmed the presence of an

organic component in recently formed particles during nucleation events in the coastal atmosphere (Vaattovaara et al., 2006). Such studies clearly point to a secondary organic aerosol source in marine aerosol. However, characterization and quantification of this organic fraction is very poorly understood at this stage. The source of the aerosol precursor is far from clear, although it is known that isoprene is also a major VOC constituent of the marine boundary layer (Yokouchi, et al., 1999). Isoprene is emitted directly by plankton, and may be indirectly produced by grazing zooplankton (Broadgate et al, 1997). Terpenes and monoterpenes are also present in lesser amounts. Although little is known about the aerosol formation potential via secondary organic processes in marine air, it is unlikely that there is sufficient organic mass to dominate PM levels. Estimates of total carbon aerosol in clean marine air is of the order of 1-2 $\mu\text{g m}^{-3}$ (Yoon et al., 2006).

Anthropogenic Sources

Transport/Industry/biomass combustion

Although globally, anthropogenic VOC emissions are significantly lower than biogenic VOC emissions, in terms of a European Budget, anthropogenic VOC comprise up to about 30% of the total concentration, suggesting a significant source of anthropogenic secondary organic aerosol over Europe, as inferred from data from a number of sources (CAFÉ Report, 2004; Putaud et al, 2004; CARBOSOL, 2006; EMEP data – Yttri, private communication, 2006). The most important anthropogenic sources relate to transportation, industrial/chemical processing and biomass combustion processes. From these processes, the dominant precursor emissions are in the form of aromatics (toluene, xylenes, trimethylbenzenes, etc) which are readily oxidised to produce particulate matter (Odum et al., 1997). A recent evaluation of the relative contributions of each of these anthropogenic activities and sources to secondary organic aerosol formation, considering only aromatic oxidation, concluded that solvent use contributed 16-23%, printing 3.5% and transport 75-81% (Dusek, 2000).

Recently benzene has also been positively identified as a precursor of SOA (Martin- Reviejo and Wirtz, 2005) and it should be noted that several oxygenated compounds as well as alkenes and acetylene have been identified as secondary organic aerosol precursors.

In summary, with the current poor capability in identification of secondary organic aerosol products, it is difficult to estimate the relative contributions to PM loadings of anthropogenic or natural sources. Furthermore, it should be noted that little is known at the present time about the chemical composition of secondary organic aerosol and its potential chemical transformations during its atmospheric lifetime and so only limited information can be gained from chemical composition measurements at this stage.

4.2 How could the contribution of SOA to PM change over time?

1. A strong seasonal cycle is expected in emissions and in photochemical processes leading to both natural and anthropogenic SOA.
2. Policy measures to reduce anthropogenic VOCs in order to control ozone formation will also reduce SOA formation.
3. Over longer time scales climate change and land-use change are expected to impact on biogenic emissions leading to SOA (see Question 3.3).

4.3 How well can the SOA contributions to levels of PM be quantified, for different source regions in Europe?

1. Poorly. There are no operational measurements that distinguish SOA from total, i.e. primary plus secondary particulate organic matter (POM). In fact there are no accepted operational measurements for POM.
2. A compilation of research projects in which particulate matter (PM), particulate organic matter (POM) and elemental/black carbon (EC/BC) were measured indicates that in the urban environment SOA might contribute up to about 20% in both PM₁₀ and PM_{2.5}.
3. According to the same compilation, the chemical composition of a significant fraction of PM₁₀ and PM_{2.5}, about 25 and 15 % respectively, remains un-identified. Part of this fraction might also consist of SOA. Hence the final upper limits for the SOA contributions to PM₁₀ and PM_{2.5} might be higher than 20%.
4. Models of transport and chemistry of the atmosphere attempt to evaluate the SOA contribution to POM and PM levels, however, the SOA concentrations calculated by the available models typically differ by a factor 3 to 4.

Supporting material

Operational measurements currently do not quantify the fraction of organic carbon accounted for by SOA. In terms of both natural and anthropogenic SOA contributions, a strong seasonal cycle is expected in most regions for both biogenic and anthropogenic emissions and photochemical processes leading to SOA production.

The chemical characterization measurements of PM mass do often not achieve mass closure which implies that some of the mass is not accounted for. The missing mass amounts to typically 30% of the total mass, (Putaud et al., 2004) and SOA may contribute to this. Missing mass in estimates may arise from the conversion of total carbon, where total carbon mass measurements are available along with the main inorganic species, to total organic mass (i.e. taking into account the oxygen and other atoms associated with the carbon atoms). The conversion used varies from typically from 1.2 to 2 (depending e.g. on water soluble fraction), with 1.4 being the more common choice, (Zhang et al., 2005).

Total particulate organic matter consist of primary organic aerosol plus secondary organic aerosol (POM = POA+SOA). Certain analytical techniques determine elemental carbon (EC or Black Carbon) as a part of POA. EC is believed to be derived from primary particles (soot) in combustion. Hence by subtracting elemental carbon from total particulate organic matter one obtains an upper limit for SOA ($SOA < POM - EC$)

Measurements from research projects indicate that in the urban background environment 25% of PM₁₀ and 30% of PM_{2.5} can be identified as POM. 5% of PM₁₀ and 8 % of PM_{2.5} is identified as EC (Putaud et al. ,2004; Zhang et al., 2005; Pang et al., 2006)

Hence a first upper limit for SOA might be 20% of PM₁₀ and 22% of PM_{2.5}. It should be noted that a significant fraction of PM₁₀ and PM_{2.5}, 28 and 17 % respectively, remains un-identified. It is expected that part of this fraction consists of SOA. (see Fig. 1) Hence the final upper limits for the SOA contributions might be significantly higher.

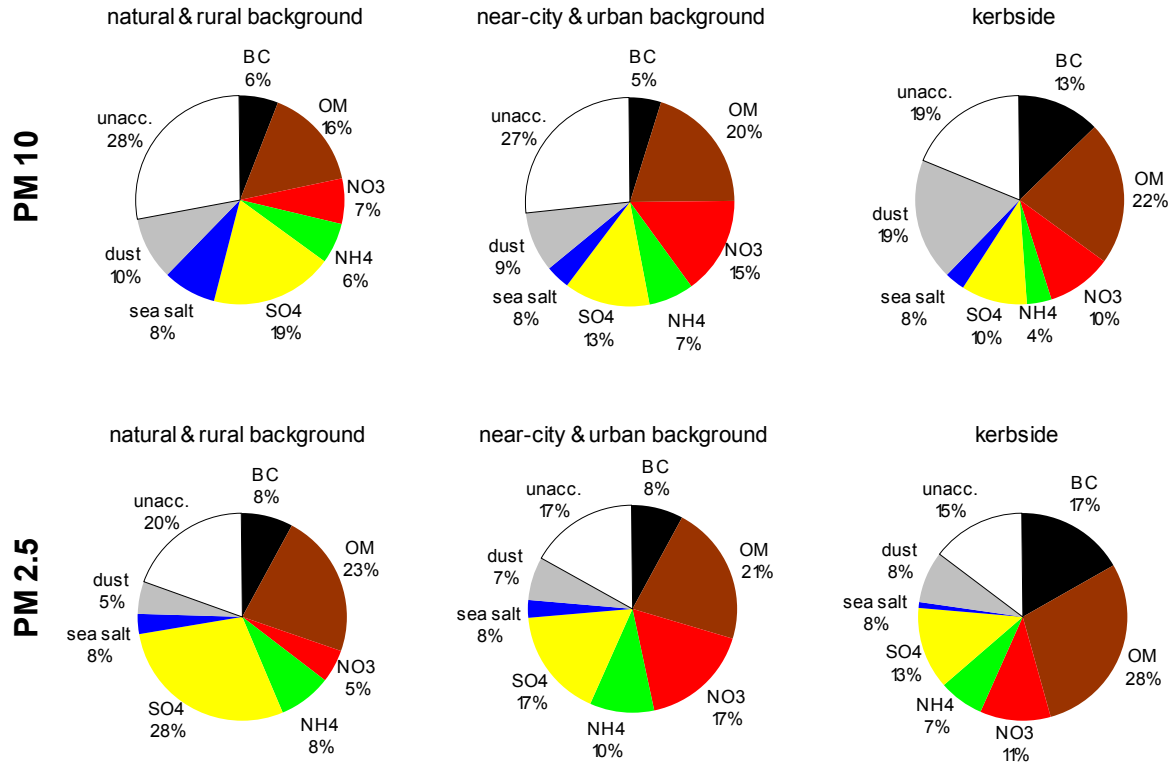


Figure 4.1.

See answers to question 3.1 and 3.2 for more supporting material.

4.2 How could the contribution of SOA to PM change over time?

1. A strong seasonal cycle is expected in *emissions* and in photochemical processes leading to both natural and anthropogenic SOA.
2. Policy measures to reduce anthropogenic VOCs in order to control ozone formation will also reduce SOA formation.
3. Over longer time scales climate change and land-use change are expected to impact on biogenic emissions leading to SOA (see Question 3.4).

4.3 How well can the SOA contributions to levels of PM be quantified, for different source regions in Europe?

1. Poorly. There are no routine monitoring techniques that distinguish SOA from total (i.e. primary + secondary) particulate organic matter (POM). In fact there are no accepted monitoring techniques for POM.
2. A compilation of research projects in which particulate matter (PM), particulate organic matter (POM) and elemental/black carbon (EC/BC) were measured indicates that in the urban environment SOA might contribute up to about 20% in both PM10 and PM2.5.
3. According to the same compilation, the chemical composition of a significant fraction of PM10 and PM2.5, about 25 and 15 % respectively, remains un-identified. Part of this fraction might also consists of SOA. Hence the final upper limits for the SOA contributions to PM10 and PM2.5 might be higher than 20%.

4. Models of transport and chemistry of the atmosphere attempt to evaluate the SOA contribution to POM and PM levels. However, the SOA concentrations calculated by the available models typically differ by a factor 3 to 4.

4.4 Are there biases introduced in the analysis leading to the Strategy due to the lack in scientific understanding?

1. The current analysis does not consider secondary organic aerosols from natural and anthropogenic VOC emissions. Hence the absolute PM_{2.5} values in the baseline scenario are underestimated. Reduction scenarios for anthropogenic VOCs are considered because of their role in ozone formation, but their potential effect on the anthropogenic part of SOA is not considered. Hence the PM_{2.5} reductions calculated in the policy scenarios will also remain underestimated .

4.5 Which research within the next 3-4 years could improve future analyses?

1. There is enough research in this area to engage in an intercomparison of existing reaction and gas-aerosol partitioning schemes used in chemical transport models, to calculate secondary organic aerosol formation. Testing such schemes against laboratory data remains a requirement.
2. Progress can be made in developing, testing and applying measurements of secondary *and* primary organic aerosols, including robust techniques that can be deployed in routine monitoring networks.

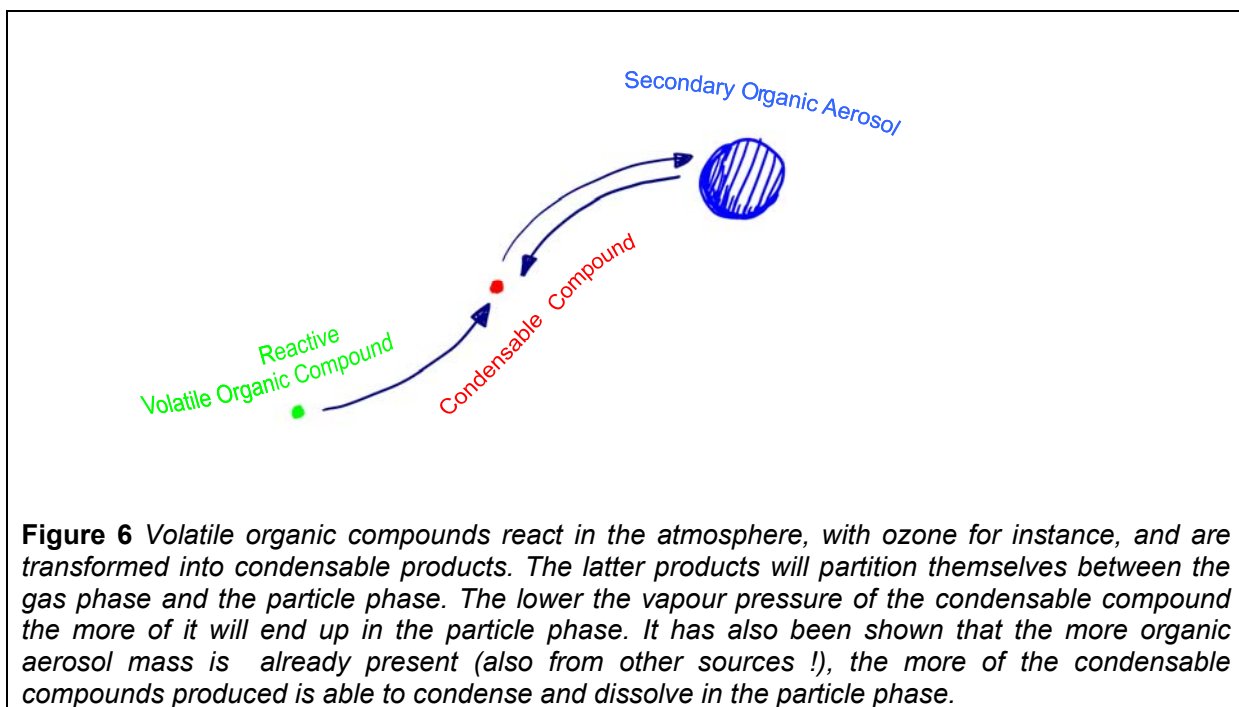


Figure 6 Volatile organic compounds react in the atmosphere, with ozone for instance, and are transformed into condensable products. The latter products will partition themselves between the gas phase and the particle phase. The lower the vapour pressure of the condensable compound the more of it will end up in the particle phase. It has also been shown that the more organic aerosol mass is already present (also from other sources !), the more of the condensable compounds produced is able to condense and dissolve in the particle phase.

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